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Safer operating conditions and optimal scaling-up process for cyclohexanone peroxide reaction

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ABSTRACT

The cyclohexanone peroxide reaction process, one of the eighteen hazardous chemical processes identified in China, is performed in indirectly cooled semibatch reactors. The peroxide reaction is added to a mixture of hydrogen peroxide and nitric acid, which form heterogeneous liquid–liquid systems. A simple and general procedure for building boundary and temperature diagrams of peroxide process is given here to account for the overall kinetic expressions. Such a procedure has been validated by comparison with experimental data. Thermally safer operating parameters were obtained at laboratory scale, and the scaled-up procedure was performed to give the minimum dosing time in an industrial plant, which is in favor of maximizing industrial reactor productivity. The results are of great significance for governing the peroxide reaction process apart from the thermal runaway region. It also greatly aids in determining optimization on operating parameters in industrial plants.

1. Introduction

To completely control heat evolution during a chemical process, fast and strong exothermic reactions are usually performed in indirectly cooled semibatch reactors (SBRs). The conversion rate of SBRs can be properly controlled based on dosing one of the reactants at an effective rate so that the accumulation is low, which is advantageous for the cooling system to remove the being heat evolved [1,2]. During above conditions, reactant accumulation in the system is governed with a low level and the hazard of thermal runaway in secondary reaction is consequently minimized. Operation of the system in the SBRs is crucial when a hazardous chemical process is carried out, such as peroxide reaction which is almost strongly heat releasing and low decomposition threshold temperature of intermediates and products, implying hazardous thermal loss control of the reactors.

In searching for process safety references of the past 30 years, a number of thermal loss controls of SBRs have been developed for paying attention on single reaction scheme [3–19]. These criteria can be classified into two parts. One is boundary diagrams (BDs), and the other is temperature diagrams (TDs), which could provide the end users a safer and simpler selection at laboratory scale [17]. However, in industry practice, numerous reaction systems involve complex and autocatalytic reactions. The new procedure for building up BDs and TDs was developed to account for arbitrary kinetic expressions and multiple reactions. The aforementioned methods have been validated as able to solve complex problems of efficient safety at laboratory scale. Moreover, an accurate kinetic characterization of the reaction system is crucial as a reliable application with these methods. If the overall reaction kinetic parameters can be obtained, the selected process parameters could be safely scaled-up at laboratory to the full-scale reactor. Therefore, a simple optimization scaled-up procedure has been developed, which is on the basis of generalized forms of BDs and TDs [1]. It can allow end users to prudently and safely scaled-up process conditions to industrial scale, optimizing the real conditions. The limited reliable kinetic parameters, as a scaled-up method, have only been used to solve the nitration process [2], which is one of eighteen dangerous chemical processes [20]. The other hazardous reaction processes, such as peroxide reaction, have been ignored in virtue of experimental and practical limitations.

In this study, the above-mentioned procedure is applied for the analysis of peroxide reaction process, which is performed in chemical industries. The synthesis of cylcohexanone peroxide (CYHPO)

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Nomenclature

A	heat transfer area of the reactor (associated to the jacket and/or the coil) (m^2) species A or pre-exponential factor (s^{-1})
B	species B (dimensionless)
BDs	boundary diagrams
C	molar concentration ($kmol\,m^{-3}$), or species C (dimensionless)
C_0	cooling number (dimensionless)
C_p	specific heat capacity ($kJ\,kg^{-1}\,K^{-1}$)
D	species D (dimensionless)
Da	$Da = \kappa_{n,m} t_D C_{B,0}^{n+m-1}$ (Damkohler number) (dimensionless)
E_a	apparent activation energy ($kJ\,kmol^{-1}$)
E_x	in Eq. (4), exothermicity number (dimensionless)
EMAT	EMAT = (1 – tool)MAT, effective maximum allowable temperature (K)
$f_{slow,c/d}$	$(\theta - \xi_B)^n (1 - \xi_B)^m / (\varepsilon\theta)^{n-1}$, dimensionless concentration function of reaction
$FF(\tau_{cool})$	$FF(\tau_{cool}) = \tau_{max}(\tau_{cool}) - \tau_{ta}(\tau_{max}) = 0$ generating function of reaction
MAT	maximum allowable temperature (K)
$RE_{slow,c/d}$	$(\nu_B/\nu_A)^{1-n} m_A^n$, reactivity enhancement factor of peroxide reaction (dimensionless)
R	gas constant, 8.314 ($kJ\,kmol^{-1}\,K^{-1}$)
R_H	$R_H = \rho_d C_{P,d} / \rho_c C_{P,c}$, heat capacity ratio (dimensionless)
R_y	reactivity number expressed in Eq. (5) (dimensionless)
St	$St = (UA)_0 t_D / \rho_c C_{P,c} V_c$, Stanton number (dimensionless)
t	time (s)
t_D	closing time (min)
T	temperature (K)
TDs	temperature diagrams (dimensionless)
T_R	reference temperature (K)
U	overall heat transfer coefficient ($kW\,m^{-2}\,K^{-1}$)
V	volume (m^3)

Greek symbols

$\Delta\tau_{ad,0}$	$\Delta\tau_{ad,0} = (-\Delta H_r) n_{B,0} / \nu_B \rho_c C_{P,c} V_c T_R$ dimensionless adiabatic temperature rise of reaction
γ	$\gamma = E/(RT_R)$, dimensionless concentration function
ξ	$\xi = n_i / n_{A,dos}$, dimensionless concentration of species i
ε	$\varepsilon = V_D/V$, relative volume increase at the end of the semibatch period
$\kappa_{n,m}$	$\kappa_{n,m} = \exp[\gamma(1 - 1/\tau)]$, dimensionless kinetic constant
ρ	molar density ($kmol\,m^{-3}$)
θ	$\theta = t/t_{dos}$, dimensionless time
τ	$\tau = T/T_R$, dimensionless temperature
τ_{cool}^{eff}	$\tau_{cool}^{eff} = U * Da(1 + \varepsilon\theta)\tau_{cool} + R_H \varepsilon \tau_D / (U * Da(1 + \varepsilon\theta) + R_H \varepsilon)$, effective dimensionless coolant temperature
ψ	$\psi = (T_{max}/T_0)_{max}$, dimensionless maximum temperature rise

Subscripts and superscripts

ad	adiabatic
c	continuous phase or referred to continuous phase
cool	coolant
d	dispersed phase or referred to dispersed phase
dos	dosing stream or dosing time
eff	effective
ind	at the industrial scale
max	maximum value of a quantity or at the maximum value of a quantity
MI	marginal ignition
QFS	quick onset, fair conversion, smooth temperature profile
R	referred to as the reference conditions
slow	slow reaction regime
ta	target
toll	safety parameter for MAT value
0	start of the dosing period

is via peroxide oxidation reaction using cyclohexanone mixed with hydrogen peroxide (H_2O_2) by acid catalysis of HNO_3. The cyclohexanone peroxide reaction belongs to the top level of Stoessel's classification of runaway reactions [9]. The thermal loss of control in peroxide synthesis reaction implies the triggering of peroxide product, which has low decomposition temperature due to weak oxygen–oxygen bond.

In the first part of this study, thermal stability of the involved chemical species was investigated under experimental conditions, which were accomplished based on the differential scanning calorimetry (DSC) and accelerating rate calorimeter (ARC). Meanwhile, microkinetic parameters calculated by Levenberg–Marquardt algorithm were estimated through reaction calorimeter (RC1^e) experiments under kinetically controlled conditions. In this study, the general optimization scaled-up procedure was applied to the selection of safer operating conditions at laboratory scale. Then, the verified safer operating conditions at laboratory scale were used to acquire the optimal scaled-up parameters applied in industrial plants.

2. Mathematical model

2.1. Reaction system

To obtain BDs and TDs, the cyclohexanone peroxide reaction is assumed to be in heterogeneous phase, which belongs to the kinetically controlled reaction regime. The overall stoichiometry is characterized by the following expression:

$$\nu_A A + \nu_B B \rightarrow C + \nu_D D \tag{1}$$

The microkinetic rate expression is as follows:

$$r = k_{n,m} C_A^n C_B^m \tag{2}$$

The reaction process occurs in the heterogeneous phase, following a slow reaction regime, and mass and energy balances can be written in a dimensionless form annotated as follows [17]:

$$\begin{cases} \dfrac{d\xi_B}{d\theta} = \nu_A Da RE_{slow,c/d} f_{slow,c/d} \kappa_{n,m} \\ (1 + R_H \varepsilon\theta)\dfrac{d\tau}{d\theta} = \Delta\tau_{ad,0}\dfrac{d\xi_B}{d\theta} - [U * Da(1 + \varepsilon\theta) + R_H\varepsilon] \times (\tau - \tau_{cool}^{eff}) \\ IC \quad \xi_B(\theta = 0) = 0 \quad \tau(\theta = 0) = \tau_0 \end{cases} \tag{3}$$

In the above equations, $f_{slow,c/d}$ represents functions that depend on the dimensionless time and dimensionless concentrations. The meaning of all symbols is given in nomenclature.