Safe Operating Conditions of isoperiodic Homogeneous Semi-Batch Reaction Based on Parameter Uncertainties Analysis

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Abstract. Proper operating conditions have a significant impact on the process state of semi-batch reaction. However, various error and bias lead to the uncertainties of parameter, which affect process safety of the semi-batch reaction. In this work, the effect of dimensionless parameters dimensionless adiabatic temperature rise ($\Delta\tau_{ad,0}$), Westerterp number (Wt), $\nu_A \mathrm{DaRE}$, dimensionless activation energy (γ), volumetric heat capacity ratio (RH) and relative volume increase (ε) on the temperature of the isoperiodic homogeneous semi-batch reaction are investigated by local sensitivity analysis. The sensitivity of the dimensionless maximum temperature to global parameters is analyzed using the scatter plot method based on Monte-Carlo sampling. Parameter sensitivity results are further quantitatively calculated by the eFAST method. The results indicate that there is a strong linear relationship between the maximum reaction temperature and △τad,0, which exhibits the highest sensitivity index compared to the other parameters. The safety boundary diagram and adiabatic temperature diagram are constructed by considering parameter uncertainty and the effect of parameter uncertainty on the critical criteria is analyzed.

Keywords: Parameter uncertainty; Safety boundary diagram; Adiabatic temperature diagram.

1. Introduction

In the fine chemical and pharmaceutical industry, it is necessary to control the dosing rate to prevent thermal runaway. Therefore, SBR is the most frequently used reactor [1]. However, thermal runaway involving exothermic reactions in the SBRs was still happen [2,3], especially when the operating conditions reached a certain critical value [4].

The operating conditions predicted by the thermal runaway critical criterions as the first line of defense could effectively prevent thermal runaway [5]. Steensma et al. proposed target temperature (Tta) concept to study the operating conditions of SBR based on material accumulation [6]. The dimensionless exothermic number (Ex) and reaction number (Ry) were introduced to construct a generalized safety boundary diagram. However, when the maximum reaction temperature exceeded the maximum allowable temperature (MAT), safe conditions could not be ensured. Therefore, Rota proposed the use of temperature diagrams to estimate the suitable operating conditions when the maximum reaction temperature exceeded the MAT [7,8]. In the case of cooling failure, the adiabatic temperature diagram was established to obtain the corresponding safe operating conditions [9,10].

However, when the safe operating conditions were calculated, the uncertainty of the data can affect the results. These uncertainties were usually described by probability distributions in the actual processing process [11]. Safe conditions caused by uncertainties could be analyzed by parametric uncertainty analysis methods. Which mainly involved polynomial chaos expansion and Monte-Carlo methods [12]. Monte-Carlo method was based on the probability density function to determine the likelihood of a variable. Local and global sensitivity analyses were used to analyze quantitatively the effect of input data on output results. The effect degree of the individual model inputs and the overall model inputs on the output results was investigated by local and global sensitivity analysis [13].

2. Analysis method

2.1 Thermal behavior identification criterions

2.1.1 Safety boundary diagrams

The *Ex* and *Ry* are used to build safety boundary diagrams.

$$Ex = \frac{\gamma}{\tau_{cool}} \frac{\Delta\tau_{ad,0}}{\varepsilon(Wt + R_H)} \tag{1}$$

$$Ry = \frac{\nu_A Da RE \kappa(\tau_{cool})}{\varepsilon(Wt + R_H)} \tag{2}$$

Where Da=κn,mtDCB,0n+m-1 is the Damköhler number, this paper takes the (1,1) order reaction as an example n=m=1,RE=1is the reactivity enhancement factor, κn,m=exp[γ/(1-1/τ)] is the dimensionless reaction rate constant, γ=E/(RTR) dimensionless activation energy, τ=T/TR dimensionless reaction temperature, T is the reaction temperature, TR=300 Kis reference temperature, ε=(Vend-V0)/V0 is the relative volume increment at the end of the addition, RH=(ρCp)D/(ρCP)0 is specific heat ratio of components A and B, △τad,0=(-△HrnB,0)/(vBρ0CP,0V0TR) is dimensionless adiabatic temperature rise, Wt=(UA)0tD/[ε(ρCp)0V0] is the Westerterp number.

The variable parameter is the cooling temperature(τcool), the relationship between exothermicity number and reactivity number can be determined as Ry = Φ(Ex). By changing the values of the parameter sets νADaRE, ε, γ, Δτad,0, different Ry = Φ(Ex) can be obtained. Repeating the same process as above, two curves of safety boundary diagram can be generated.

2.1.2 Adiabatic temperature diagram

The information solely obtained from boundary diagram is insufficient when the reaction temperature exceeds MAT. Adiabatic temperature diagram is used to predict the thermal behavior when cooling failure.

For a set of adiabatic temperature diagrams, the parameters RH, Wt, n and m are fixed and the parameters νADaRE, ε, γ and △τad,0 are assigned a value within an acceptable range. Ry remains constant in a single line. When the data set is generated, the value of τcool can be computed using Ry expression. The values of Ex and MTSR0(dimensionless maximum temperature of the synthesis reaction) from the corresponding expressions and the point of (Ex, MTSR0/τcool) can be obtained. Different data sets are selected by repetition of the same process to produce other points, the curve of (MTSR0/τcool)max= Φ(Ex) can be generated.

2.2 Sensitivity and uncertainty propagation analysis of parameters

The local parameter sensitivity analysis is carried out by the one-factor-at-a-time method. The effect of a single operating parameter on the reaction temperature was analyzed by changing the value of an input parameter of homogeneous semi-batch reaction system. At the same time, Monte Carlo sampling scatterplot method and eFAST method were used to analyze the global parameter sensitivity to determine the effect of parameter interaction on the dimensionless maximum temperature during the semi-batch reaction process.

3. Results analysis

3.1 Parameter sensitivity analysis for semi-batch reaction system

3.1.1. Local parameter sensitivity analysis for semi-batch reaction system

The effect of the operating parameters such as △τad,0, Wt, νADaRE, γ, ε and RH on the semi-batch reaction system is carried out by only changing one parameter. The maximum temperature (Tmax) and the time to reach the maximum temperature (θTmax) are shown in Fig. 1.

As can be seen from Fig. 1 (a)~(f), when △τad,0 of the reaction system increases from 0.5 to 0.7, Tmax changes from 294.4 K to 401 K and θTmax changes from 1.35 to 1.02. When the value of Wt is reduced from 10 to 5, θTmax increases from 315.9 K to 390.7 K, θTmax changes from 1.46 to 0.92. When the value of νADaRE decreases from 15 to 2.5, Tmax increases from 324 K to 370.9 K, θTmax increases from 0.35 to 1.1. When γ, RH and ε change, θTmax and Tmax changes less. It can be seen that the values of △τad,0, Wt, νADaRE have a great effect on the reaction temperature than on RH and ε during the semi-batch reaction.

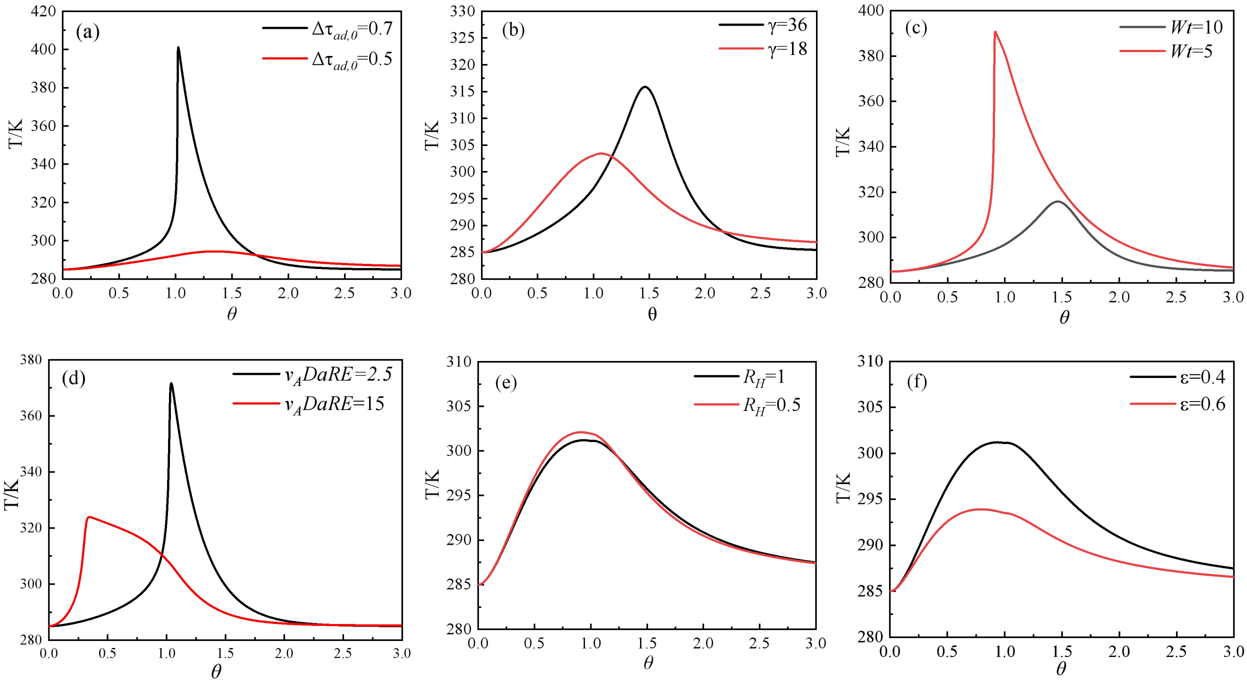

Fig. 1 Effect of parameters on the reaction temperature. T_{cool}=285 K,(a): *Wt*=10，$v_A DaRE$ =2，γ=36，ε=0.4，R_H =1;(b): $v_A DaRE$ =2, $\triangle\tau_{ad,0}$=0.6, *Wt*=10, ε =0.4, R_H =1; (c): $v_A DaRE$ =2, γ=36, $\triangle\tau_{ad,0}$ =0.6, ε =0.4, R_H =1;(d):*Wt* =10, $\triangle\tau_{ad,0}$=0.6， ε=0.4, γ=36, R_H =1; (e): *Wt*=10, $v_A DaRE$ =2, $\triangle\tau_{ad,0}$=0.6, ε=0.4, γ=36 ;(f): *Wt*=10, $v_A DaRE$ =2, $\triangle\tau_{ad,0}$=0.6, γ =36， R_H =1.

3.1.2. Global parameter sensitivity analysis for semi-batch reaction system

The dimensionless maximum temperature for the semi-batch reaction system can be described by the function: τmax=f(x1,x2,x3,x4,x5,x6), τmax is the dimensionless maximum temperatures and x1~x6 are the input parameters △τad,0, Wt, νADaRE, γ, RH and ε for the global parameter sensitivity analysis. Table 1 shows the parameter distribution and value ranges.

Table 1. The input parameter distribution for the global parameter sensitivity analysis

Symbol	Distribution	Statistical parameters	Value range
Wt	Uniform distribution	/	[9,11]
γ	Normal distribution	μ=37.5, σ=2.5	[30,45]
$\triangle\tau_{ad,0}$	Normal distribution	μ=0.4, σ=0.08	[0.1,0.7]
$v_A DaRE$	Uniform distribution	/	[0.025,18]
R_H	Uniform distribution	/	[1,1.2]
ε	Uniform distribution	/	[0.1,0.6]

Dimensionless maximum temperatures are obtained by substituting input sampling samples based on the distribution of the input parameters into balance model of the semi-batch reaction system. Statistical characteristics of dimensionless maximum temperatures are shown in Table 2. When the sample number (nS) exceeds 300, the average reaction temperature value remains relatively unchanged. In order to improve the confidence of the statistical model, the sample size of the scatter plot is set to 500. Scatter plots of the dimensionless maximum temperature of the semi-batch reaction system with the input parameters for are shown in Fig.2. It is observed that maximum reaction temperature exhibits a strong linear relationship with △τad,0, while maximum reaction temperature has a weak linear relationship with the other parameters.

Table 2. Statistical characteristics of dimensionless maximum temperatures

Samples number	Average	Median	Maximum	Minimum	Variance	Standard deviation	Kurtosis
100	1.127	1.118	1.348	1.0166	0.0039	0.063	0.4199
200	1.125	1.119	1.4157	1.0166	0.0044	0.066	1.4788
300	1.125	1.117	1.4157	1.0166	0.0041	0.0637	1.2290
400	1.123	1.114	1.4157	1.0166	0.0039	0.0626	0.9018
500	1.123	1.113	1.4157	1.0166	0.0038	0.0621	0.8255

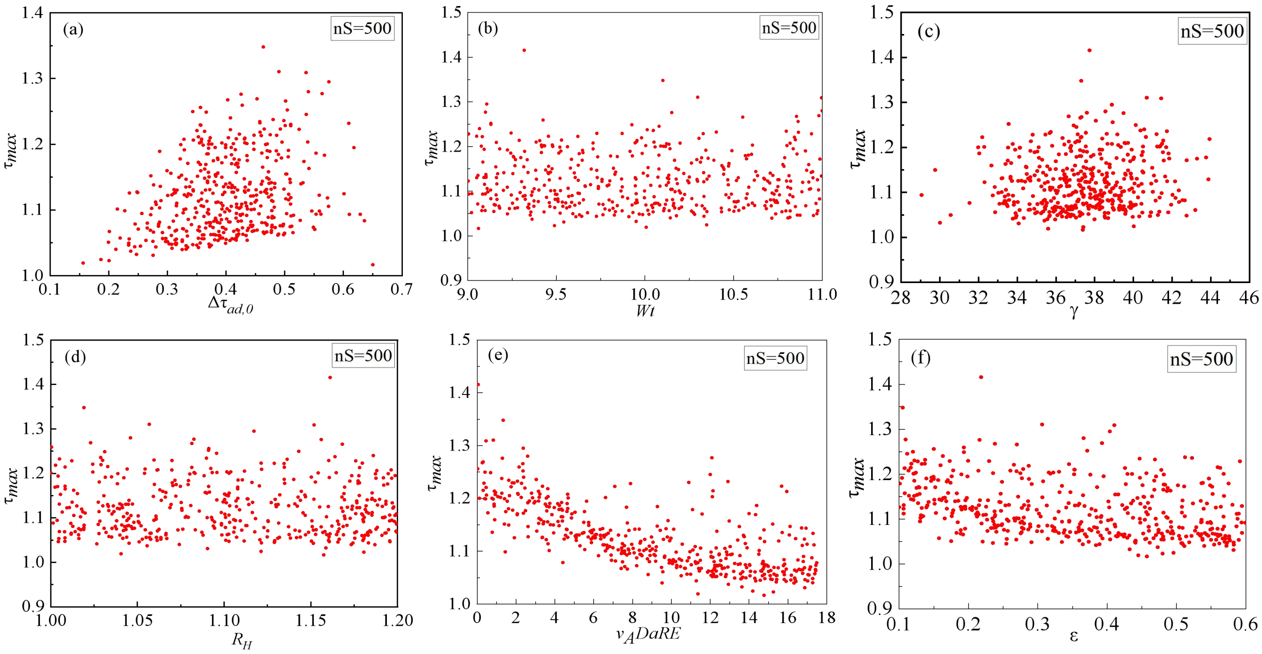

Fig. 2 Scatter plot of the dimensionless maximum temperature of the reaction system with the input parameters. 0.025< $\nu_A DaRE$ <18, 0.1< ε <0.6, 32< γ <45, 0.1< $\triangle\tau_{ad,0}$ <0.7, 9< Wt <11,1< R_H <1.2.

The eFAST method is used to quantitatively investigate the effect of uncertainty parameters on the maximum temperature of the semi-batch reaction system. The first order sensitivities Si and total sensitivities STi of each parameter are shown in Fig. 3. It can be seen that the order of STi is the same as that of Si: △τad,0> Wt >γ>νADaRE >RH>ε. △τad,0 is the highest sensitive parameter, it has the greatest effect on the maximum reaction in the semi-batch reaction system. △τad,0, Wt, γ and νADaRE have a significant effect on the maximum temperature of the semi-batch reaction system, whereas RH and ε have little effect on the maximum reaction temperature. The global sensitivity analysis shows that adiabatic temperature rise, activation energy and heat transfer coefficient have a significant effect on the reaction temperature.

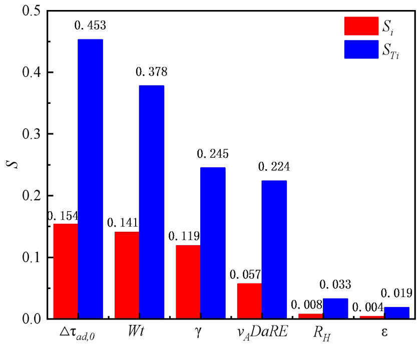

Fig. 3 The sensitivity analysis for each parameter.

3.2 The effect of parameter uncertainty on thermal runaway criticality criterion

3.2.1 The effect of parameter uncertainty on safety boundary diagram

The corresponding safety boundary diagrams are constructed by considering the uncertainty of the parameters. Fig. 4 shows the effect of parameter uncertainty on the safety boundary diagram. When taking the 5th percentile of the reaction heat, activation energy and heat transfer coefficient, the values of Exmin increase, the values of RyQFS decrease compared with the actual value. The TR region becomes smaller and the IS region becomes larger. When taking the 95th percentile of the parameters, the results opposite.

When RH=1, Wt=5 and RH=1, Wt=20, the TR region and IS region change more obvious. The inherently safe region of the safety boundary diagram overlaps with the thermally runaway region, which may lead to misjudgment of the reaction thermal safety state. If the reaction occurs near the critical position, ignoring parameters uncertainty during the reaction may lead to the wrong judgment of the thermal safety state, resulting in thermal runaway.

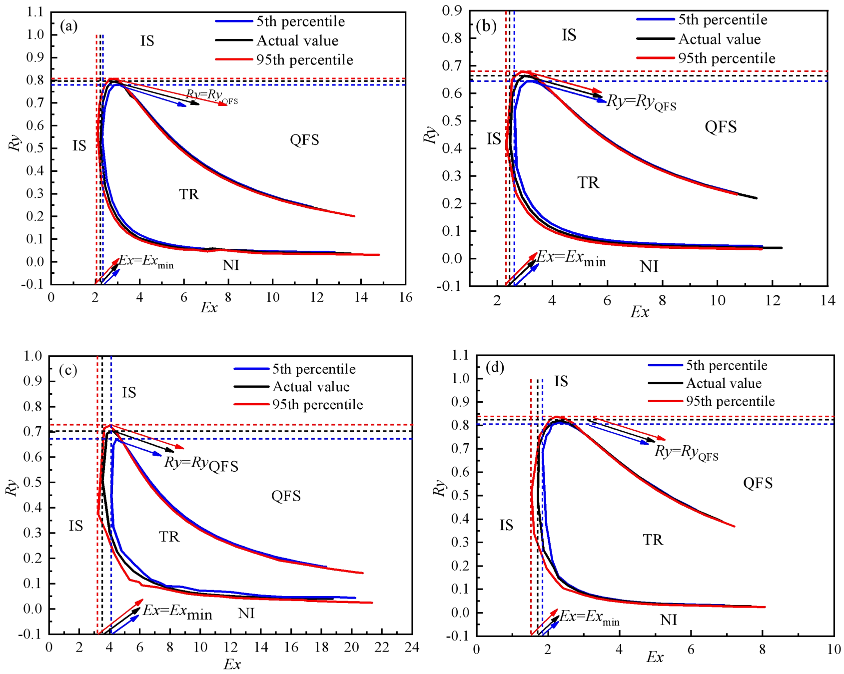

Fig. 4 The effect of parameter uncertainty on the safety boundary diagram. $0.025< v_A DaRE <18$, $0.1< \varepsilon <0.6$, $32< \gamma <45$, $0.1< \triangle\tau_{ad,0} <0.7$. (a)$Wt$=10, R_H=1, (b)Wt=10 R_H=2, (c)Wt=5, R_H=1, (d)Wt=20, R_H=1.

3.2.2 The effect of parameter uncertainty on adiabatic temperature diagram

The results are shown in Fig. 5. The 5th and 95th percentiles of △τad,0, γ and Wt are considered in the model calculations to analyze the effect of the parameter uncertainty on the adiabatic temperature diagram. It can be observed that the curve trend of the adiabatic temperature diagram does not change much compared to the adiabatic temperature diagram without considering the parameter uncertainty. However, with the increase of Ex and the decrease of Ry, the effect of parameter uncertainty on (MTSR0/τcool)max is more obvious.

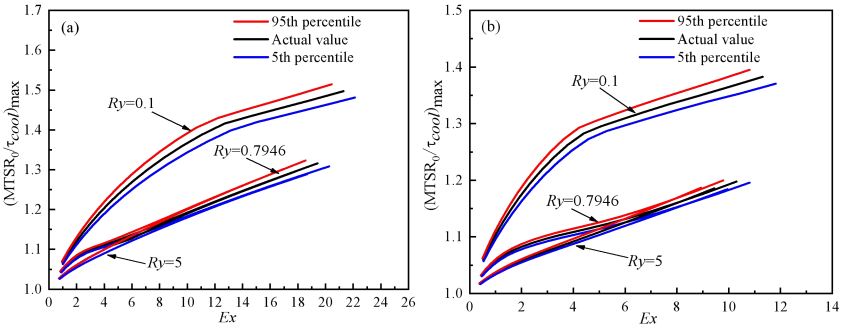

Fig. 5 The effect of parameter uncertainty on the adiabatic temperature diagram. 0.025< $\nu_A DaRE$ <18, 0.1< ε <0.6, 32< γ <45, 0.1< $\triangle\tau_{ad,0}$ <0.7, R_H=1, (a) *Wt*=5, (b) *Wt*=10.

4. Summary

In this work, the effect of parameter uncertainty on the critical conditions of thermal runaway in semi-batch homogeneous reactions is studied. The effect of △τad,0, Wt, νADaRE, γ, RH and ε on the temperature are investigated by local and global sensitivity analysis. The local sensitivity analysis and the global sensitivity analysis show △τad,0, Wt and νADaRE have great effect on the reaction temperature. The effect of parameter uncertainty on the safety boundary diagram and adiabatic temperature diagram is analyzed by numerical simulation. The results show that the parameter uncertainty may affect the thermal safety state of the reaction.

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