

Computer Aided Design of Thermally Safe Operating Conditions for Heterogeneous Semibatch Reactors

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Semibatch reactors (SBRs) are widely used to control the heat generation rate of exothermic reaction by tuning the dosing rate. To avoid the undesirable thermal runaway accidents, designing thermally safe operating conditions for SBRs is of high importance. In this work, a new simple computer aided method is developed to facilitate the process of designing safe conditions for liquid-liquid reactions that occur in the continuous phase following a slow reaction regime. The information required to design the safe operation parameters of dosing time (t_b) and jacket coolant temperature (T_j) just include ϵ , R_H , $\Delta T_{ad,0}$ and MAT, which can be simply obtained from the reaction recipes or calorimetry tests. This method is developed on the basis of a deep insight into the thermal behaviors for isoperibolic SBRs. Two cases are conducted to verify the validity of the developed approach in this article.

1. Introduction

In the fine chemical and pharmaceutical industries, semibatch reactors (SBRs) are widely used to control the heat generation during the reaction process. To prevent the undesirable thermal runaway accidents, designing thermally safe operating conditions for SBRs is of high importance. In the last decades, a number of works have been reported concerning this issue.

Hugo and Steinbach (1985) are the first who observed that an accumulation of the reactants at low reactor temperature was the main cause of the thermal runaway in homogeneous SBRs. Steensma and Westerterp (1990,1991) developed the boundary diagrams for liquid-liquid reaction systems that followed second order kinetics to assist designing thermal safe operating conditions for SBRs. Recently, Bai et al. (2017) constructed a new set of boundary diagrams for homogeneous semibatch reactions on the basis of their finding that, with respect to QFS and no ignition scenarios, the maximum temperature of synthesis reaction under adiabatic conditions (MTSR) appeared at the stoichiometric point of dosing period, whereas MTSR always occurred before this time point for thermal runaway scenario.

Applying the above methods to design safe operating conditions requires knowledge on the kinetic parameters, at least, the apparent kinetic parameters. However, determination of the kinetic parameters in realistic cases requires professional expertise, especially in the cases of heterogeneous reaction systems, which strongly restricts the application of the above method. Therefore, it is desirable to develop approaches without requirement of kinetic parameters and solubility of reactants to design thermally safe operating conditions. In this sense, Maestri et al. (2017, 2018) developed an integrated criterion aiming to simply monitor SBRs. Guo et al. (2017) recently developed the practical procedures to design thermally safe operating conditions for SBRs without kinetic parameters.

Although a great progress in this research field has been reached, the ambition to develop more reliable and simple approaches to design thermally safe operating conditions for SBRs is perpetual. In this work, a new simple method is developed to facilitate the process of designing safe conditions for liquid-liquid reactions that occur in the continuous phase following a slow reaction regime. This method is developed on the basis of the deep insights into the thermal behaviors of QFS operating conditions for isoperibolic SBRs. The validity of this method will also be verified by two case studies.

2. Dimensionless mathematic model for kinetically controlled liquid-liquid semibatch reactions that occur in the continuous phase

Let's first assume that a single bimolecular kinetically controlled liquid-liquid reaction is carried out in SBRs.



where v_i is the stoichiometric coefficient of the reactant. Component C is assumed to be the product, accordingly the value of v_i with respect to component C can be set to 1. In addition, we assume that reactant B is loaded into the reactor initially and reactant A is dosed at a constant rate until the stoichiometric amount of A is added.

The micro-kinetic rate expression can be described by a generic power law expression:

$$r = k C_A C_B \quad (2)$$

where r is the reaction rate, k is the reaction rate constant, C_i is the molecular concentration of reactant i . To deduce the dimensionless mathematic model, more assumptions should be made. These assumptions could be found elsewhere. (Maestri et al., 2005; Guo et al., 2017) The mass and energy balances for isoperibolic SBRs involving kinetically controlled liquid-liquid reactions that occur in the continuous phase can be written in a dimensionless form as follows:

$$\begin{cases} \frac{dX_B}{d\theta} = v_A DaRE \cdot f \cdot \kappa \\ \frac{d\tau}{d\theta} = \frac{1}{1 + \varepsilon R_H \theta} (\Delta\tau_{ad,0} \frac{dX_B}{d\theta} - \varepsilon(Wt(1 + \varepsilon\theta)(\tau - \tau_j) + R_H(\tau - \tau_D))) \end{cases} \quad (3)$$

3. Theoretical tools to design thermally safe operating conditions for isoperibolic SBRs involving kinetically controlled liquid-liquid reactions that occur in the continuous phase

It is well known that there are three operation regions in isoperibolic SBRs: no ignition(NI), thermal runaway(TR), and QFS(quick onset, fast conversion, smooth temperature profile), which are defined as a result of comparison of the reaction temperature profile with a so-called "target temperature" (T_{ta}) profiles. QFS operating conditions are usually considered as the desirable one in practice. (Steensma and Westerterp, 1990)

Six dimensionless parameters are present in the dimensionless model of isoperibolic SBRs: $v_A DaRE$, ε , γ , R_H , $\Delta T_{ad,0}$ and Wt . If we set the values of ε , R_H , $\Delta T_{ad,0}$ as $R_H=1$, $\varepsilon=0.4$, $\Delta T_{ad,0}=0.7$, then a safety boundary diagram that separate the three scenarios by the so-called Ry (reactivity number) vs Ex (exothermicity number) lines can be constructed following the procedure developed by Steensma and Westerterp, (1990) as shown in Figure.1. Herein, the expressions of Wt , Ry and Ex are

$$Wt = \frac{(UA)_0 t_D}{\varepsilon(\rho c_p)_0 V_0} \quad (4)$$

$$Ry = \frac{v_A DaRE \cdot \kappa|_{\tau_j}}{\varepsilon(R_H + Wt)} \quad (5)$$

$$Ex = \frac{\gamma}{\tau_j^2} \left[\frac{\Delta\tau_{ad,0}}{\varepsilon(R_H + Wt)} \right] \quad (6)$$

Table 1: The corresponding Wt_{min} to different sets of ε , R_H and $\Delta T_{ad,0}$

	ε	$R_H=0.5$	$R_H=1$	$R_H=2$
$\Delta T_{ad,0}=0.5$	0.2	42	41	39
	0.3	26	25	22.5
	0.4	19	18	15
	0.5	14	13	10.5
	0.6	11	10	7.5
$\Delta T_{ad,0}=0.3$	0.2	19.5	18	14
	0.3	11.5	9.5	<5
	0.4	7.5	7	<5
	0.5	5.5	<5	<5
	0.6	<5	<5	<5

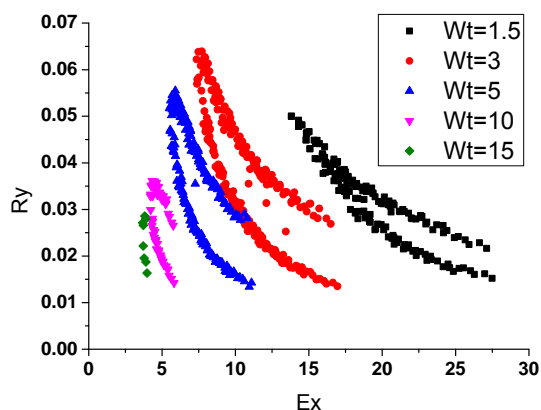


Figure 1: Boundary diagrams for isoperibolic liquid-liquid SBRs in which kinetically controlled reactions occur in the continuous phase. $R_H=1$, $\varepsilon=0.4$, $\Delta T_{ad,0}=0.7$, $0.025 < v_A Da RE < 15$, $27 < \gamma < 45$.

From Figure.1, it can be reasonably expected that if $R_y > R_{y_{min}}$, the isoperibolic SBRs must be in the QFS scenario. Herein, $R_{y_{min}}$ refers to the maximum value of R_y with respect to each R_y vs Ex line in Figure.1. In addition, it is obvious that when the value of Wt is higher than a critical point, for example $Wt=3$, both the values of $R_{y_{min}}$ and the numbers of R_y vs Ex points rapidly decrease. This tendency indicates that the required $R_{y_{min}}$ will decrease with Wt increasing up to be higher than the critical point.

We find that when the value of Wt increases up to 28, the R_y vs Ex points in Figure.1 completely disappear, indicating that no thermal runaway will occur as long as $Wt \geq 28$ for this case. In fact, different sets of ε , R_H , $\Delta T_{ad,0}$ correspond to different values of such critical Wt , which will be denoted to Wt_{min} in the following. Table 1 show the corresponding Wt_{min} to different sets of ε , R_H , $\Delta T_{ad,0}$. This table provides a simple approach to design safe operating conditions for isoperibolic semibatch liquid-liquid reactions that occur in the continuous phase following a slow reaction regime. Once the values of ε , R_H , $\Delta T_{ad,0}$ had been determined, thermal runaway operating conditions can be avoided as long as Wt is higher than the corresponding Wt_{min} .

3.1 Effect of reaction order

It should be kept in mind that the values of Wt_{cri} in Table 1 are developed on the basis of second-order kinetics assumption. Since most of organic reactions may not rigorously obey second order kinetics, discussion of the effect of reaction order on Wt_{cri} is essential. For this purpose, the values of ε , R_H and $\Delta T_{ad,0}$ are set to be constant and the effects of reaction orders of n and m are investigated separately. One typical example of $\varepsilon=0.3$, $R_H=1$ and $\Delta T_{ad,0}=0.5$ is shown in Figure.2.

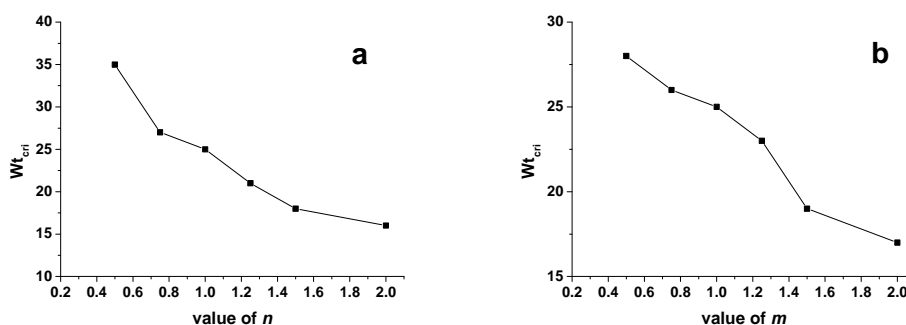


Figure. 2: Effect of kinetic order of (a) n and (b) m on the values of Wt_{cri} for the reactions with $\varepsilon=0.3$, $R_H=1$, $\Delta T_{ad,0}=0.5$

One can see from Figure.2 that the values of Wt_{cri} decrease with the reaction orders increasing, indicating that, for reactions with kinetic orders of $n > 1$ and $m > 1$, no thermal runaway will occur as long as the practical Wt is higher than the Wt_{cri} in Table 1.

For reactions with orders of $n < 1$ or $m < 1$, the Wt_{cri} in Table 1 can't guarantee that thermal runaway event must be avoided.

In fact, the values of Wt_{cri} in Table 1 can also be applied to reactions of an order lower than 2. When the second-order reactions are in QFS situation, the reactions of an order lower than 2 must be also in QFS situation. This can be ascribed to the fact that, when the reactant concentrations are identical, the reaction rates for the reactions of an order lower than 2 are faster than that for the second-order reactions.

In short, though the values of Wt_{cri} in Table 1 are determined on the basis of second-order reactions, they can also be applied to reaction of other kinetic order. In other words, the applicability of the Wt_{cri} in Table 1 is independent on the reaction orders. However, we have to highlight that, when coming crossing the autocatalytic reactions, the Wt_{cri} in Table 1 cannot be applied because autocatalytic reactions show a completely different behavior.

4. The facile approach for designing thermally safe operating conditions

Thermally safe operating conditions also require that the undesirable exothermic side or decomposition reactions, usually accompanied with strong heat and gas generation, are not triggered. Hence, the thermal stability of reactants, products and/or reactive mixtures should be investigated. This can be achieved by carrying out dynamic DSC (differential scanning calorimetry) and ARC (adiabatic rate calorimeter) tests. These thermal analysis techniques can offer the MAT (maximum allowable temperature) parameter, which is defined to prevent the triggering of dangerous decompositions or strongly exothermic side reactions.

Then information on $\Delta T_{ad,0}$, R_H and ϵ should be obtained first. With respect to $\Delta T_{ad,0}$, at least one effective reaction calorimetry (RC1) tests should be conducted to determine the heat of reaction. Then $\Delta T_{ad,0}$ can be calculated by the following expression

$$\Delta T_{ad,0} = \frac{(-\Delta H_r)n_{B,0}}{T_R(\rho c_p)_0 V_0} \quad (7)$$

In fact, RC1 tests can also provide information on heat capacity (c_p) of the reaction mass through a calibration procedure, as a result, R_H can be easily obtained. As for the information on ϵ , it can directly be determined from the specific reaction recipes.

Now that information on $\Delta T_{ad,0}$, ϵ and R_H have been determined, Wt_{min} can be obtained from Table 1. Then the minimum value of dosing period, $t_{D,min}$ can be calculated from Eq. 4, namely

$$t_{D,min} = \frac{Wt_{min} \cdot \epsilon(\rho c_p)_0 V_0}{(UA)_0} \quad (8)$$

Then one can reasonably expect that regardless of the value of T_j , as long as $t_D > t_{D,min}$, no thermal runaway events will occur in the isoperibolic SBRs.

Now that $t_{D,min}$ has been determined, then the other important operating constraint, namely $T_{j,max}$, which means the maximum allowable jacket coolant temperature, should be determined. This can be achieved on the basis of the fact that the maximum of reaction mixture temperature, T_{max} , should be lower than MAT. With respect to no ignition and QFS operations in isoperibolic SBRs, the value of T_{max} must be lower than the maximum value of T_{ta} , namely $T_{ta,max}$, which refers to the target temperature occurs at the initial period. Hence, the above constraint of $T_{max} < MAT$ can be guaranteed as long as $T_{ta,max} < MAT$. The value of $T_{ta,max}$ can be calculated by

$$T_{ta,max} = T_j + \frac{1.05\Delta T_{ad,0}}{\epsilon(R_H + Wt)} \quad (9)$$

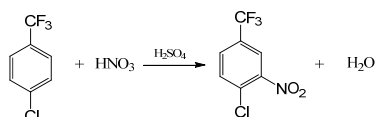
Substituting Eq.9 into the constraint of $T_{ta,max} < MAT$ gives the values of $T_{j,max}$ as follows

$$T_{j,max} < MAT - \frac{1.05\Delta T_{ad,0}}{\epsilon(R_H + Wt)} \quad (10)$$

From the above analysis, one can obtain the fact that as long as the two constraints of $t_D > t_{D,min}$ and Eq.10 are confirmed, thermally safe operating conditions can be ensured. However this still can't ensure that the operations correspond to QFS situation. To obtain QFS operations, operating condition with relatively high values of T_j or t_D can be reasonably considered and then at least one isoperibolic reaction calorimetry test needs to be conduct..

5. Case study

In this case, pure 4-chloro benzotrifluoride (BTF) is dosed into an anhydrous mixture of sulfuric and nitric acid at 9% w/w of nitric acid.



The reaction occurs in the continuous acid phase. Maestri et al. (2009,2016) has experimentally demonstrated that this aromatic nitration is kinetically controlled and reported the reaction rate expression as follows

$$r = 3.228 \times 10^{12} \exp\left(-\frac{87260[\text{J/mol}]}{RT}\right) m_A C_{A,d} C_{B,c} \quad (11)$$

where $C_{A,d}$ and $C_{B,c}$ are the concentrations of 4-chloro BTF in the dispersed phase and of nitric acid in the continuous phase, respectively, and $m_A=0.01$ is the distribution coefficient of 4-chloro BTF, which is the ratio of the concentrations in the continuous and in the dispersed phases). The initial concentrations of 4-chloro BTF in the dispersed phase and HNO_3 in the continuous phase are 7.495 kmol/m^3 and 2.623 kmol/m^3 , respectively.

The reaction temperature must be limited within $80 \text{ }^\circ\text{C}$, because above this temperature an undesired second nitration of the reaction product could partially take place. If the reaction temperature doesn't exceed this threshold value, the overnitration of the product by nitric acid is kinetically negligible even with a large excess of mixed acids.

Table 2: Geometry and operating conditions of the RC1 reactor

Parameters	Value
Volume of the reactor	1.2 L
Volume of continuous phase, V_c	382.9 cm^3
Volume of dispersed phase, V_d	134 cm^3
Mass of mixture acid, m_c	688.05 g
Mass of 4-chloro BTF, m_d	181.3 g
Specific heat capacity of mixture acid, $C_{p,c}$	$1.477 \text{ J/(g}\cdot^\circ\text{C)}$
Specific heat capacity of 4-chloro BTF, $C_{p,d}$	$1.257 \text{ J/(g}\cdot^\circ\text{C)}$
Initial UA	3.15 W/K
Final UA	4.25 W/K

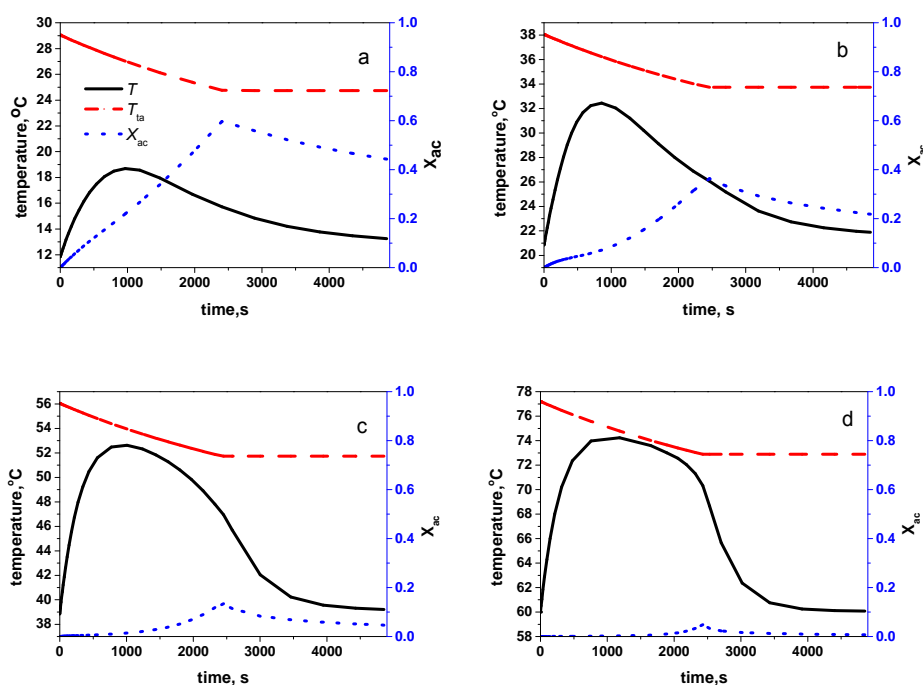


Figure 3: Temperature, target temperature and accumulation profiles of nitration of 4-chloro benzotrifluoride. $\varepsilon=0.35$, $\gamma=35$, $R_H=0.6444$, $v_{ADaRE}=0.986$, $\Delta T_{ad,0}=0.43$, $T_j=T_D$. (a) $T_j=11.85^\circ\text{C}$; (b) $T_j=20.85^\circ\text{C}$; (c) $T_j=38.85^\circ\text{C}$; (d) $T_j=60^\circ\text{C}$.

The reaction is conducted at a laboratory scale calorimetric reactor, that is RC1. The geometry and operating conditions of RC1 are listed in Table 2. The reaction heat is equal to -123 kJ/mol. The initial adiabatic temperature rise can be calculated as follows

$$\Delta T_{ad,0} = \frac{(-\Delta H_r) \times n_{4\text{-chloro BTF}}}{(mc_p)_c} = 129^\circ\text{C} \quad (12)$$

According to the above knowledge, the dimensionless parameters are: $\epsilon=0.35$, $\gamma=35$, $\Delta T_{ad,0}=0.43$, $R_H=0.644$. For the sake of conservation, substitute the values of $\epsilon=0.35$, $R_H=0.5$ and $\Delta T_{ad,0}=0.5$ into Table 1 and give $Wt_{\min}=21.5$. Accordingly, the minimum dosing time ($t_{D,\min}$) can be calculated to be 2427 s. Then the value of $v_A DaRE$ can be calculated to be 0.986. In addition, substituting $MAT=80^\circ\text{C}$ into Eq.10 gives the corresponding value of $T_{j,\max}=62.52^\circ\text{C}$.

The temperature, target temperature and accumulation profiles of nitration of 4-chloro benzotrifluoride at dosing time ($t_D=2427$ s) and four different T_j are shown in Figure.3. It is obvious that none of all the temperature profiles is in the thermal runaway situations. As the value of $T_{j,\max}$ increases, the accumulation decreases. Particularly, the profiles in Figures.3d can be considered as the QFS operation. The maximum reaction temperature T_{\max} in Figure.3d is equal to 77.2°C , which is lower than the $MAT=80^\circ\text{C}$.

6. Conclusion

In summary, a facile approach is developed in this article to design thermally safe operating conditions for liquid-liquid reactions that occur in the continuous phase following a slow reaction regime. The information required for this purpose just include ϵ , R_H and $\Delta T_{ad,0}$, which can be simply obtained from the reaction recipes or an isothermal RC1 test. By substituting these three parameters into Table 1, the value of Wt_{\min} can be determined and the value of $t_{D,\min}$ can also be calculated by Eq.8. To avoid the triggering of the second side or decomposition reaction, the maximum temperature of jacket coolant $T_{j,\max}$ can be derived from Eq.10. In addition, two cases are conducted, which clearly verify the validity of the developed approach in this article. To the end, we would like to underline that the approach in this article are developed on the basis of the kinetics of second order.

Acknowledgments

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