



A new criterion to identify safe operating conditions for isoperibolic homogeneous semi-batch reactions

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HIGHLIGHTS

- A new runaway criterion to distinguish different reactor behaviors (IS, MI, TR and QFS) is proposed.
- The chemical process may be in a potential runaway situation if $\theta_{\text{MTR}} < 1$.
- A robust procedure to identify generalized inherently safe (GIS) operating conditions for isoperibolic homogeneous SBRs is proposed with limited kinetic information.
- The determined GIS operating conditions involve the information of both a sufficiently low accumulation and MTR lower than MAT.

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ABSTRACT

The maximum temperature of a synthesis reaction (MTR) is an important criterion for process risk assessment and reactor design. In this paper, the variation of the dimensionless MTR_0 and θ_{MTR} (the instant corresponding to MTR_0) for isoperibolic processes is studied in detail. A new runaway criterion, denoted as MTRC, is proposed. Based on the proposed operating diagrams, a robust procedure to identify generalized inherently safe operating conditions (GIS) characterized by both a sufficiently low accumulation and MTR lower than MAT, is developed and used with limited kinetic information. These kinetic parameters are conveniently measured by performing only one adiabatic and two isothermal experiments at laboratory scale. Comparison between MTRC and other safety criteria is performed. In conclusion, it is demonstrated that MTRC is an efficient and robust criterion to identify inherently safe operating conditions.

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1. Introduction

In the fine and pharmaceutical chemical industries the most commonly used type of reactor, in which highly exothermic reactions are involved, is the semi-batch reactor (SBR) for which the isoperibolic operating mode is the most common. However, runaway reactions caused by excessive feeding rate, improper jacket temperature, cooling failure, loss of agitation, and even mal-operation cannot be completely avoided. Runaway reactions can result in loss of containment and significant risk to human life, equipment and corporation assets. Hence, much attention has been paid to identification and prevention of runaway reactions.

The maximum temperature of a synthesis reaction after a cooling failure occurs (denoted as MTR) initially proposed based on the cooling failure scenario [1] is a useful criterion for process risk

assessment and reactor design. Stoessel [2] determined that MTR must be lower than the maximum allowable temperature (MAT) which is associated to the boiling point in an open system (MT) and the consecutive decomposition temperature of reacting mixture (T_{D24}).

MTR is a function of the process temperature (T_p), the accumulation degree (ζ_{ac}) and the adiabatic temperature rise (ΔT_{ad}):

$$\text{MTR} = (T_p + \zeta_{ac} \Delta T_{ad})_{\max} \quad (1)$$

It was suggested by Hugo et al. that the process temperature and the accumulation degree have an inverse relationship, meaning MTR probably decreases with the increase of process temperature [3] and the comprehensive investigation into the variation of MTR with process temperature for isothermal reactions in our previous paper [4] further verified this conclusion. Nevertheless, the knowledge about the variation of MTR for isoperibolic reactions is not clear.

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Nomenclature

A	heat exchange surface area, m^2	ε	relative volume increase at the endpoint of the feed period
C	instantaneous concentration, $\text{mol}\cdot\text{m}^{-3}$	θ	dimensionless time, $\theta = t/t_{\text{dos}}$
C_p	specific heat capacity, $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$	θ_{MTR}	dimensionless instant corresponding to MTR_0
Da	Damköhler number at the reference temperature (T_R), $Da = k_R t_{\text{dos}} C_{B,0}$	κ	dimensionless reaction rate constant, $\kappa = \exp(\gamma(1-1/\tau))$
E	activation energy, $\text{J}\cdot\text{mol}^{-1}$	ν	stoichiometric coefficient
Ex	exothermicity number, $Ex = \Delta\tau_{\text{ad},0}/(\tau_j^2 \varepsilon (R_H + Wt))$	ξ	Grecian fractional conversion
f	function of the dimensionless time and conversion of component B, $f = (1 - \xi_B)(\theta - \xi_B)/(1 + \varepsilon\theta)$ ($\theta < 1$) or $(1 - \xi_B)^2/(1 + \varepsilon)$ ($\theta > 1$)	ρ	density of the reaction mixture, $\text{kg}\cdot\text{m}^{-3}$
FF	a function to identify the critical jacket temperatures	τ	dimensionless temperature, $\tau = T/T_R$
k	kinetic rate constant, $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$\phi_{V,A}$	volumetric dosing rate of the component A, $\text{m}^3\cdot\text{s}^{-1}$
MAT	maximum allowable temperature, K	ΔH_r	enthalpy of the reaction, $\text{J}\cdot\text{mol}^{-1}$
MTR	maximum temperature of synthesis reaction under adiabatic conditions, K	$\Delta T_{\text{ad},0}$	adiabatic temperature rise at initial conditions, $\Delta T_{\text{ad},0} = (-\Delta H_r)n_{B,0}/(\nu_B(\rho C_p)_0 V_0)$, K
MTR_0	dimensionless form of MTR	$\Delta\tau_{\text{ad},0}$	dimensionless form of $\Delta T_{\text{ad},0}$, $\Delta\tau_{\text{ad},0} = \Delta T_{\text{ad},0}/T_R$
MTT	maximum temperature for technical reasons, K	<i>Subscripts and superscripts</i>	
n_B	number of moles of the component B	ac	accumulation
r	instantaneous reaction rate, $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$	A, B, C and D	components
R_H	ratio of the volumetric heat capacities of the dosed component A and B, $R_H = (\rho C_p)_A/(\rho C_p)_B$	cf	cooling failure
R_E	the reactivity enhancement factor	dos	dosing
R_y	reactivity number, $R_y = Da \exp(\gamma(1-1/\tau_j))/(\varepsilon(R_H + Wt))$	0	initial or dimensionless
t	time, s	f	final
T	temperature, K	j	jacket
T_{D24}	temperature at which TMR_{ad} is 24 h, K	$m-1, m, n, n+1$	the $(m-1)_{\text{th}}, m_{\text{th}}, n_{\text{th}}, (n+1)_{\text{th}}$ points of the jacket temperature in its changing range
U	overall heat transfer coefficient, $\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$	max	maximum
V	actual volume of the reactor content, m^3	min	minimum
Wt	Westerterp number, $Wt = (UA)_0 t_{\text{dos}}/(\varepsilon(\rho C_p)_0 V_0)$	MI-TR	transformation from MI case to TR case
<i>Greek symbols</i>		p	process
γ	dimensionless activation energy, $\gamma = E/RT_R$	r	reaction
		rm	reacting mixture
		TR-QFS	transformation from TR case to QFS case

A thoroughly discussed in the literature [5,6], the dangerous accumulation in an isoperibolic semi-batch reactor was the key cause for the occurrence of runaway reaction. The too low jacket temperature results in a huge accumulation. For this reason, in semi-batch condition a higher jacket temperature is often safer than a lower one. However, if the jacket temperature is too high, a situation can arise in which the accumulation is confined below critical values but the process temperature itself is too close to the MAT values.

For the identification of low accumulation in SBRs, Westerterp and co-workers [7–12] developed the so-called boundary diagrams based on a target temperature which was introduced and defined as follows:

$$T_{\text{ta}} = T_j + \frac{1.05\Delta T_{\text{ad},0}}{\varepsilon[Wt(1 + \varepsilon\theta) + R_H]} \quad (2)$$

Additionally, the inherently safe region was proposed and a systemic procedure for identifying inherently safe operating conditions was developed and elaborated for laboratory and industrial reactors.

It is noted that the boundary diagrams which is devoted to the low accumulation is lacking in the information that MTR should lower than MAT. Therefore, Rota and co-workers [13–18] developed a new kind of diagrams called temperature diagrams to complement the boundary diagrams. However, the temperature diagrams involve the maximum temperature only under normal operation rather than in an adiabatic condition.

In the papers by Copelli et al. [19–21] a topological criterion for arbitrary kinetic schemes was developed and verified to be actually the most powerful tool to detect QFS (quick onset, fair conversion and smooth temperature profile) region and even temperature control can be inserted. Successively, with integrating dosing and jacket temperature equations, mixing rules, global material balance and cooling jacket energy balance, this criterion allows for optimizing processes at full plant scale [22]. Recently, this extended tool was used to the decomposition kinetics case [23]. However, unfortunately, it requires huge experimental efforts. In this sense, the problem can be considered still open.

In addition, over the past few decades many works have been devoted to detect the runaway boundary, especially sensitivity criterion [24] and divergence criterion [25–27]. Recently, Casson et al. [28] summarized these works and compared these runaway criteria to investigate the runaway boundary for the acid catalyzed esterification of acetic anhydride and methanol. Nevertheless, these criteria mainly aimed to detect runaway situation, not considering process optimization, namely simultaneously the low accumulation and proper temperature threshold.

As a consequence, it would be useful to find a way to integrate the information of the low accumulation deduced from the boundary diagrams and the temperature threshold that MTR lower than the MAT value.

In this paper, firstly, the variation of the dimensionless MTR_0 and θ_{MTR} (the meaning of these terms will be explained below) for isoperibolic reactions is studied in detail. Secondly, a new runaway criterion is proposed and subsequently a systemic and robust

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