Chemical Engineering Science 142 (2016) 269–276

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Thermal stability and dynamic analysis of the acetic anhydride hydrolysis reaction ☆

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HIGHLIGHTS

- Rigorous dynamic analysis was performed for acetic anhydride hydrolysis reaction.
- Thermal and bifurcation diagrams were calculated.
- The oscillatory instability of the reaction was demonstrated.
- An excellent agreement between simulation and experimental data was achieved.

ARTICLE INFO

Article history:
Received 3 September 2015
Received in revised form
21 November 2015
Accepted 7 December 2015
Available online 17 December 2015

Keywords:
Dynamic modeling
Hopf bifurcation
Acetic anhydride hydrolysis
Oscillatory behavior
Thermal sensitivity

ABSTRACT

In this work, a rigorous dynamic analysis was performed for the acetic anhydride hydrolysis reaction. It allowed identifying its safe operational conditions in a Continuous Flow Stirred-Tank Reactor (CSTR). Some parameters were introduced and the dimensionless variables and model equations (material and energy balances) were defined. The temperature and conversion profiles were calculated using the experimentally validated kinetic expression and typical operating conditions. Subsequently, thermal and bifurcation diagrams were obtained. All thermal states were recognized: stability (unique and multiple solutions) and instability, bifurcation points, saddle-node bifurcations, turning points (limit points) and oscillatory behavior. The obtained results demonstrated high sensitivity of reactive system (thermal runaway) and predominant oscillatory instability.

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1. Introduction

Acetic anhydride is an organic compound widely used in the production of cellulose acetate, explosives, aspirin, acetic acid, and in others organic synthesis (Ullmann's Encyclopedia of Industrial Chemistry, 2011). Its handling can be dangerous. It is an irritant and highly flammable liquid and, in gaseous phase, it can release toxic vapors. Moreover, the acetic anhydride vapor/air mixtures, at temperatures above 322 K, may become explosive (IPCS-INCHEM, 2015).

Several events caused by acetic anhydride emergency discharges and runaway reactions have been reported in the open literature. Recently, in 2010, an incident was reported in the Chemistry Department at Northwestern University during a modified synthesis of 2-(tert-butylsulfonyl)iodosylbenzene (C&EN, 2015). Apparently, an excess of acetic anhydride reacted with a secondary product (peracetic acid) forming highly shock sensitive and explosive diacetyl peroxide, a compound with high thermal instability (CDC-NIOSH, 2015). The acetic anhydride hydrolysis is another reaction with high thermal sensitivity. Haldar and Rao (1991) studied experimentally its thermal behavior in a Continuous Flow Stirred-Tank Reactor (CSTR). The existence of two steady states, the upper one being oscillatory and the lower one stable, was confirmed. Nevertheless, they could not explain all experimental data with the proposed mathematical model. More recently, based on experimentally validated kinetic data, Jayakumar et al. (2011) reported on the parametric sensitivity (coolant flow rate and the wall capacitance) and dynamic analysis of this reaction. Basing on classical ignition theory, uniqueness and multiplicity regions were reported and sensitivity profiles vs. time were calculated. However, their analyses do not represent completely the real dynamics of the system. In fact, even if the

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http://dx.doi.org/10.1016/j.ces.2015.12.003
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oscillatory behavior is a clear intrinsic property of this reactive system (Haldar and Rao, 1991), process dynamics and rigorous mathematical stability analysis was totally ignored. Therefore, it can be argued that the Jayakumar et al. (2011) study can be considered as simplified and inappropriate. Clearly, classic ignition theory cannot reveal oscillatory thermal instability of thereactive system (Elnashaie and Uhlig, 2007; Ball, 2011, 2013; Ball and Gray, 2013; Ojeda-Toro et al., 2016).

The dynamic behavior of a CSTR can be more complex than multiple steady states with ignition, extinction, and hysteresis. Actually, at a given operating conditions, all steady states may be unstable and the reactor may exhibit sustained oscillations or limit cycles (Rawling and Ekerdt, 2013). The recent studies over the intrinsic dynamics of CSTR have included the comprehensive concepts of bifurcations and attractors. New mathematical tools have been introduced and used to analyze experimental information and to study reactor's mathematical models, making possible to understand, in a unified way, the description of reactive systems. Thus, their dynamics can be described through bifurcation parameters and diagrams which, properly modified, define the regions of different stability and oscillatory behavior. Consequently, it can be expected that a rigorous dynamic analysis sets the specific limits between the operating point and the critical boundaries.

Considering that the acetic anhydride hydrolysis reaction can present serious operative hazards, in this work we reexamine experimental data, previously published by Haldar and Rao (1991) and Jayakumar et al. (2011), using a rigorous thermal stability and dynamic analysis. In order to explain the observed reaction behavior, the predictive capability of bifurcation analysis was tested against experimental data. The reported experimental and simulated steady states, of temperature and conversion profiles, were taken as initial points for the dynamic modeling. Then, the thermal stability (unique and multiple solutions) and instability states (bifurcation points, saddle-node bifurcations), turning points (limit points and oscillatory behavior) were identified. Thus, over the relevant operating parameter space, safe regions for reactor operation were completely established.

2. Reactive system

The hydrolysis of acetic anhydride, $(CH_3CO)_2O$, to acetic acid, CH_3COOH, is an exothermic reaction ($-\Delta H_{rxn} = 58.62$ kJ/mol of acetic anhydride), in liquid phase catalyzed by sulfuric acid. It can be written as follows:

$$(CH_3CO)_2O_{(l)} + H_2O_{(l)} \xrightarrow{H_2SO_4\ \text{catalyst}} 2CH_3COOH_{(l)} \tag{1}$$

Its mechanism has been extensively studied and described in the organic chemistry literature (Asprey et al., 1996; Hirota et al., 2010; Asiedu et al., 2013; Wade, 2013). It is not considered a classical substitution reaction but rather as an addition one.

Haldar and Rao (1991) and Jayakumar et al. (2011) have investigated experimentally this reaction in a CSTR. The experimental data were fitted to a first order rate law with respect to acetic anhydride as follows:

$$-r_A = 1.85 \times 10^{10} C_s \exp\left(\frac{-11243.9}{T}\right) C_A \tag{2}$$

where $-r_A$ is the rate of consumption of acetic anhydride (mol/(m^3 s)), T is the reaction temperature (K), and C_s and C_A are the sulfuric acid and acetic anhydride concentrations (mol/m^3), respectively.

3. Mathematical modeling for dynamic analysis

Assuming a homogeneous CSTR, which concentration and spatial gradients are negligible and the reactive volume is constant, the transient material balance can be written as follows:

$$V_R \frac{dC_A}{dt} = \upsilon(C_{A_0} - C_A) - A_0 C_s \exp\left(\frac{-E}{RT}\right) C_A V_R \tag{3}$$

where t is the time (s), V_R is the reactor volume (m^3), υ is the volumetric flow (m^3/s), A_0 is the pre-exponential factor (1.85×10^{10} m^3/mol s), E is the activation energy (J/mol), R is the ideal gas constant (J/mol K), with $E/R = -11243.9$ K. Similarly, the following energy balance for the reaction side can be defined:

$$(V_R \rho C_p + w_s)\frac{dT}{dt} = \upsilon \rho C_p (T_0 - T) + (-\Delta H_{rxn}) A_0 C_s \exp\left(\frac{-E}{RT}\right) C_A V_R - Ua(T - T_c) \tag{4}$$

where ρ is the mixed reactive density (kg/m^3), C_p is the specific heat of reaction mixture (J/kg K), w_s is the wall capacitance (J/K), ΔH_{rxn} is the reaction enthalpy (J/mol), and Ua is the heat transfer coefficient (W/K). The subscripts 0 and c indicate feed and cooling conditions, respectively.

The CSTR is equipped with a cooling coil and water is used as refrigerant medium. Thus, the energy balance for the heat transfer fluid can be written as follows:

$$V_c \rho_c C_{p_c} \frac{dT_c}{dt} = Ua(T - T_c) + \upsilon_c \rho_c C_{p_c} (T_{c_0} - T_c) \tag{5}$$

The Eqs. (3)–(5) are tied to the following initial conditions:

$$t = 0, \quad C_A = C_{A_0}, \quad T = T_0, \quad T_c = T_{c_0} \tag{6}$$

This mathematical model (Eqs. (3)–(6)) can be expressed in a more tractable form, by maintaining the experimentally variable quantities as independent dimensionless parameters. However, the features of a nondimensionalized parameter space are not absolute (Gray and Roberts, 1988). They strongly depend on their designation. Consequently, in order to propose a direct relation between the model and the real system, the following dimensionless variables and bifurcation parameters were defined.

$$x_A = \frac{C_{A_0} - C_A}{C_{A_0}} \quad \text{Acetic anhydride conversion} \tag{7}$$

$$\gamma = \frac{E}{RT_0} \quad \text{Dimensionless activation energy} \tag{8}$$

$$\theta = \left(\frac{T - T_0}{T_0}\right)\gamma \quad \text{Dimensionless reaction temperature} \tag{9}$$

$$\theta_c = \left(\frac{T_c - T_0}{T_0}\right)\gamma \quad \text{Dimensionless cooling temperature} \tag{10}$$

$$\alpha = k(T_0)t_r = A_0 C_s \exp\left(-\frac{E}{RT_0}\right) t_r \quad \text{Dimensionless rate constant} \tag{11}$$

$$\psi = \frac{(-\Delta H_{rxn}) C_{A_0} V_R \gamma}{Ua t_r T_0} \quad \text{Semenov number, representing the ratio between the rate of heat production and of cooling.} \tag{12}$$

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