

Thermal stability of the DPT reaction system synthesized by acetic anhydride method

Zhi Wang¹, Shaohua Jin¹, Guanghui Gu², Xinping Zhao², Yulin Wei²,
Zhiyan Lu², Kun Chen*^{1, a}, Shusen Chen¹

¹ Beijing Institute of Technology, School of Materials, Beijing 100081;

² Gansu Yinguang Chemical Industry Group Co., Ltd., Baiyin, 730900, Gansu.

^a kchen@bit.edu.cn

Abstract. The adiabatic decomposition of a reaction mixture prepared in DPT using the acetic anhydride method was analyzed using an Accelerating Rate Calorimeter (ARC) to determine the thermal decomposition characteristics and kinetic parameters of the reaction solution at different reaction times. The adiabatic decomposition kinetics were modeled using TSS software, and the corresponding kinetic parameters were derived. Subsequently, a numerical simulation was employed to predict the critical ambient temperature of the reaction liquid in the reactor in case of cooling failure. The results indicated that the CT value was lowest at a feeding time of 10 minutes, highest at a holding time of 15 minutes, and closest to the cooling temperature of the reactor at a feeding time of 30 minutes.

Keywords: DPT; nitration reaction mixture; thermal decomposition; Critical ambient temperature.

1. Introduction

1,3,5,7-tetranitro-1,3,5,7-tetrazocane, commonly known as octogen (HMX), stands out as a highly promising single-component explosive due to its exceptional properties. It boasts a high density of 1.903 g/cm³, which contributes to its potent explosive force. Its detonation velocity is remarkably high at 9110 m/s, indicating the rapid release of energy upon explosion. Additionally, HMX has a decomposition temperature of 279 °C, showcasing its thermal stability under normal conditions[1]. The exceptional density, detonation velocity, and thermal stability of HMX make it an indispensable component in high-energy explosives, solid propellants, and nitramine-based launch agents. Its ability to enhance the performance and reliability of these materials underscores its importance in both military and aerospace applications[2–5]. The production of HMX typically involves the nitrolysis of hexamine using the acetic anhydride method, which is also known as the Bachmann progress[6–8]. 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane, also known as DPT, serves as a crucial intermediate for producing HMX. This compound takes the form of white rhombic crystals, boasting a molecular weight of 218.18 and a density of 1.63 g/cm³. DPT exists in two crystalline forms, each demonstrating less impact sensitivity compared to HMX and RDX[9]. The recorded melting points are 222-223°C and 204-205 °C, respectively[10]. DPT is soluble in acetic acid and N, N-dimethylformamide, but insoluble in water[11]. The synthesis of DPT can be achieved through various methods, including the reaction of sulfuric acid with hexamine dinitrate (HADN), the nitrolysis of hexamine (HA), and the condensation of small molecules such as nitrourea[7,12–14]. DPT possesses potential as an energetic material, attributed to the nitroamine groups and cyclic structural strain within its molecules. Throughout the storage period, the thermal stability and safety of storage will undergo gradual alterations. At present, there are many studies on the thermal stability of DPT. Svatopluk[10] performed tests on the thermal decomposition of DPT under a nitrogen environment utilizing DSC, and in an air environment through DTA. The initial temperature recorded for DPT decomposition ranged between 120-190 °C, with the decomposition heat measured at approximately 117.20±15.50 kJmol⁻¹. Radhakrishna[15] noted that DPT's maximum decomposition temperature reaches 220 °C, and its activation energy for thermal decomposition is 174.6 kJmol⁻¹. Hall[16] performed a DSC analysis of DPT at a scanning rate of 4 K/min, where the decomposition temperature reached 197.85 °C, the energy liberated was

146.50±25.11 kJmol⁻¹, and the activation energy ranged from 418.58 to 1255.74 kJmol⁻¹. Kruglyakova[17] applied LC-MS to explore, while Duan [18] utilized ReaxFF molecular dynamics simulations coupled with TG-FTIR-MS techniques to study the pyrolysis mechanisms of DPT, each contributing distinct insights into its thermal behavior. Due to investigating the thermal stability of the reaction mixture is particularly important. These data significantly influence the assessment of reaction risks. In the study of the thermal safety of the N-nitropyrazole synthesis process, Yan[19] used ARC to test the thermal decomposition of the reaction solution under adiabatic conditions. The activation energy and pre-exponential factor of the reaction mixture are reported as 118.81 kJmol⁻¹ and 6.94×10¹³ s⁻¹, respectively. The temperature, TD24, corresponding to the maximum reaction rate achieved after 24 h under adiabatic conditions, was determined to be 48.11 °C. By analyzing the test data of thermal decomposition, the thermal decomposition kinetic parameters necessary for simulating the critical threshold of thermal decomposition in various environments can be obtained. This method is extensively employed in the study of various energetic materials. Zhao[20] examined non-isothermal DSC data through nonlinear optimization to study the thermal decomposition kinetics of the CL-20/HMX cocrystal. Zhang[21] developed a kinetic model for the thermal decomposition of N-nitrodihydroxyethyl dinitrate (DINA) based on DSC results, and used numerical simulations with this model to assess the potential risks of thermal explosion under various conditions.

In the study of the thermal safety of DPT synthesis via the acetic anhydride method and the thermal stability of the reaction system, there is limited literature on the thermal stability data of the reaction solution. Therefore, in this study, ARC was employed to test samples of DPT synthesized via the acetic anhydride method at various reaction times, obtaining the thermal stability data of the reaction mixture under adiabatic conditions. The thermal decomposition kinetics equation for the reaction mixture was formulated. Utilizing numerical simulation of thermal decomposition kinetics, the potential risk of a thermal explosion in the reaction mixture was predicted, providing crucial data for assessing the thermal risk of DPT synthesized via the acetic anhydride method. It provides support for chemical safety and environmental safety. According to the obtained hazard threshold, the combustion or even explosion of the reaction system can be avoided.

2. Experiment

Experiments were conducted in accordance with the reaction conditions for DPT synthesis via the acetic anhydride method as described in literature [22]. The feeding time and holding time were set at 30 minutes and 15 minutes, respectively, while maintaining the reaction temperature at 44 °C. Based on the requirements of ARC tests, various experiments are conducted periodically.

Reaction mixtures at different reaction times of 10, 20, 30, and 15 minutes during the feeding stage and the holding stage were analyzed using ARC. The test samples were titanium alloy balls (model: Ti-LCQ), each weighing 5.97 g with a specific heat of 0.52 J/g/K. The ARC testing parameters included a temperature range of 30-350 °C, a heating rate of 5 °C/min, and a sensitivity of 0.02 °C/min. The reaction solution weighed 0.75 g with a specific heat capacity of 2.17 J/g/K.

3. Summary

3.1 Thermal stability of the reaction mixture

The thermal decomposition results of each sample in the adiabatic environment are shown in Fig.1. Fig.2 shows the exothermic stage of each sample in the ARC test. According to the test results, the reaction liquid during the feeding stage exhibits a single distinct exothermic process, whereas the reaction liquid during the holding stage displays two exothermic processes. Because the sample and the sample cell achieve thermal equilibrium, as described in thermodynamic principles:

$$m_s C_{vs} \Delta T_s = (m_s C_{vs} + m_b C_{vb}) \Delta T \quad (1)$$

Here, m_s is the mass of sample, g; C_{vs} is the average specific heat capacity of the sample, $\text{Jkg}^{-1}\text{K}^{-1}$; ΔT_s is the adiabatic temperature rise of the sample, K; m_b is the mass of sample cell, g; C_{vb} is the specific heat capacity of the sample cell, $\text{Jkg}^{-1}\text{K}^{-1}$; ΔT is the measured adiabatic temperature rise of the whole test system including the sample and the sample cell, K.

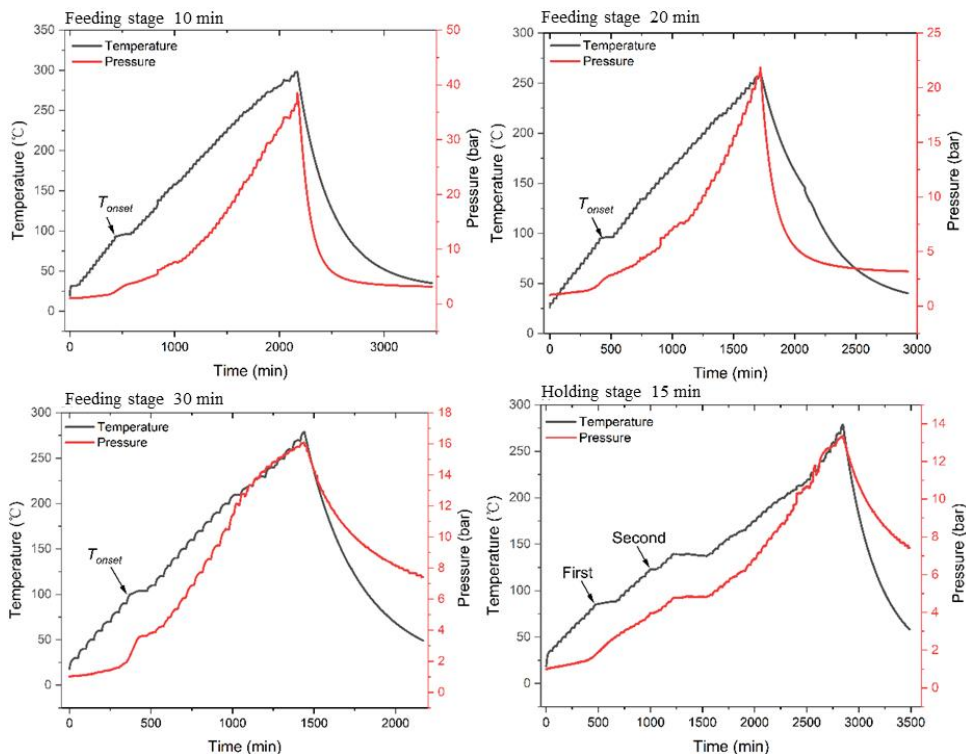
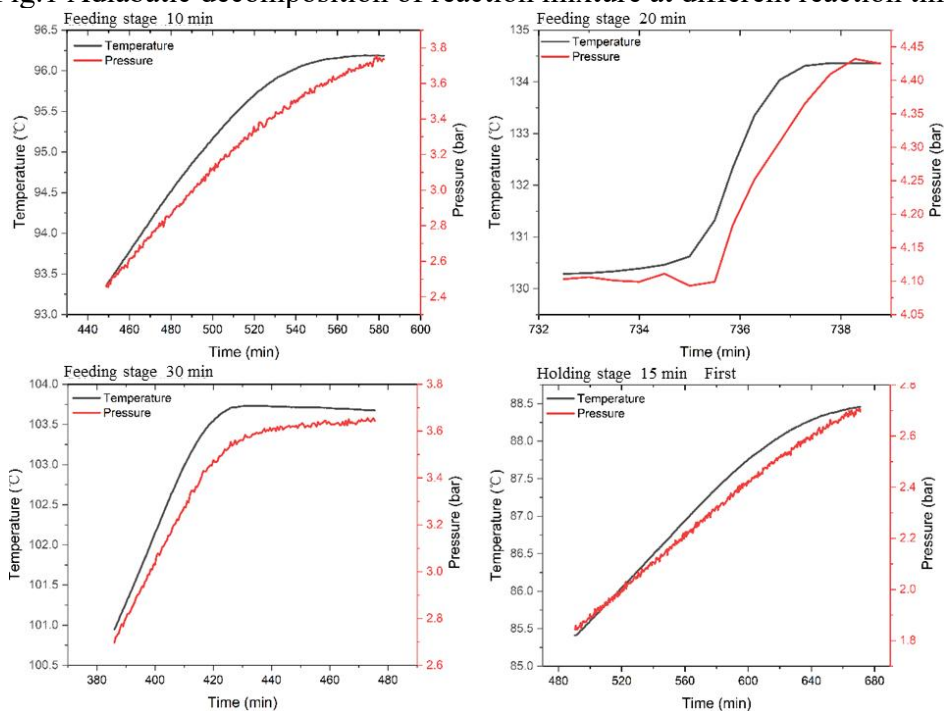


Fig.1 Adiabatic decomposition of reaction mixture at different reaction time



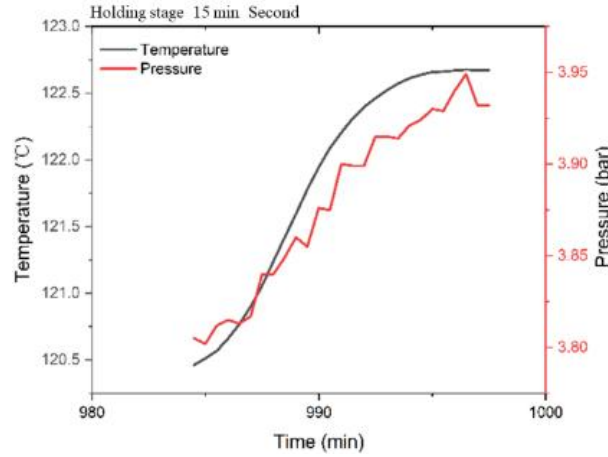


Fig.2 The exothermic process of each sample in the reaction mixture

Transpose the Eq. (1):

$$\Delta T_s = \left(1 + \frac{m_b c_{vb}}{m_s c_{vs}}\right) \Delta T \quad (2)$$

In the Eq. (2), $\varphi = 1 + \frac{m_b c_{vb}}{m_s c_{vs}}$ called thermal inertia factor of the sample reactor. When $m_s \geq m_b$, $\varphi \approx 1$. thermal decomposition data do not require correction; however, corrections must be made if φ differs from 1.

For the sample in question, the temperature at which it reaches an adiabatic state is denoted as T_{fs}

$$T_{fs} = T_0 + \varphi \Delta T \quad (3)$$

The equation illustrates how the thermal inertia factor φ of the reactor affects the system's temperature under adiabatic conditions.

Additionally, the parameter φ similarly influences the adiabatic temperature rise rate of the sample. The adiabatic temperature rise rate, denoted as $\sigma_{0,s}$ is:

$$\sigma_{0,s} = \varphi \sigma_0 \quad (4)$$

The maximum reaction rate reaches time θ :

$$\theta_s = \frac{\theta}{\varphi} \quad (5)$$

θ_s represents the time at which the maximum reaction rate is reached when only the sample is present.

The adiabatic decomposition characteristic parameters of the reaction liquid after calibration according to the φ values are shown in Table 1.

Table 1: Adiabatic decomposition characteristic parameters of the corrected reaction mixture

Parameters	Feedin g/10min	Feedin g 20min	Feedin g 30min	Holding 15min	
				First	Second
Initial decomposition temperature /°C	93.34	130.29	100.95	85.41	120.46
Initial thermal decomposition rate /°C·min ⁻¹	0.04	0.03	0.08	0.02	0.59
End temperature of thermal decomposition /°C	101.54	142.62	109.64	95.09	127.46
Maximum pressure /MPa	38.40	21.80	16.06	13.32	
Maximum rate /°C·min ⁻¹	0.15	8.57	0.34	0.04	0.37
Adiabatic temperature rise per unit mass /K·g ⁻¹	10.53	17.14	13.87	14.39	10.40
Maximum temperature rise rate reaches time /min	16.72	0.99	5.91	17.03	1.57
Thermal inertia factor	2.90	3.03	3.30	3.17	

According to the corrected data, the maximum temperature rise rate for the adiabatic decomposition of the reaction liquid is 8.57 °C/min, observed in the reaction liquid after 20 minutes of feeding. At this stage, the decomposition rate of the reaction mixture reaches its peak, making it the most challenging to control once decomposition commences. Comparing the adiabatic temperature rise of the reaction mixture per unit mass, the highest adiabatic temperature rise occurs when the reaction solution is fed for 20 minutes. If cooling failure occurs during the reaction process, the damage resulting from the adiabatic decomposition of the reaction system will be maximal. The initial decomposition temperature of the reaction mixture reached its lowest point after a holding stage of 15 minutes, during which two distinct decomposition phases were observed. This occurs as the feeding and reaction processes advance, increasing the complexity of the reaction system; most of the raw materials undergo transformation, and an increase in by-products and intermediate products is noted. In the study of the thermal decomposition of the reaction mixture at holding stage of 15 minutes, the initial decomposition phase was prioritized as the primary focus. This prioritization is due to the lowest initial decomposition temperature and highest adiabatic temperature rise observed during this phase, which also correlates with the decomposition risk. Consequently, the thermal safety data derived from this focus are the most conservative and reliable.

3.2 Calculation of kinetic parameters of thermal decomposition

To conduct numerical simulations, it is essential to establish a thermal decomposition kinetic model utilizing data derived from ARC tests. The accuracy and reliability of the simulation results are significantly influenced by the kinetic model. Owing to the absence of detailed information on the decomposition process, a simplified kinetic model is employed. Although this model does not detail the mechanism, it accurately depicts the main characteristics of the reaction. The model is capable of representing a complex multi-stage reaction, encompassing several independent, parallel, or sequential stages, describable through the rate and temperature of the thermal decomposition reaction conform to the Arrhenius equation:

$$k = Ae^{-E_a/(RT)} \quad (6)$$

Here, k is the reaction rate, A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, T is the temperature. For the n -order decomposition reaction, the reaction rate follows the law of Eq. (7).

$$r = ke(1 - \alpha)^n \quad (7)$$

$$r = Ae^{-\frac{E_a}{RT}}(1 - \alpha)^n \quad (8)$$

r is the rate of thermal decomposition reaction, α is the degree of decomposition of thermal decomposition.

The Thermal Safety Software (TSS) was employed to fit the curve in accordance with Eq. (8), facilitating the calculation of thermal decomposition kinetic parameters for the reaction mixture under adiabatic conditions. Table 3 presents the thermal decomposition kinetic parameters for the reaction mixture at each stage. Figure 3 illustrates the thermal decomposition experiments and their fitting results for the reaction solution.

Reaction mixture	$\ln(A)(\ln(\frac{1}{s}))$	n	E_a (kJ/mol)	Q(J/g)
Feeding 10min	53.04	0.58	187.15	17.78
Feeding 20min	90.45	1.95	316.85	26.76
Feeding 30min	83.39	0.54	282.84	19.36
Holding 15min	45.91	0.50	163.73	7.37

Table 3 Thermal decomposition kinetic parameters

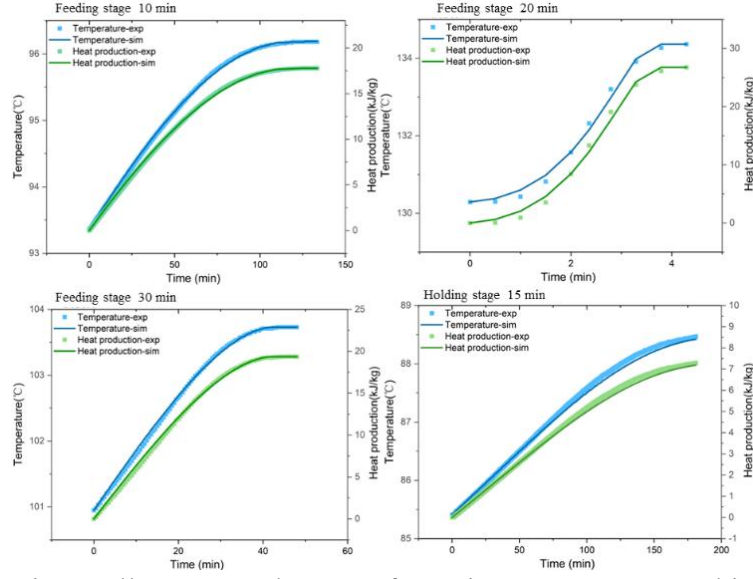


Fig.3 The experimentally measured curve of reaction temperature and its fitting values.

Analysis reveals that the reaction mixture of feeding stage 20 minutes exhibits the highest apparent thermal decomposition activation energy and releases the greatest amount of heat during thermal decomposition. Conversely, the reaction mixture of holding stage 15 minutes demonstrates the lowest apparent activation energy for thermal decomposition, rendering it most susceptible to decomposition, albeit with a comparatively small amount of heat released.

3.3 Possibility of thermal runaway reaction

Time to maximum rate under adiabatic condition (TMR_{ad}) represents the time at which thermal decomposition achieves the maximum reaction rate under adiabatic conditions following the onset of secondary decomposition. The time θ , marking the maximum reaction rate, is defined as the difference between t_m , the time when the material attains this maximum rate, and t , the time at a specified temperature.

$$\theta = t_m - t = \int_t^{t_m} dt \quad (9)$$

According to the self-heating rate equation, it can be obtained:

$$\theta = \int_t^{t_m} dt = \int_T^{T_m} \frac{dT}{A \left(\frac{T_f - T}{\Delta T} \right)^n \Delta T c_0^{n-1} \exp\left(-\frac{E_a}{RT}\right)} \quad (10)$$

T_m is the temperature corresponding to the maximum reaction rate. By using the method of numerical integration to calculate T_m , the Eq. (11) can be obtained:

$$\theta = \frac{RT^2}{\sigma E_a} - \frac{RT_m^2}{\sigma_m E_a} \quad (11)$$

σ is the maximum heating rate. In the exothermic reaction system, the first term on the right side of the Eq. (11) is much larger than the second term on the right side, which can be ignored.

$$\theta = \frac{RT^2}{\sigma E_a} \quad (12)$$

Given that the reaction system is adiabatic, all heat generated by the reaction or decomposition contributes to the increase in the system's temperature. the adiabatic equation is:

$$H \frac{dc}{dt} = -C_p \frac{dT}{dt} \quad (13)$$

c represents the concentration of the unreacted substance, mol/L. As c diminishes over time, the corresponding term on the right side of the equation is negative. n is the reaction order. R is gas constant, J/K/mol. C_p is the average volume-specific heat capacity, J/L/K. H is the reaction heat, J/mol.

In the adiabatic reaction system:

$$\frac{dT}{dt} = \frac{H}{C_p} A c^n \exp\left(-\frac{E_a}{RT}\right) \quad (14)$$

$$\text{Reaction velocity } \sigma = \frac{dT}{dt} = \frac{H}{C_p} A c^n \exp\left(-\frac{E_a}{RT}\right) = \frac{H}{C_p} k$$

$$\theta = \frac{C_p R T^2}{H k E_a} \quad (15)$$

θ representing TMR_{ad} , serves as a critical parameter for the thermal hazard assessment in chemical reaction processes. Consequently, by using the determined thermal decomposition kinetic parameters, the TMR_{ad} curve for the reaction mixture involved in the synthesis of DPT via the acetic anhydride method can be plotted, as depicted in Fig. 4.

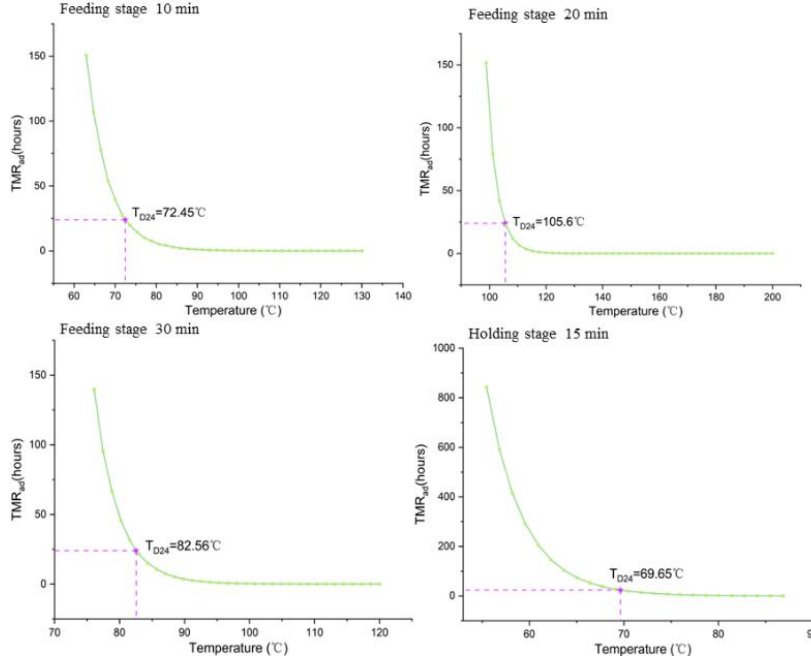


Fig. 4 The TMR_{ad} curve

The TMR_{ad} curve facilitates the prediction of temperatures corresponding to TMR_{ad} values over 24 hours and 8 hours, respectively. These temperatures, designated as T_{D24} and T_{D8} , are crucial parameters in thermal risk assessment. The T_{D24} and T_{D8} of each test sample are listed in table 4. It is found that under adiabatic conditions, the lowest T_{D24} is the reaction mixture at the holding stage of 15 min, that is, under the adiabatic condition of 69.65 °C, the reaction liquid at this time will reach the maximum decomposition temperature after 24 hours, and the reaction system has the risk of thermal explosion.

Reaction mixture	$T_{D24}/ ^\circ\text{C}$	$T_{D8}/ ^\circ\text{C}$
Feeding 10min	72.45	78.82
Feeding 20min	105.60	108.24
Feeding 30min	82.56	87.06
Holding 15min	69.65	74.57

Table 4 Thermal risk assessment parameters T_{D24} and T_{D8}

During thermal explosion simulations, the heat transfer model is represented by the thermal conductivity Eq. 16, integrated with Eq. 6 and 7

$$\rho C_p \frac{\partial T}{\partial t} = \text{div}(\lambda \Delta T) + W \quad (16)$$

ρ is density; C_p is the specific heat capacity; λ thermal resistance; W is thermal power; ΔT is temperature difference.

Employing kinetic parameters and equations derived from TSS under adiabatic conditions, the stability of the reaction mixture under isothermal conditions has been simulated and predicted. In the simulation process, the third type of boundary conditions is selected. Time to conversion limit

(TCL) represents the duration required for reaction mixture decomposition to achieve a specific conversion ratio at a constant temperature. Fig. 5 illustrates the relationship between the times required to achieve 5%, 10%, and 15% conversion and the corresponding temperatures. It is evident that as the temperature increases, the time to reach the conversion limit decreases correspondingly. Table 5 enumerates the typical durations required to reach the three specified conversion limits and their corresponding temperatures.

Table 5 Times and corresponding temperatures reach the TCL

Reaction mixture	conversion limit /%	TCL		
		Exceed 10 years	1 year	1 day
Feeding 10 min	5	≤ 23.14 °C	34.12 °C	60.78 °C
	10	≤ 26.27 °C	37.25 °C	65.49 °C
	15	≤ 27.84 °C	38.82 °C	67.06 °C
Feeding 20 min	5	≤ 74.71 °C	82.94 °C	102.94 °C
	10	≤ 75.88 °C	84.12 °C	104.12 °C
	15	≤ 77.06 °C	85.00 °C	105.29 °C
Feeding 30 min	5	≤ 47.06 °C	54.12 °C	75.29 °C
	10	≤ 48.82 °C	54.50 °C	77.06 °C
	15	≤ 50.59 °C	58.52 °C	78.82 °C
Holding 15 min	5	≤ 15.00 °C	25.00 °C	53.33 °C
	10	≤ 16.67 °C	26.67 °C	56.67 °C
	15	≤ 18.33 °C	30.00 °C	60.00 °C

For a conversion limit of 5%, the results indicate that the reaction mixtures from the feeding stages 20 min and 30 min require more than 10 years to reach this limit at an optimal isothermal storage temperature of 25 °C. Conversely, the reaction mixture from the holding stage 15 min achieves this limit within one year. The reaction mixture from the feeding stages 10 min reaches the limit value within 10 years. By comparing the conversion limits of T_{D24} and TCL over one day, it was determined that the conversion limits of various reaction mixtures exceed 15% in the event of a thermal explosion.

3.4 Simulation of thermal hazard parameters of reaction mixture

Upon determining the thermal decomposition characteristic parameters of the reaction liquid, its thermal stability was simulated using TSS software, which employs thermal decomposition kinetics. In a 5000 L reactor constructed from Hastelloy alloy, the reaction system behaves as an adiabatic storage tank in the event of a cooling failure of the reaction. Concurrently, the ambient temperature of the sample approximately matches that of the reaction cooling system[23]. The simulation selects the third boundary condition for the heat transfer process. It models the scenario where the critical ambient temperature (CT) of the reaction system increases by at least 6 °C within a maximum of seven days[24,25]. The simulation presumes uniform initial distributions of temperature and component concentrations within the sample container. Standard continuous boundary conditions for temperature and heat flux are established on the inner wall surface, with both velocity components constrained to zero at this boundary[26]. The reactor and reaction mixture content used in the simulation are shown in Fig. 6. The simulation results are shown in Table 6.

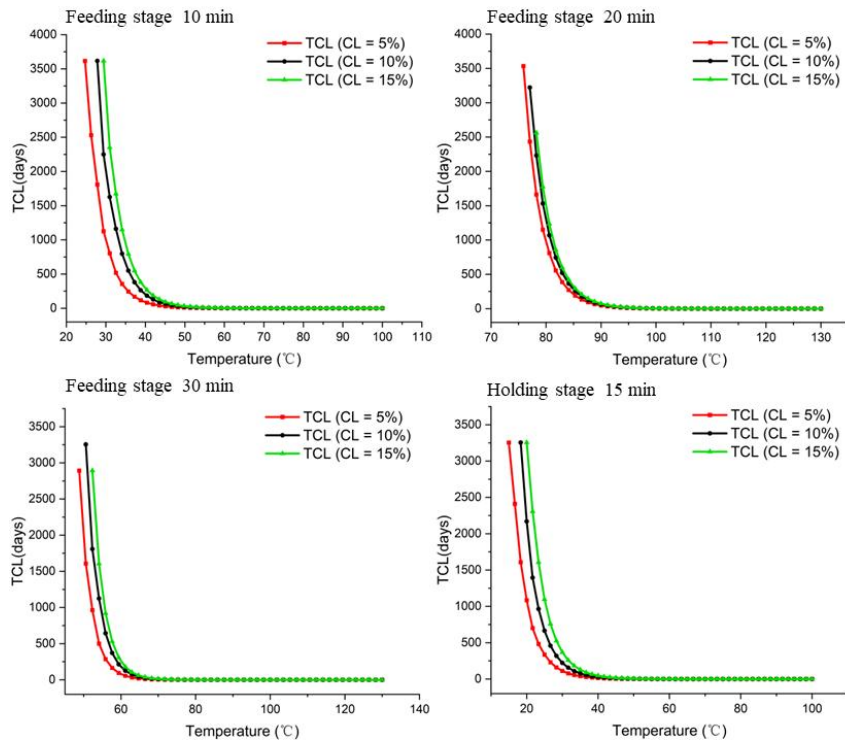


Fig. 5 Time to conversion limit curves vs. Temperature

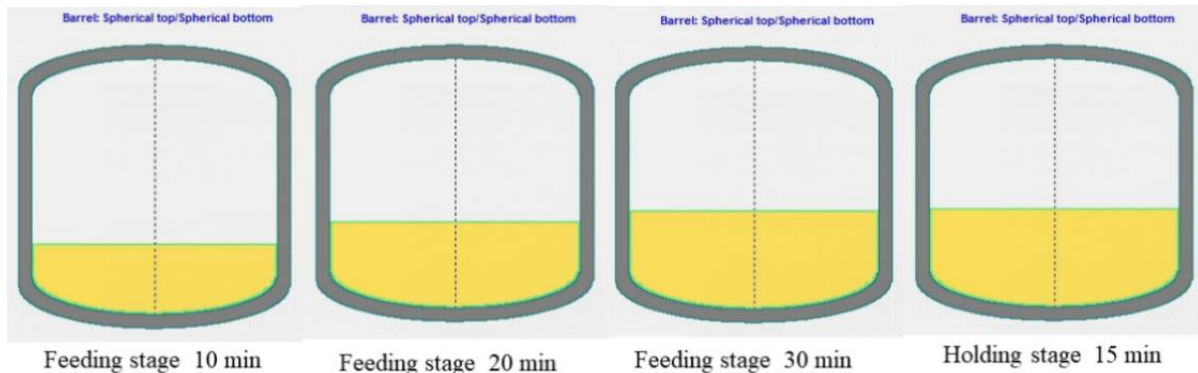


Fig.6 Simulated reactor and reaction mixture content

Table 6 Simulation of critical temperature

Reaction mixture	Ambient temperature /°C	CT/°C
Feeding 10min	20.00	49.36
Feeding 20min	30.00	75.55
Feeding 30min	40.00	59.80
Holding 15min	44.00	200.00

Through simulation, it has been determined that the CT value is lowest when the feeding time is 10 minutes, indicating that at an ambient temperature of 49.36°C, thermal decomposition will cause the temperature of the reaction mixture in the reactor to rise by more than 6°C. This indicates the poorest stability of the reaction system, with the ambient temperature of 49.36°C causing significant decomposition of the reaction mixture. The sample exhibiting the highest CT value corresponds to the holding stage 15 min. Significant heating of the reaction system occurs only when the system temperature reaches 200.00°C. This results from the minimal heat released during the decomposition at this stage and the maximum mass of the reaction system. Consequently, the gradual temperature increase caused by this slow decomposition process is less pronounced. When the reaction mixture is holding 15 min, the differential between the ambient temperature and the

critical ambient temperature is minimized. Consequently, in the event of a cooling system failure, the system is highly likely to reach the CT value.

4. Summary

Reaction mixture at various stages of DPT synthesis via the acetic anhydride method were analyzed using ARC. The reaction mixture with a holding time of 15 minutes exhibited the lowest initial decomposition temperature under adiabatic conditions, recorded at 85.41°C. When fed for 20 minutes, the reaction mixture demonstrated the highest maximum temperature rise rate during adiabatic decomposition, measured at 8.57 °C/min, the temperature increase during adiabatic decomposition is the most pronounced, and the severity of the post-decomposition effects is the greatest. Simulations of TCL indicate that only samples with feeding times of 20 and 30 minutes can maintain conversion limits within 5% at room temperature.

Thermal stability simulations reveal that when the reaction mixture is feeding stage 10 min at an ambient temperature of 49.36 °C, thermal decomposition induces a temperature increase in the reactor's contents of more than 6 °C. When the sample is holding stage 15 min, a noticeable temperature rise in the reaction system occurs only if the temperature reaches 200.00 °C. When the reaction mixture is feeding stage 30 min, the temperature differential between the ambient and CT is minimized, resulting in the highest likelihood of significant heating in the system.

References

- [1] D Tian, F Zhao, J Liu. Energetic materials and related materials manual [M]. Energetic materials and related materials manual, 2011.
- [2] K Zhang, Z Yang, G Wang, et al. Technology of precision pressing HMX explosive with armor-piercing projectile [J]. Ordnance Automation, 2015, 34 (04): 78-80.
- [3] YHuang, X Wang, S Xu, et al. Study on the critical initiation pressure of HMX-based propellants [J]. Explosives, 2020,49 (1): 34-39.
- [4] D Zhao, X Tian, Y Huang, et al. Study on the performance of civil heat-resistant explosives prepared from recycled HMX-based explosives [J]. Shanxi Chemical Industry, 2014, 34 (4): 17-18.
- [5] S Cao, Z Li, W Xiong, et al. Design and properties of low-vulnerability cast HMX-Al-based PBX explosives [J]. Energetic materials, 2021, 29 (7) : 650-657.
- [6] Bachmann W E, Jenner E L. 1-Acetoxyethyl-3, 5, 7-trinitro-1, 3, 5, 7-tetraazacyclooctane and its Reactions. Significance in the Nitrolysis of Hexamethylenetetramine and Related Compounds1[J]. Journal of the American Chemical Society, 1951, 73(6): 2773-2775.
- [7] Bachmann W E, Sheehan J C. A New Method of Preparing the High Explosive RDX[J]. Journal of the American Chemical Society, 1949, 71(5): 1842-1845.
- [8] Bachmann W E, Horton W J, Jenner E L, et al. Cyclic and Linear Nitramines Formed by Nitrolysis of Hexamine 1[J]. Journal of the American Chemical Society, 1951, 73(6): 2769-2773.
- [9] Choi C S, Bulusu S. The crystal structure of dinitropentamethylenetetramine (DPT)[J]. Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry, 1974, 30(6): 1576-1580.
- [10] Vagenknecht J, Zeman S. Some characteristics of 3,7-dinitro-, 3,7-dinitroso- and dinitrate compounds derived from 1,3,5,7-tetraazabicyclo[3.3.1]nonane[J]. Journal of Hazardous Materials, 2005, 119(1-3): 1-11.
- [11] Xue M, Wu S, Liu W, et al. Solubility of 3,7-Dinitro-1,3,5,7-tetraazabicyclo [3.3.1] Nonane in Ethanenitrile, Methanol, 1,1-Dichloroethane, Dimethyl Sulfoxide, Acetone, and Mixed Solvents[J]. Journal of Chemical & Engineering Data, 2015, 60(6): 1683-1687.
- [12] P Wang, H Song, Z Meng, et al. One-pot synthesis of dinitropentamethylenetetramine [J]. Journal of Beijing University of Technology, 2011,31 (5) : 603-605 + 617.
- [13] Il'yasov S G, Lobanova A A, Popov N I, 等. Chemistry of urea nitro derivatives: III. Reactions of N, N'-dinitrourea with bases[J]. Russian journal of organic chemistry, 2002, 38(12): 1731-1738.

- [14] Brockman F J, Wright G F, Downing D C. NITROLYSIS OF HEXAMETHYLENETETRAMINE: III. PREPARATION OF PURE CYCLONITE[J]. Canadian Journal of Research, 1949, 27b(5): 469-474.
- [15] Radhakrishnan S, Talawar M B, Venugopalan S, et al. Synthesis, characterization and thermolysis studies on 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT): A key precursor in the synthesis of most powerful benchmark energetic materials (RDX/HMX) of today[J]. Journal of Hazardous Materials, 2008, 152(3): 1317-1324.
- [16] Hall P G. Thermal decomposition and phase transitions in solid nitramines[J]. Transactions of the Faraday Society, 1971, 67: 556.
- [17] Kruglyakova L A, Stepanov R S, Kekin Yu V, et al. Kinetics of Thermal Decomposition of 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane[J]. Russian Journal of General Chemistry, 2019, 89(2): 194-198.
- [18] Duan X, Jin G, Zhang L, et al. Insight into the pyrolysis of 3,7-dinitro-1,3,5,7-tetraazabicyclo [3,3,1] nonan (DPT) based on ReaxFF MD simulations and TG-FTIR-MS techniques[J]. Fuel, 2023, 331: 125860.
- [19] Y Yan. Study on thermal safety in the synthesis of 3,4-dinitropyrazole. [D]. North University of China, 2024.
- [20] Zhao L, Yin Y, Sui H, et al. Kinetic model of thermal decomposition of CL-20/HMX co-crystal for thermal safety prediction[J]. Thermochemica Acta, 2019, 674: 44-51.
- [21] Zhang J, Ma Y-Y, Chen L-P, et al. Experimental and numerical simulation to identify the thermal hazards and hazardous scenarios of N-Nitrodihydroxyethyl dinitrate[J]. Process Safety and Environmental Protection, 2021, 145: 211-221.
- [22] H Peng. Study on thermal hazard of synthesis of Octogen by acetic anhydride method [D].Nanjing University of Science and Technology, 2016.
- [23] Stoessel F. Thermal safety of chemical processes: risk assessment and process design[M]. John Wiley & Sons, 2021.
- [24] Kossoy A A, Sheinman I Ya. Comparative analysis of the methods for SADT determination[J]. Journal of Hazardous Materials, 2007, 142(3): 626-638.
- [25] Kossoy A. CISP-Newsletter N10 Kinetics-based simulation approach. More about applying simulation for evaluating reactive hazard of Li-ion battery[Z](2016).
- [26] Kossoy A A, Belokhvostov V M, Koludarova E Y. Thermal decomposition of AIBN: Part D: Verification of simulation method for SADT determination based on AIBN benchmark[J]. Thermochemica acta, 2015, 621: 36-43.