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Kinetic-parameters-free determination of thermally safe operation conditions for isoperibolic homogeneous semibatch reactions: A practical procedure

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HIGHLIGHTS

- Semibatch reactors are commonly used to prevent thermal runaway.
- Kinetic parameters of exothermic reactions are often unavailable in practice.
- A kinetic-parameters-free procedure to determine safe conditions is developed in this work.
- This procedure just needs several isothermal RC1 tests.

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ABSTRACT

In the fine and pharmaceutical chemical industries, the kinetic parameters of exothermic reactions are often unavailable because this process is time-consuming and money-consuming. Hence, it is essential to develop kinetic-parameters-free procedure to determine thermally safe operating conditions for exothermic semibatch reactions. In this work, a practical procedure without any reaction kinetic parameter information required has been developed and presented. It just needs several isothermal RC1 (reaction calorimetry) tests, which are convenient to conduct in practice. Such a practical procedure, based on two crucial theoretical tools: Ry_{min}-Wt plot and $\nu_A Da R_E \kappa$-X_{ac} plot, allows one not only to keep safe conditions but also to optimize the reactor productivity. In addition, this method is also feasible for the cases of the exothermic reactions with low value of Ex and low mixing heat. Moreover, this method is supposed to be inapplicable when encountering autocatalytic reactions.

1. Introduction

In the fine and pharmaceutical chemical industries, semibatch reactor (SBR) is the most commonly employed type of reactors in order to prevent the reaction runaway caused by thermal loss of control of exothermic reactions. However, the occurrence of runaway phenomena is not completely vanished by now. The number of fatalities and injuries as a result of thermal runaway incidents has increased by ~325% and ~279%, respectively, in the last 25 years even though the number of incidents was significantly decreasing [1].

In general, to prevent reactor incidents and runaways, three lines of defense can be considered in the design and operation of SBRs: a suitable system to handle running away reaction, an early warning detection system (EWDS) and choice of the safe operating conditions [2]. The first one means taking measures to minimize the negative results after runaway reactions have occurred. For example, if vapors are developed, we need a blow down system with catch tanks. The second line of defense can give an early warning to the operator to anticipate a runaway to occur within a shorter period, say for example, 20–200 min in advance of reaching the maximum runaway temperature. In the last decades, great advances in this field have been made. The most advanced technique in this field is the divergence criterion developed by Zaldívar and coworkers [3], which have been applied to several practical cases [4–6]. The third line of defense maybe plays the most important role in this field. Many authors have been devoted to design inherently safe operating conditions for SBRs.

In practice, most of SBRs are operated in a so-called isoperibolic operation mode, which means the coolant temperature keeps constant and the reactive mixture temperature varies. Hence, it is of particular importance to develop a practical method for determination of thermally safe operating conditions of isoperibolic SBRs.

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Nomenclature

A	heat exchange surface area, m^2
C	instantaneous concentration, $mol \cdot m^{-3}$
C_p	specific heat capacity, $J \cdot kg^{-1} \cdot K^{-1}$
Da	Damköhler number at the reference temperature (T_R), $Da = k_R t_d C_{B,0}$
E	activation energy, $J \cdot mol^{-1}$
Ex	exothermicity number
F	function of the dimensionless time and conversion of component B, $f = (1 - \xi_B)(\theta - \xi_B)/(1 + \varepsilon\theta)$ $(\theta < 1)$ or $(1 - \xi_B)^2/(1 + \varepsilon)$ $(\theta > 1)$
K	kinetic rate constant, $m^3 \cdot mol^{-1} \cdot s^{-1}$
MAT	maximum allowable temperature, K
$MTSR$	maximum temperature of synthesis reaction under adiabatic conditions, K
n_B	number of moles of the component B
r	instantaneous reaction rate, $mol \cdot m^{-3} \cdot s^{-1}$
R_H	ratio of the volumetric heat capacities of the dosed component A and B, $R_H = (\rho C_p)_A/(\rho C_p)_B$
R_E	the reactivity enhancement factor
Ry	reactivity number
T	time, s
T	temperature, K
T_{D24}	temperature at which TMR_{ad} is 24 h, K
U	overall heat transfer coefficient, $W \cdot m^{-2} \cdot K^{-1}$
V	actual volume of the reactor content, m^3
Wt	Westerterp number, $Wt = (UA)_0 t_d/(\varepsilon(\rho C_p)_0 V_0)$
X	conversion

Greek Symbols

Γ	dimensionless activation energy, $\gamma = E/RT_R$
ε	relative volume increase at the endpoint of the feed period
θ_{MTSR}	dimensionless instant corresponding to MTSR
θ	dimensionless time, $\theta = t/t_{dos}$
κ	dimensionless reaction rate constant, $\kappa = \exp(\gamma(1 - 1/\tau))$
ν	stoichiometric coefficient
ρ	density of the reaction mixture, $kg \cdot m^{-3}$
τ	dimensionless temperature, $\tau = T/T_R$
$\phi_{V,A}$	volumetric dosing rate of the component A, $m^3 \cdot s^{-1}$
ΔH_r	enthalpy of the reaction, $J \cdot mol^{-1}$
$\Delta T_{ad,0}$	adiabatic temperature rise at initial conditions, $\Delta T_{ad,0} = (-\Delta H_r) n_{B,0}/(\nu_B(\rho C_p)_0 V_0)$, K
$\Delta\tau_{ad,0}$	dimensionless form of $\Delta T_{ad,0}$, $\Delta\tau_{ad,0} = \Delta T_{ad,0}/T_R$

Subscripts and Superscripts

ac	accumulation
A, B, C and D	components
c	coolant
d	dosing
0	initial
f	final
max	maximum
min	minimum
p	process
r	reaction

The pioneers in this research field are Hugo and Steinbach [7,8] who observed that an accumulation of the dosed component at too low reactor temperatures is the cause of the runaway in homogeneous semibatch reactors. They presented a line in a diagram, which separates the region with a runaway from the region with a smoothly operating SBR with only a small harmless accumulation of the dosed reactant. Steensma and Westerterp [9–11] then developed full safety diagrams for both homogeneous and heterogeneous semibatch reactions. In their safety diagrams they plotted the Reactivity, *Ry*, as a function of the Exothermicity, *Ex* and surrounded the region of runaways by a boundary line. Based on these safety diagrams, they developed a practical procedure to determine the inherently safe operating conditions [12]. These boundary diagrams(BD) method for heterogeneous reactions has been then extended to the case of multiple heterogeneous reactions by Van Woezik and Westerterp [13,14]. Maestri and Rota [15–17] demonstrated that for homogeneous as well as heterogeneous SBRs, the reaction order of the two reactants can influence the shape and location of the boundary diagrams. To prevent the triggering of dangerous decomposition and side reactions, they also developed new diagrams, called temperature diagrams (TD) [18]. Accordingly they proposed a procedure based on the use of BD and TD for selecting safe operating conditions for homogeneous as well as heterogeneous exothermic SBRs [19,20]. Recently, Bai and co-workers [21] proposed a new method for predicting the generalized inherently safe operating conditions based on a runaway criterion, denoted as MTSRC, which is based on the variation of the dimensionless *MTS*R (maximum temperature of synthesis reaction under adiabatic conditions) and θ_{MTSR} (dimensionless instant corresponding to *MTSR*).

All the above methods are workable on the premise that kinetic parameters, at least apparent kinetic parameters are known. However, since the determination process of kinetic parameters is time-consuming and money-consuming, kinetic parameters are often unavailable in practice. Therefore, it is highly urgent to develop kinetic-parameters-free method to determine thermally safe operating conditions. Along this line, Copelli and co-workers [22–24] introduce the concept of the topological curve, which is a plot of T_{max}/T_c versus the conversion in the point where the T_{max} has been reached. On such a curve the area for QFS (quick onset, fair conversion and smooth temperature profile) reactions can be identified. Moreover, Maestri and Rota [25,26] recently developed a general method on the basis of a so-called ψ number criterion, which allows for ongoing detection of the displacement of the SBR operating regime from safe target condition.

In this work, we propose a new practical procedure for determining thermally safe operating conditions of isoperibolic homogeneous SBRs without any information about the reaction kinetic parameter required. Just several times of isothermal reaction calorimetry (RC1) tests are needed. Two crucial tools, namely Ry_{min}-Wt plot and $\nu_A Da R_E \kappa$-X_{ac} plot, are employed to develop this procedure, which will be introduced in detail in the third part of this work.

The work will be constructed as followed: Firstly, the mathematical model of SBR is introduced; Secondly, Ry_{min}-Wt plot and $\nu_A Da R_E \kappa$-$X_{ac,max}$ plot will be introduced in detail; Thirdly, we will interpret how the kinetic-parameters-free procedure works; Finally, some more discussions with respect to this procedure will be present.

2. Dimensionless mathematical model

Assuming that a single reaction is performed in a semi-batch homogeneous stirred reactor equipped with the cooling jacket:

$$\nu_A A + \nu_B B \rightarrow C + \nu_D D \quad (1)$$