



## Kinetics-based simulation approach to evaluate thermal hazards of benzaldehyde oxime by DSC tests



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### ABSTRACT

To evaluate thermal hazards of benzaldehyde oxime (BO), dynamic experiments were carried out by differential scanning calorimeter (DSC) to obtain thermodynamic parameters. A kinetic model was evaluated by fitting experimental curves. Finally, thermal behaviors under isothermal, adiabatic and conditions of limited intensity of heat exchange were simulated. The results indicate that BO decomposes rapidly in liquid phase, and releases a large amount of thermal energy. The reaction model of full autocatalysis has been created comprising two parallel stages: initiation stage of the  $n$ -order type, and the autocatalytic stage. Contribution of the two stages are also presented. Simulation results demonstrate low stability of BO in liquid phase, it decomposes at low temperature right above melting and results in thermal explosion even for a small container. Estimation of time to maximum rate (TMR<sub>ad</sub>) demonstrates the operational temperature should not be higher than 42 °C during production and usage.

### 1. Introduction

The self-reactive substance is defined as a substance that decomposition or intermolecular oxidation-reduction reactions may occur without the aid of external oxygen, representing special class of hazardous chemicals. [1,2].

Numerous severe accidents (thermal explosion, fire) involving self-reactive substances have been triggered by factors such as external heating, mechanical impact, etc. Self-accelerating decomposition can occur under the conditions of natural storage, releasing large amounts of thermal energy, or producing flammable gases, resulting in runaway accidents [3–5]. In order to avoid the thermal explosion incidents caused by self-heating during manufacturing, usage, transportation and storage of self-reactive substances, it is necessary to properly assess their thermal hazards. Therefore, the study on the thermal decomposition characteristics and the reaction kinetics of self-reactive substances is of great significance for providing safe production, storage and transportation of chemical products, preventing disaster and mitigating their consequences, and protecting people's property [6,7].

Benzaldehyde oxime (BO) is a widely used material in the chemical synthesis reactions to produce various compounds, mostly applied in medicine and agriculture. In addition, more and more benzaldehyde oxime-based compounds have been found involving a variety of biological activities, including analgesia, lipid-lowering, vascular

expansion, progesterone, anti estrogen, herbicides, anti fungal, anti bacterial, anti-virus and other aspects. Therefore, immense application value of benzaldehyde oxime-based compounds has been gradually recognized. As a self-reactive substance, BO is prone to a highly exothermic runaway reaction. During the manufacturing process, usage, transportation and storage, thermal decomposition will be induced if the temperature cannot be controlled properly, then it will release a large amount of heat and produce flammable gases, leading to thermal explosion. At present, the research of BO is mainly focused on the molecular structures and syntheses. K. Jalaja et al. [8] researched the molecular structure and spectroscopic characterization of 4-[2-(5-Ethylpyridin-2-yl) ethoxy] BO, and investigated its reactive properties by DFT calculations and molecular dynamics simulations. M.G. Okala Amombo et al. [9] studied the reactions of lithiated methoxyallene with different oxime derivatives, such as E-benzaldehyde oxime. However, there are few reports paying attention to its thermal hazards and reaction model. J.P. Deng et al. [10] mainly studied the thermal behavior of BO by using high-performance adiabatic calorimeter (PHI-TECII), determined the self-accelerating decomposition temperature (SADT) for the standard packages of 25 kg BO, calculated the pressure-controlled and temperature-controlled bottom relief areas by the Boyle's Law and the Tangren's Law, respectively. But the decomposition kinetic model of BO has not been studied.

The main purpose of this paper is to evaluate thermal hazards of BO

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by applying calorimetric methodology and kinetics-based simulation. In this study, differential scanning calorimeter (DSC) was employed for implementing dynamic scanning experiments to obtain the thermodynamic parameters of BO decomposition, such as overall reaction heat, and temperature range of the reaction. Then the reaction kinetic model was evaluated on the basis of experimental data at several heating rates by applying non-linear optimization method. As a result, the structure of the kinetic model was identified and the corresponding kinetic parameters were estimated. Finally, thermal behaviors under isothermal, adiabatic and conditions of limited intensity of heat exchange were simulated separately based on the reaction model. Furthermore, thermal explosion characteristics such as induction period and some hazard indicators such as time to conversion limit (TCL) and adiabatic time to maximum rate (TMR<sub>ad</sub>) were estimated to provide effective safety information concerning liquid BO during production and usage [11].

## 2. Experimental and methods

### 2.1. Sample

Benzaldehyde oxime (E-type, 97%) used in the tests was a white crystal, with a molecular formula of C<sub>7</sub>H<sub>7</sub>NO, produced by SEGEMA.

### 2.2. Apparatus

All the tests were carried out by a heat flux differential scanning calorimeter (DSC131 Evo), manufactured by SETARAM, France. Stainless steel high-pressure crucible, which can resist high pressure of 15 MPa, was used as test cell. About 2–3 mg of the sample was added in the crucible and sealed. The flow of nitrogen was set as 100 ml/min to provide a similar environment for each test. DSC was performed in the temperature range 20–300 °C at the heating rates of 1, 2, 4, 10 K/min.

### 2.3. Kinetics-based simulation approach

The kinetics-based simulation is an advanced and effective approach for solving complex challenge with reliable estimation of thermal hazards. As the name suggests, the first step is evaluation of the kinetic model from experimental data. As long as the precise reaction kinetics is obtained, thermal hazards under various conditions could be predicted. Being free of essential simplifications, this approach can be applied to a wide variety of practical problems [12,13]. Of course, kinetics-based simulation approach is not for complete replacement of the simplified empirical methods. On the contrary, they mutually complement each other. For example, kinetic model can be estimated and simulation results can be verified by the experiments, at the same time, the experimental results can also be supplemented through kinetics-based simulation, and simulation will be most helpful when the potential danger of a reaction or process has been revealed by using simplified empirical methods [14]. In this paper, kinetics-based simulation was accomplished by employing the thermal safety software (TSS) [15].

The thermal safety software (TSS) series, developed by CISP Company in Russia, could be employed to process experimental data, to estimate reaction kinetics, to simulate the reactions under various operation conditions, and so on. The key step is the creation of kinetic model. At first a plausible reaction model is created by taking into account the features of experimental data. Then the model's parameters are estimated by non-linear optimization method with the aim to provide the best possible fit of experimental data. The detailed information about kinetic model can be found in the reference [16].

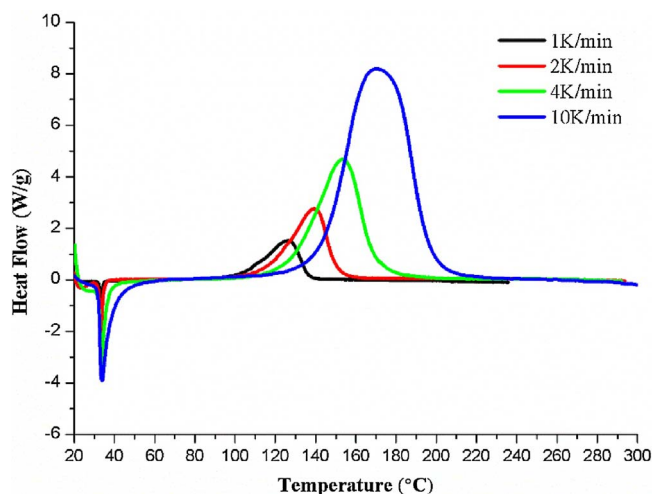


Fig. 1. Dynamic DSC curves of BO.

## 3. Results and discussion

### 3.1. DSC experimental results

Fig. 1 shows DSC curves of BO at heating rates of 1, 2, 4 and 10 K/min. The characteristic parameters of thermal decomposition are shown in Table 1.

As seen in Fig. 1, there are two distinct peaks on the DSC curves during the linear heating. According to the physical properties of BO, the melting temperature is about 30–33 °C. The first peak is an endothermic peak of phase transition, which is usually considered as the melting of BO. Therefore, BO should be stored at temperatures below the melting. The second is an exothermic peak of decomposition. It means that the decomposition of BO occurs in liquid phase. Combining Fig. 1 and Table 1, it can be seen that with the increase of heating rates, the onset decomposition temperature ( $T_0$ ), peak temperature ( $T_p$ ), and maximum heat production rate of BO increase. The average of heat production is 1828 J/g, in addition, incondensable gases are generated in the decomposition of BO [10], according to the criterion in the reference [17], severe consequences will be caused once the thermal runaway reaction of BO occurs.

### 3.2. Thermal decomposition kinetics

DSC data undergo all the necessary steps of initial data processing to provide reliable basis for kinetics evaluation [18–21]:

- (1) correction of original data on the position of experimental base line (blank subtraction) to mitigate the impact of device;
- (2) reconstruction and subtraction of the “under peak” base line;
- (3) reconstruction of sample temperature: the sample temperature deviate from the reference (linear) temperature, due to part of the heat generated by the reaction is accumulated in the sample, reconstruction of the sample temperature is to calculate the real sample temperature taking into account the deviation;

Table 1  
Thermal decomposition characteristic parameters of BO.

| $\beta$ (K/min) | $m$ (mg) | $T_{endo}$ (°C) | $\Delta H_{endo}$ (J/g) | $T_0$ (°C) | $T_p$ (°C) | $\Delta H_d$ (J/g) |
|-----------------|----------|-----------------|-------------------------|------------|------------|--------------------|
| 1               | 2.35     | 29.6            | −124.7                  | 87.9       | 126.6      | 1830.34            |
| 2               | 2.30     | 29.8            | −109.5                  | 95.5       | 139.3      | 1814.40            |
| 4               | 2.31     | 29.6            | −113.9                  | 105.5      | 153.4      | 1838.64            |
| 10              | 2.31     | 29.7            | −120.5                  | 114.2      | 170.2      | 1832.26            |

(4) data deconvolution, the time constant is estimated by dynamic calibration of the instrument and has been found equal to 30 s.

Kinetic analysis of data involved two steps. At first the Friedman isoconversional method was applied for preliminary analysis. Then the reaction kinetic model has been created by applying non-linear optimization method.

### 3.2.1. Friedman method

The Friedman method was employed to evaluate the model-free kinetics without any assumption of reaction model. Friedman [22] proposed to apply the logarithm of the conversion  $d\alpha/dt$  as a function of the reciprocal temperature at any conversion, as shown in Eq. (1) and Eq. (2):

$$d\alpha/dt = Af(\alpha)\exp(-E/RT) \quad (1)$$

$$\ln(d\alpha/dt) = \ln A + \ln f(\alpha) - (E/RT) \quad (2)$$

where  $A$  is pre-exponential factor,  $E$  is activation energy,  $f(\alpha)$  is the reaction model.  $f(\alpha)$  is a constant at any fixed value of conversion  $\alpha$ , and the dependence of  $\ln(d\alpha/dt)$  on  $1/T$  shows a straight line with the slope equal to  $(-E/R)$  and the intercept equal to  $\ln[Af(\alpha)]$ . Therefore, linear fitting was performed to estimate the effective activation energy value for the set of different conversions. For complex multi-stage reactions, this method gives the effective activation energy which depends on conversion. Furthermore, for single-stage reaction with known function  $f(\alpha)$ , the pre-exponential factor can be calculated.

The relationship between the activation energy  $E$ ,  $\ln[Af(\alpha)]$ , and conversion  $\alpha$  for BO are shown in Fig. 2.

The conversion at the initial and termination stage of decomposition was greatly influenced by the selection of baseline and the noise of device [23,24], thus the conversions within the range 0.1–0.9 are usually used for calculation. It can be seen from Fig. 2 that the effective activation energy of BO is mainly degressive, ranging from 68.9 to 41.3 kJ/mol in the above mentioned range of conversions. The  $\ln[Af(\alpha)]$  ranges from 13.3 to 4.7 in the same range of the conversions. It implies that the decomposition of BO is a complex reaction, which can't be presented in a single-step kinetic model.

### 3.2.2. Reaction kinetic model

Friedman method can be used to obtain the activation energy value for each conversion. It doesn't require any ideas about reaction model and initial guess for kinetic parameters. Therefore, it can be applied for complex reaction, and model-free kinetics is capable of good approximation of complex experimental data. However, "Model-free" methods of kinetic analysis don't give final results but postpone the problem of identifying a suitable kinetic model until an estimate of the activation energy has been made [25]. It doesn't give any information about

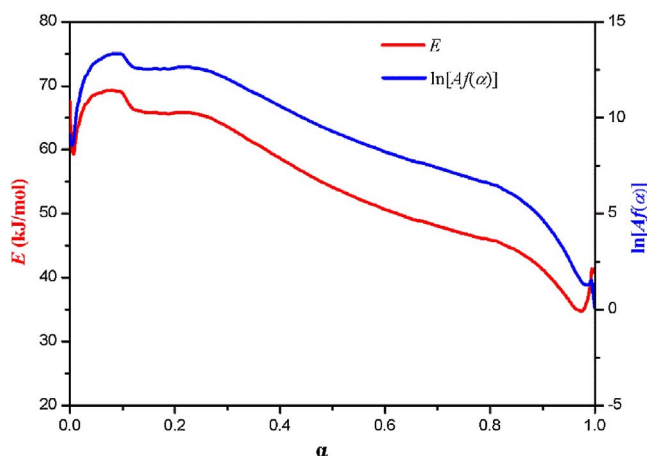
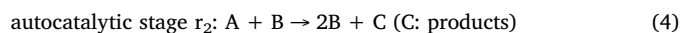
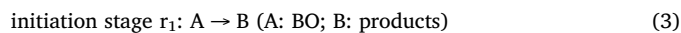


Fig. 2.  $E$  and  $\ln[Af(\alpha)]$  vs  $\alpha$  for BO.

reaction mechanism, especially for multi-stage reaction, it is hard to distinguish between self-accelerating and non-accelerating stages.

Accordingly, kinetics-based simulation approach was applied to estimate a reliable kinetic model of the BO decomposition by employing TSS software.

As shown in Fig. 1,  $T_0$  increases with the increase of heating rates, this characteristic of dynamic DSC experimental results clearly reveal autocatalytic nature of the reaction [26], therefore the model of full autocatalysis is chosen for describing thermal decomposition of BO in liquid phase. It is represented by Eq. (3)–Eq. (8):



$$d\alpha/dt = r_1 + r_2 \quad (5)$$

$$r_1 = A_1 \exp(-E_1/RT)(1 - \alpha)^{n_1} \quad (6)$$

$$r_2 = A_2 \exp(-E_2/RT)\alpha^{n_2}(1 - \alpha)^{n_2} \quad (7)$$

$$dQ/dt = Q_1 r_1 + Q_2 r_2 \quad (8)$$

where  $r_i$  and  $Q_i$  denote reaction rate and heat production of each stage respectively,  $i = 1$  and 2.

The kinetic parameters of the model have been estimated by applying nonlinear optimization method so as to provide best possible fit of experimental results.

Fig. 3 and Fig. 4 demonstrate the comparison between DSC experiments and TSS simulation results of heat production rate and heat production at various heating rates for BO, respectively.

According to Fig. 3 and Fig. 4, the TSS simulation results show a reasonable fitting of the DSC experimental data under various heating rate. It indicates that the reaction model is suitable for BO. Therefore, the decomposition of BO is considered two parallel reactions. The initiation stage is the  $n$ -order reaction, and the second stage is the autocatalytic reaction. The kinetic parameters of the reaction model for BO are shown in Table 2.

In order to more clearly reveal the reaction kinetic model of BO decomposition, Fig. 5 demonstrates the contribution of two stages in reaction progress and heat production rate at various heating rates.

As seen in Fig. 5, the contribution of two stages at various heating rates provide the similar trend. For example, at the heating rate of 4 K/min, in the beginning, contribution of the first stage prevails, reaction rate of the first stage is faster than the second stage, and therefore the

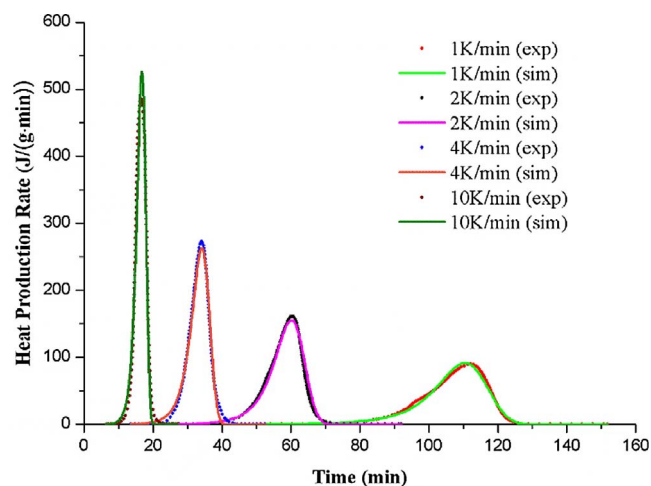


Fig. 3. Comparison between experiments and simulation of heat production rate vs time for BO.

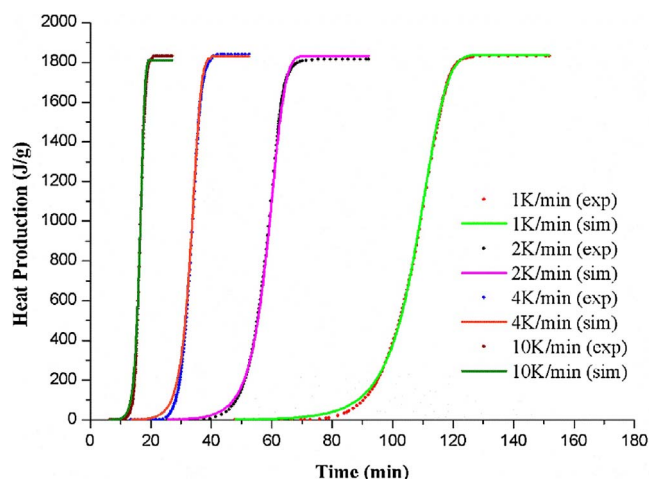


Fig. 4. Comparison between experiments and simulation of heat production vs time for BO.

Table 2  
Kinetic parameters of the reaction model for BO.

| Parameters | Units  | 1st stage ( $n$ -order)      | 2nd stage (autocatalytic)    |
|------------|--------|------------------------------|------------------------------|
| $A$        | 1/s    | $(2.39 \pm 0.04) \cdot 10^8$ | $(5.77 \pm 0.12) \cdot 10^3$ |
| $E$        | kJ/mol | $91.5 \pm 2.0$               | $48.0 \pm 1.0$               |
| $n_1$      | –      | $1.70 \pm 0.03$              | –                            |
| $n_{21}$   | –      | –                            | $1.00 \pm 0.02$              |
| $n_{22}$   | –      | –                            | $0.80 \pm 0.02$              |
| $Q$        | J/g    | $1720.6 \pm 30$              | $1853.4 \pm 35$              |

effective activation energy predicted by Friedman method at small conversions is close to  $E_1$ . After generation of some amount of product-catalyst, contribution of the second stage with smaller activation energy increases. Then after the conversion reaches 0.2, contribution of the second stage prevails, and its reaction rate becomes faster. Finally, the second stage becomes dominant after the conversion reaches about 0.7. Accordingly, this analysis explains the decline of the effective activation energy along the conversions predicted by Friedman isoconversional method. It means the results of model-based kinetic analysis are in good accord with the preliminary results obtained by model-free kinetics.

### 3.3. Thermal hazards analysis

It is known that the DSC experimental results can't be directly applied to industrial production due to heat accumulation in large amount of substance, while DSC experiments are carried out with mg-scale samples. However, the kinetic model can be employed for prediction and simulation to evaluate the thermal hazards, because the kinetics of any reaction doesn't depend on the sample mass [27].

Based on the kinetic model, applying numerical simulation by means of TSS software, thermal behaviors of BO under different conditions are predicted.

#### 3.3.1. Prediction of the isothermal conditions

Autocatalytic reactions are considered to be hazardous because of unexpected initiation and sudden heat evolution even in an isothermal environment [28]. To evaluate the thermal hazards of BO in liquid phase during production and usage, isothermal condition at low temperature should be predicted. In this simulation, it is assumed that all the reaction heat is removed in time, and the sample temperature remains ideal isothermal.

Fig. 6 shows the heat production rate and conversion vs time of BO under isothermal conditions at different temperatures. The isothermal

curves illustrate strong autocatalysis. The simulation results demonstrate that BO will decompose even at quite low temperature right above melting. According to Fig. 6 (b), the conversion will reach 100% within about 2.5 days under isothermal condition at 40 °C.

Assessment of thermal stability of a substance lies in evaluating the dependency of time instant (time to conversion limit, TCL) when conversion of a reaction reaches some predefined value-conversion limit under isothermal conditions [29]. In order to evaluate the thermal stability of BO when temperature jumped above melting, TCL was estimated.

Fig. 7 indicates the dependencies of TCL on temperature of BO calculated on the basis of the kinetic model. The results clearly show that the conversion will reach the limit value (10%) after 1.18 d at 35 °C. It means that BO has very low stability in liquid phase, the product will be rapidly consumed after melting.

#### 3.3.2. Estimation of the thermal explosion

As it was shown that decomposition of BO is quite fast at 40 °C isothermal condition, which even provided that all the reaction heat is removed from the reacting system. When heat removal from the container with the product is impeded, it results in heat accumulation and temperature increase. In this case the reaction can proceed in violent explosive mode. Therefore estimation of the thermal explosion characteristics such as critical temperature and induction period are of significant practical interest.

Thermal explosion has been simulated by ForK software (one module of TSS series), assuming uniformity of the liquid product (the well stirred container) fill in a cubic box which 10 cm side, thermal inertia  $\emptyset$  is assumed to be 1 due to the heat capacity of sample is much bigger than of container. Heat exchange with environment obeyed the Newton law with heat transfer coefficient 4.4 W/m<sup>2</sup>/K. Fig. 8 indicates the temperature vs time for decomposition of BO at different environment temperatures of 35, 40 °C.

The simulation showed that even for the small 1 l container with heat exchange surface 0.06 m<sup>2</sup> thermal explosion occurs at lowest possible temperature 35 °C which exceeds only slightly the melting temperature. This system turned out to be well within explosion domain, therefore even 10 times more intensive heat exchange couldn't prevent explosion. As seen in Fig. 8, estimation of induction period for 35 °C is about 1300 min, for 40 °C is about 900 min.

These calculations demonstrate that sudden elevation of outer temperature above melting point during transportation or storage is very dangerous, hence very strict measures should be undertaken firstly to minimize the probability of loss of storage temperature control, secondly to ensure efficient and fast means of cooling containers with BO in the case of accidental increase of temperature.

#### 3.3.3. Evaluation of the adiabatic runaway reaction

Adiabatic runaway reaction should be evaluated for analyzing thermal hazards because it represents the most dangerous conditions. Simulation of the reaction course under ideal adiabatic condition ( $\phi = 1$ ) has been performed. Fig. 9 shows the temperature vs time for decomposition of BO at different onset temperatures 40, 50, 60, 70 °C.

As shown in Fig. 9, the higher the starting temperature, the shorter the adiabatic induction period, and the higher starting temperature will result in the self-heating rate of thermal decomposition of BO increasing exponentially. Moreover, the adiabatic temperature rise is about 860 °C, the severity of runaway reaction is catastrophic according to Zurich hazard analysis (ZHA). During a chemical process in a batch reactor with liquid BO, great care should be taken to prevent cooling failure.

Further analysis of thermal hazards of BO can be implemented by estimating adiabatic time to maximum rate ( $TMR_{ad}$ ).  $TMR_{ad}$  is determined from the self-heating rate ( $dT/dt$ ) for a reaction course as the time instant that corresponds to maximal value of ( $dT/dt$ ). The dependency of  $TMR_{ad}$  on the onset temperature estimated by simulation based on the kinetic model is shown in Fig. 10.

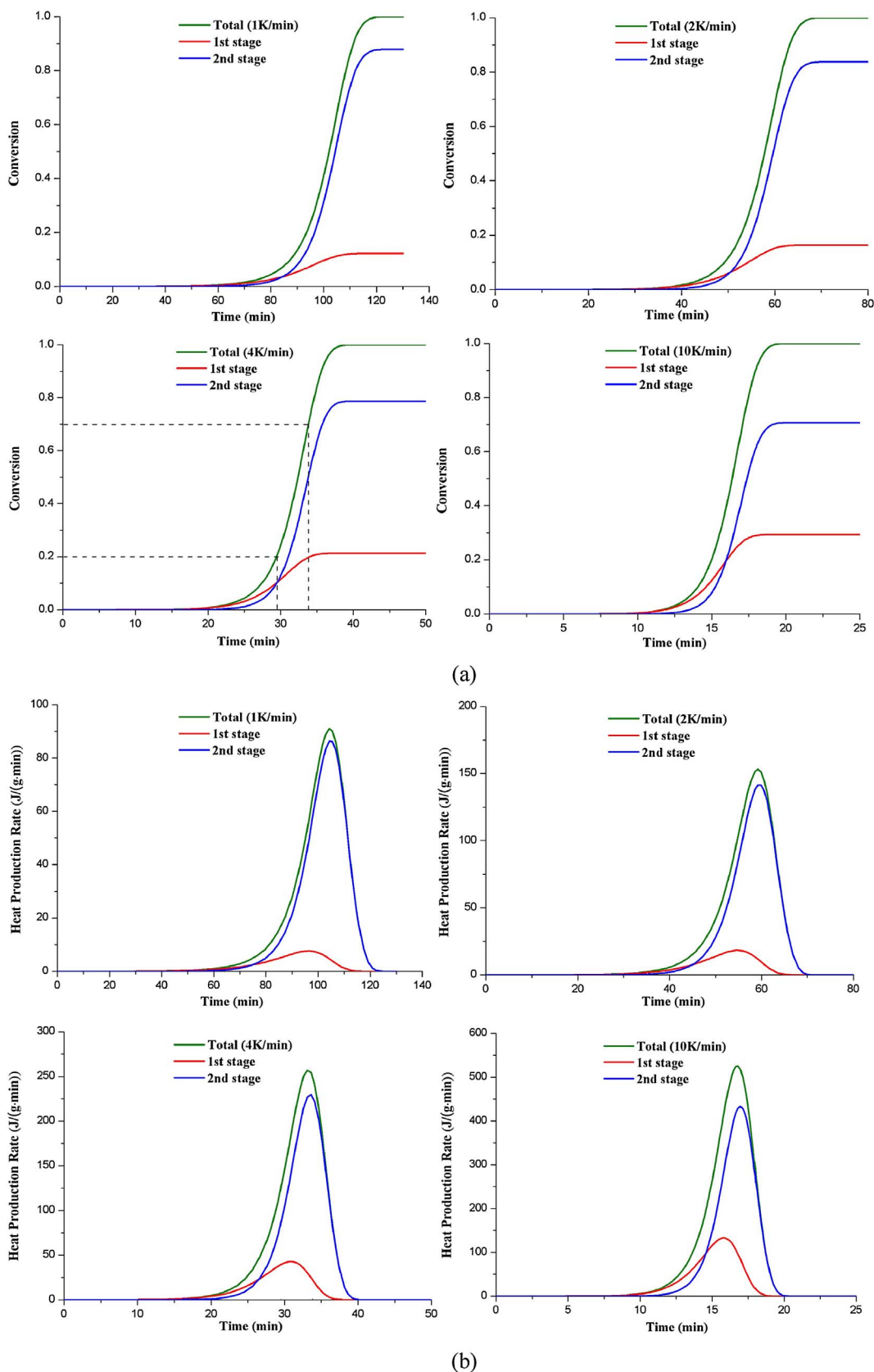


Fig. 5. Contribution of two stages in (a) reaction progress and (b) heat production rate at various heating rates for BO decomposition.

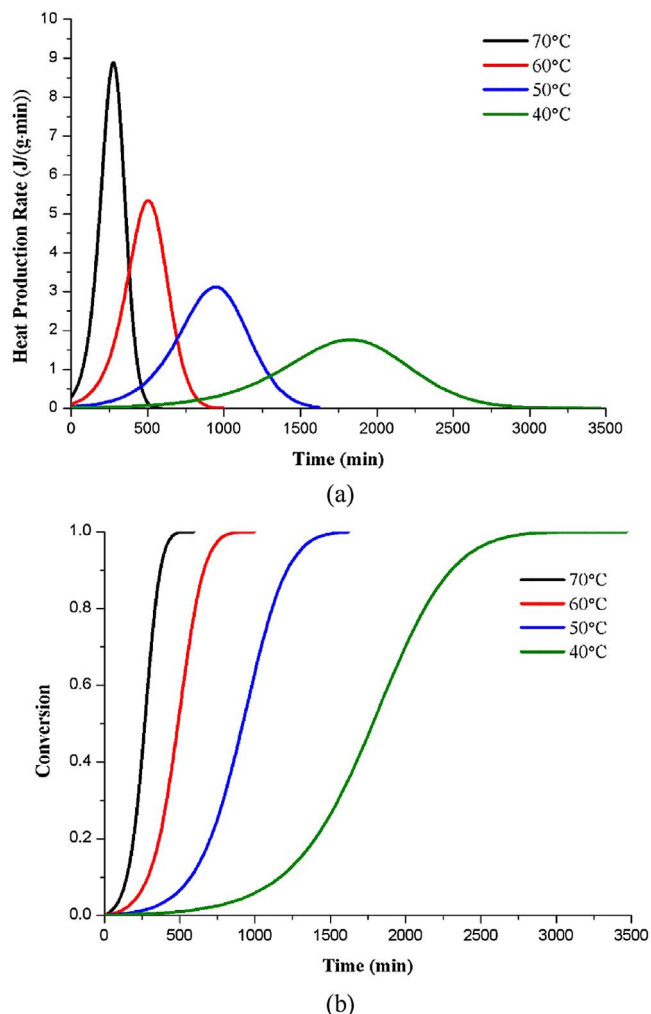


Fig. 6. (a) Heat production rate and (b) conversion vs time of BO under isothermal conditions.

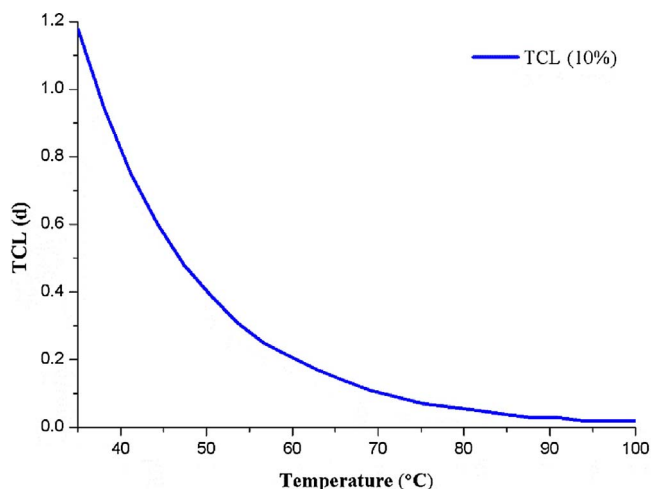


Fig. 7. Time to conversion limit (TCL) vs temperature of BO.

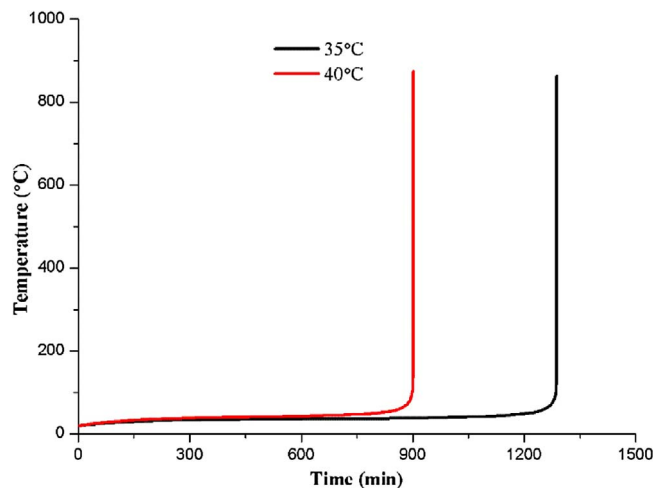


Fig. 8. Temperature vs time of BO under general conditions.

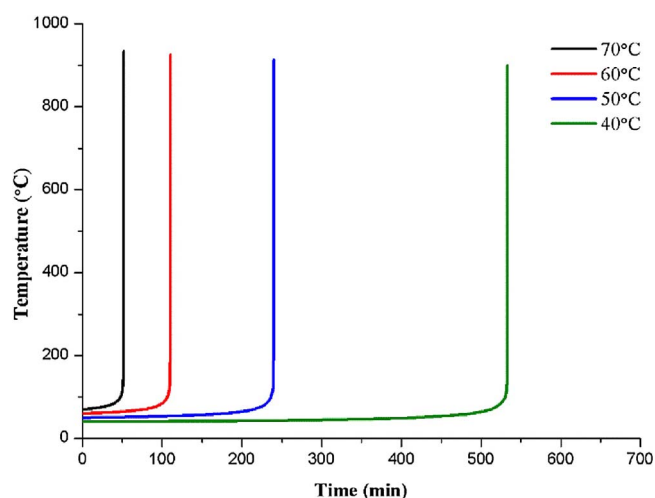


Fig. 9. Temperature vs time of BO under ideal adiabatic conditions.

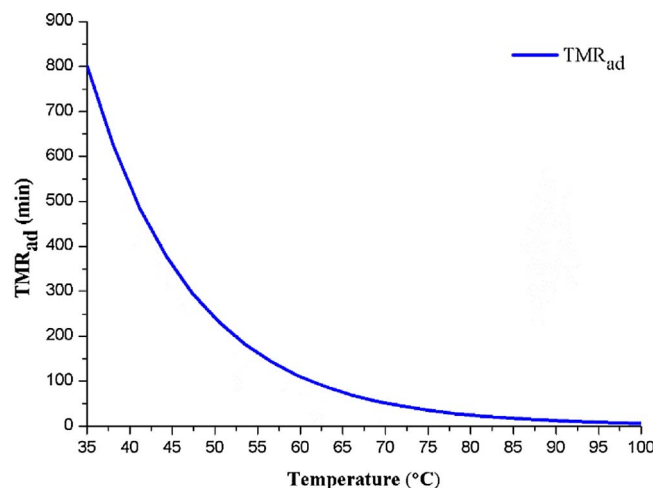


Fig. 10. Adiabatic time to maximum rate (TMR<sub>ad</sub>) vs temperature of BO.

According to the criteria for the assessment of an accident probability suggested by Stossel [17], the probability is considered to be high if TMR < 8 h. Therefore, operational temperature of BO in liquid phase during production and usage should not be higher than 42 °C.

#### 4. Conclusions

The thermal hazards of BO can be successfully evaluated by combining calorimetric experiments and kinetics-based simulation. In this study, thermal decomposition characteristics and reaction model of BO

were determined. Furthermore, thermal behaviors under different conditions were predicted based on the kinetic model. The conclusions were shown as follows:

(1) Under a linear heating condition, endothermic phase transition occurs followed by rapid exothermic decomposition of liquid BO. It should be stored at low temperature that does not exceed the melting point 30 °C.

(2) According to the Friedman method, the effective activation energy of BO is ranging from 68.9 to 41.3 kJ/mol, which implies the decomposition of BO is a multi-step reaction.

(3) The kinetics model of full autocatalysis comprising two parallel stages is capable of proper fitting all the available experimental data. The first initiation stage is represented by the n-order reaction, and the second stage is the autocatalytic reaction. The kinetic parameters are estimated by applying non-linear optimization method.

(4) Reaction course simulation of BO under isothermal condition demonstrates strong self-acceleration and low stability in liquid phase. It will be rapidly consumed after melting.

(5) Simulation results demonstrate that even for a small container with efficient heat removal, thermal explosion always occurs when the ambient temperature exceeds the melting point. Thermal explosion characteristics of BO are estimated to provide safety information.

(6) Simulation of ideal adiabatic condition shows a high adiabatic temperature rise, which means the severity of runaway reaction is catastrophic. According to  $TMR_{ad}$ , the operational temperature of BO in liquid phase during production and usage should not be higher than 42 °C.

In this paper, the kinetic model of BO was estimated at the temperature that exceeds phase transition. Accordingly, the predicted results under all conditions are suitable for proper choice of safety production and usage of liquid BO. Further study should be done to evaluate the thermal stability of solid BO during storage and transportation.

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