



Insights into maximum temperature of synthesis reactions in isothermal homogeneous semibatch reactors

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ABSTRACT

Semibatch reactors (SBRs) are commonly used to conduct exothermic reaction in the pharmaceutical and fine chemical industries. From the thermal safety point of view, low *MTSR* (maximum temperature of synthesis reactions) is desirable. We have found that *MTSR* vs process temperature (*T*) profile favorably present S-shape in isothermal homogeneous SBRs involving highly exothermic or slow reactions. However, the criterion to determine the dependency of *MTSR* on *T* has been not thoroughly studied. In this work, such a theoretical criterion will be developed based on the fact that the derivative of *MTSR* to *T* is zero at the reaction temperature at which the lowest value of *MTSR* is obtained and experimentally validated by the hydrolysis reaction of acetic anhydride. To develop such a criterion, the quantitative relationship between the maximum accumulation $X_{ac,max}$ and Damköhler number (*Da*) for isothermal homogeneous semibatch reactions of arbitrary kinetic orders is first developed and numerically verified.

1. Introduction

In the pharmaceutical and fine chemical industries, one commonly used type of reactors to prevent thermal runaway accidents is the semibatch reactors (SBRs). The safe operation of SBRs can be achieved by regulating the dosing rate to meet the cooling capacity of the cooling systems. However, thermal runaway accidents caused by systematic faults like cooling failure have not been completely vanished so far [1].

One important principle concerning thermal safety in SBRs is that the maximum temperature of synthesis reactions (*MTSR*) should be lower than the maximum allowable temperature (*MAT*) [2]. Herein, *MAT* refers to the lower one of the decomposition temperature of reaction mixture (T_D) and the maximum temperature for technical reason (*MTT*) [3]. *MTSR* was first proposed by Gyax [4] and then defined by Lerena [5] as the maximum temperature attained in the case of a cooling failure for an exothermic reaction. This principle of $MTSR < MAT$ has been widely used in industrial and academic field [6–10].

According to the definition, *MTSR* can be simply expressed as follows

$$MTSR = T + X_{ac,max} \times \Delta T_{ad} \quad (1)$$

Where *T* is the process temperature, $X_{ac,max}$ is the maximum accumulation, ΔT_{ad} is the adiabatic temperature rise. Hugo and co-workers [11] pointed out that *T* and $X_{ac,max}$ have an inverse relationship,

meaning that $X_{ac,max}$ would decrease with *T* increasing. Accordingly, Hugo [11] predicted that *MTSR* may decrease with *T* increasing for highly exothermic reactions in certain range of reaction temperature. This phenomenon has been observed in the synthesis of 3-methylpyridine-*N*-oxide by Zhang and co-workers [12], who found that if the catalyst mass and dosing rate of hydrogen peroxide kept at 10 g and 60 min, respectively, the tested *MTSR* would decrease from 171.66 °C to 140.66 °C as *T* increased from 70 °C to 90 °C. Zhang [13] observed that for synthesis of butyl acetate by acetic anhydride and butyl alcohol in semibatch reactor, when *T* increased from 35 °C to 50 °C, *MTSR* decreased from 65.9 °C to 61.9 °C. Guo and co-workers [14] experimentally investigated the esterification reaction of propionic anhydride with 2-butanl in a reaction calorimeter and found that *MTSR* decreased with *T* increasing from 70 °C to 80 °C. For deeper understanding, Guo [14] also theoretically analyzed the variation tendency of *MTSR* in homogenous SBRs, and found that the *MTSR* vs *T* profile for synthesis reactions with high exothermicity or high activation energy favorably presented S-shape while *MTSR* would monotonously increase with *T* increasing for synthesis reactions with low exothermicity or activation energy, as illustrated in Fig. 1. Stoessel [3] has also found the *MTSR* vs *T* tendencies.

From the thermal safety point of view, the most safe process temperature occurs at point B in Fig. 1b, because the value of *MTSR* at point B is relatively lower than that of the neighboring points. Accordingly,

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Nomenclature

a	constant parameter in equation 6 and 7
b	constant parameter in equation 6 and 7
C	instantaneous concentration, mol m ⁻³
c _p	specific heat capacity, J g ⁻¹ K ⁻¹
Da	Damköhler number, $Da = kn, mt_d C_{B,0}^{n+m-1}$
E	activation energy, J mol ⁻¹
f	function of the dimensionless time and conversion of component B
k	kinetic rate constant, cm ³ mol ⁻¹ s ⁻¹
k ₀	pre-exponential factor
m	the total mass of the final reaction mixture
MAT	maximum allowable temperature
MTSR	maximum temperature of synthesis reaction under adiabatic conditions
q	heat generated rate, W
Q	heat generated by the hydrolysis reaction
r	instantaneous reaction rate, mol cm ⁻³ s ⁻¹
R	ideal gas constant
t	time, s
t _d	dosing time, s

T	process temperature
T _{D24}	temperature at which TMR _{ad} is 24 h, K
V	reaction volume
X	conversion
ΔT _{ad}	adiabatic temperature rise
-ΔH _r	the reaction enthalpy, kJ/mol

Greek Symbols

ε	the volume ratio of dosing reactant A to co-reactant B
θ	dimensionless time, $\theta = t/t_d$

Subscripts and Superscripts

ac	accumulation
ad	adiabatic conditions
A, B, C and D	components
d	dosing
max	maximum
p	process
r	reaction
tot	total

development of the criterion to check whether the given process temperature correspond to the most safe process temperature is of high significance. Though these works [12–14] experimentally found the phenomenon that MTSR decreased with T increasing for highly exothermic reactions in certain range of reaction temperature, however, they didn't propose such a theoretical criterion. Hugo [11] have ever proposed such a criterion for second order homogeneous reactions as follows

$$\frac{E \cdot \Delta T_{ad}}{RT^2} > \frac{2}{X_{ac,max}} \quad (2)$$

Eq. (2) states that (1) if the left term is higher than the right one, MTSR decreases with T increasing and (2) the most safe process temperature occurs when the left term is equal to the right one.

However, the validity of Eq. (2) is suitable only to rigorous second order reactions. The reaction order of most of chemical reactions is not rigorously equal to 2. Hence, it is desirable to develop a general criterion suitable to arbitrary kinetic order. In this work, such a general criterion will be developed based on the knowledge that the derivative of MTSR to T is equivalent to zero at the reaction temperature at which the lowest value of MTSR is obtained. For this purpose, the quantitative calculation formula for X_{ac,max} will be first deduced.

2. Theory

2.1. Dimensionless model for isothermal homogeneous SBRs

Assuming that a single bimolecular homogeneous reaction is performed in a semibatch stirred reactor equipped with the cooling jacket or coil:

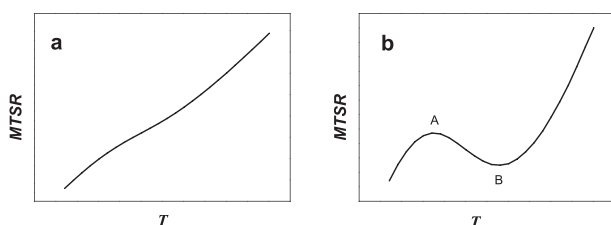
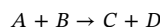


Fig. 1. The two tendencies of MTSR vs T profiles in isothermal SBRs.



where components A and B are pure or diluted with inert solvents, C and D are the products of the reaction. Moreover, we assume that the reactant B is loaded into the reactor vessel initially and then component A is dosed at a constant rate until the stoichiometric amount of A is added. The reaction heat is removed by a flow of coolant through a coil or a jacket.

In addition, some more assumptions are made as follows:

- The reaction is irreversible and non-autocatalytic;
- The reaction mass are perfectly macro-mixed;
- The reaction volume variation caused by the reaction is negligible and the increase in reaction volume is only because of the addition of component A;
- The mixing heat is negligible relative to the reaction heat. Reaction enthalpy is the only source of heat generation;
- The physicochemical properties of all the components are constant over the whole reaction.

Reaction rate can be described by a power law function:

$$r = k_{n,m} C_A^n C_B^m \quad (3)$$

The dimensionless conversion rate of component B can be expressed as follows [14]

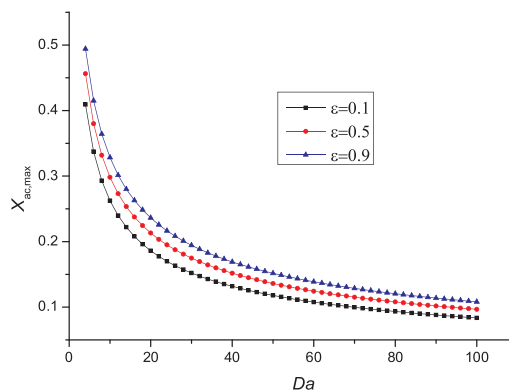


Fig. 2. The quantitative relationships between Da and X_{ac,max} at different values of ε for isothermal homogeneous SBRs with second order reactions involved.

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