Adiabatic thermal runaway and safety relief design for hexamethylene diisocyanate reaction system

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Abstract: Runaway reaction may occur for hexamethylene-diisocyanate (HDI) with two active NCO groups during the reactions or storage and transportation when run into device failure, operation error and other unexpected environments, which would damage equipment or even cause explosions. Adiabatic experiments for HDI using Vent Sizing Package 2 (VSP2) is conducted and temperature and pressure changes over time, as well as the maximum temperature rise rate and maximum pressure rise rate, are obtained. The results show that the initial exothermic temperature of the system is 50°C, and the maximum temperature is 232°C and the heat of reaction is 414.7 kJ/kg, so the severity level of HDI is classified as "medium" according to the assessment criteria for the severity of a runaway reaction. The relief type of the reaction system is determined to be a gas system by analysis of the pressure change curve during heating and cooling processes, along with the temperature at the point of loss of control, and calculated by the DIERS method and Leung's correction method through Python programming, which is applied to determine the required safety relief device for an industrial scenarios, and the minimum relief area is calculated to be 0.0028m² and 0.0019m², respectively. The study verifies the higher reliability of the safety relief design for runaway reactions based on VSP2 experimental data.

1.Introduction

Hexamethylene diisocyanate (HDI) is an important monomer in aliphatic diisocyanates and widely used in the preparation of polyurethane materials in various fields such as aviation, automotive, construction, wood, plastics, and leather [1]. Isocyanate compounds, due to the presence of -N=C=O unsaturated bonds in their structure, exhibit high reactivity and pose certain thermal hazards [2]. There have been reports of explosion accidents at home and abroad, such as the Bhopal incident that shocked the world, that is, the safety valve of methyl isocyanate underground storage tank broke, resulting in thousands of deaths and hundreds of thousands of injuries, which is the most terrible toxic substance leakage accident in the 20th century

Safety valves are crucial safety release devices in industrial production, capable of promptly releasing the energy or materials generated by overpressure from confined spaces, thereby preventing hazardous incidents caused by equipment overpressure damage in industrial production. Since the 1970s, the Design Institute for Emergency Relief Systems (DIERS) in the United States has been conducting research on relief releases for chemical reaction runaway incidents. Gradually, they have developed a methodology system based on a combination of runaway experiments and empirical formulas, which constitutes the primary approach for safety relief valve design.

Currently, there is a primary focus on the optimization of production processes and application research regarding HDI, with limited literature available on studies related to safety relief. In this study, we conducted adiabatic release experiments on hexamethylene diisocyanate (HDI) using VSP2. Subsequently, based on these experiments and corresponding release theories, we further developed a safety relief design model. This model aims to provide design and selection references for safety relief devices related to the production and transportation of HDI.

2.Experiment

2.1.Experimental equipment

The experimental setup utilized the VSP2 adiabatic calorimeter developed by the FAI company in the United States. This apparatus is capable of simulating various conditions that may lead to chemical reaction runaway. Commonly used for thermal hazard analysis of substances [3]. The physical setup is depicted in Fig 1, comprising key components such as temperature control system, pressure control system, super magnetic stirrer, and high-pressure vessel (containing the test pool).

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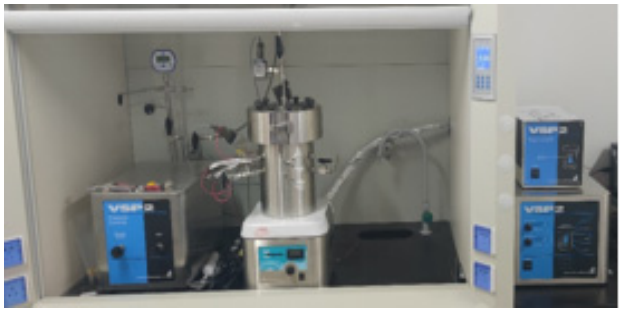

Figure 1. VSP2 device diagram.

During measurements, the sample was introduced into the test pool within the high-pressure vessel, and thorough mixing of the material in the test pool was achieved using a super magnetic stirrer. Upon occurrence of exothermic reactions or gas evolution within the sample in the pool, the pressure and temperature control systems regulated the corresponding changes in temperature and pressure within the vessel, ensuring consistency between the internal and external temperature and pressure of the test pool. This facilitated the determination of conditions leading to reaction runaway.

Compared to other calorimetric devices, its superiority lies in the unique pressure balance mechanism, which enables the walls of the test pool to be very thin. Consequently, its thermal inertia factor is remarkably low. Therefore, the data obtained from the measurements can typically be directly extrapolated to industrial scale without the need for cumbersome correction calculations.

2.2.Sample source and testing conditions

Sample source: Hexamethylene diisocyanate (HDI): industrial grade, provided by the Central Research Institute of Wanhua Chemical Group.

This study employed a sealed test cell made of 304 stainless steel (volume: 116 mL, mass: 40 g).

Experimental Procedure:

(1) Assemble the VSP2 instrument according to the standard operation programming (SOP). Perform pressure calibration, airtightness testing, and test cell insulation procedures. Then, add the sample to the test cell, place it into the high-pressure vessel, connect all joints, and seal the device.

(2) Set the experimental parameters in the computer control program: rotor speed of 300 rpm, using standard mode, and enable the Auto Heat-Wait-Search (AHWS) option.

(3) Commence the experiment and monitor the exothermic reaction. Wait for the completion of the exothermic reaction while the instrument automatically records the temperature and pressure data of the sample.

(4) Upon completion of the exothermic reaction, stop the experiment. Disassemble the instrument and clean the pipelines strictly following the SOP.

2.3.Results and Analysis

The experimental data obtained are presented in the figure 2 below:

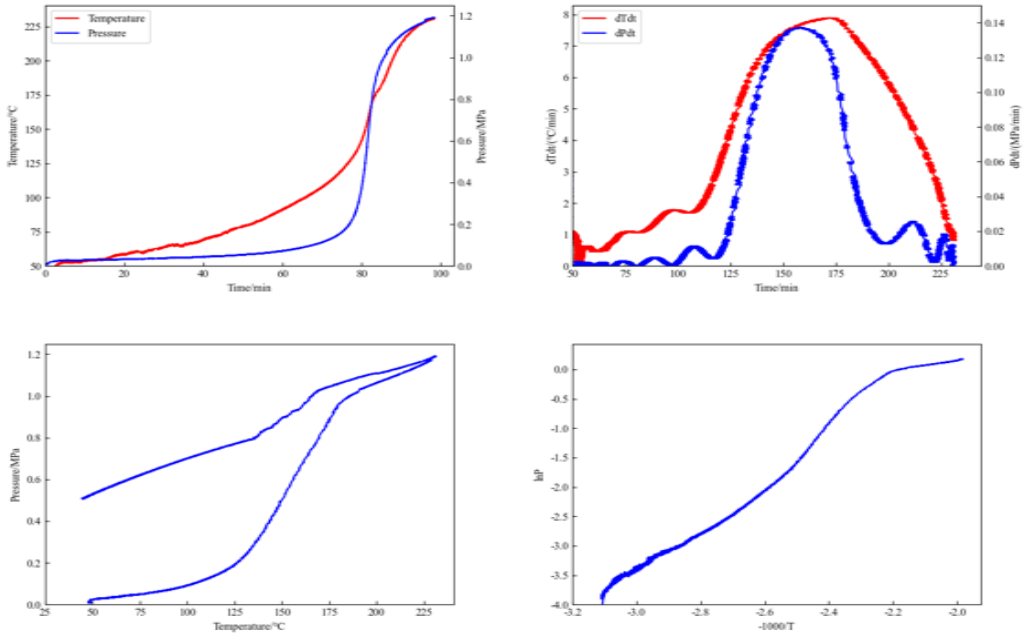

Fig. 2. The experimental data plot

The key data obtained from the plot include the initial temperature T0, the maximum temperature reached Tmax, the maximum pressure Pmax, the adiabatic temperature rise ΔTad, as well as the maximum temperature rise rate (dT/dt)max and pressure rise rate (dP/dt)max. These data are listed in Table 1.

The heat of reaction Q for the sample system can be calculated using Equation (1).

$$Q = \phi \Delta T_{ad} C_r \quad (1)$$

Wherein, the thermal inertia factor Φ is calculated using Equation (2).

$$\phi = 1 + \frac{m_{cell} \times C_{cell}}{m_s C_r} \quad (2)$$

In the equation, m_s represents the mass of the sample, which is 35.80g; m_{cell} denotes the mass of the test cell,

which is 40g; C_r is the specific heat capacity of the sample, which is 1.78 kJ·kg^{-1}·K^{-1}; C_{cell} stands for the specific heat capacity of the test cell, which is 0.45 kJ·kg^{-1}·K^{-1}.

Table 1. Thermal data in an adiabatic state.

T_0 /(℃)	T_{max} /(℃)	ΔT_{ad} /(℃)	$(dT/dt)_{max}$ /(℃·min^{-1})	P_{max} /(MPa)	$(dP/dt)_{max}$ /(MPa·min^{-1})	Q /(kJ·kg^{-1})
50	232	182	6.94	1.2	0.129	414.7

According to the severity assessment criteria for runaway reactions (Shown in Table 2), with an adiabatic temperature rise ΔT_{ad}=182℃, it can be observed that, in the event of a thermal runaway phenomenon, the severity level of the runaway reaction is classified as "medium" [4].

Table 2. .Assesment criteria for the severity of a runaway reaction

ΔTad/℃	Severity
> 200	High
50 < ΔTad < 200	Medium
< 50	Low

3.Release calculation based on VSP2 experimental data

3.1.Classification of release types

The discharge device commonly used in industrial production has safety valve and bursting disc, and the discharge quantity and discharge area are important parameters in its design and manufacture. The purpose of safety release study is to determine the release amount of safety release device and to design the release area on this basis. If the design area is too large, it will easily cause the waste of resources; If the design area is too small, it will lead to insufficient discharge capacity, and overpressure protection can not be achieved well when the reaction occurs thermal runaway. Based on the data of runaway experiment, the safe release is calculated by using the release theory proposed by DIERS.

According to the pressure-temperature variation curve, if the system pressure at the end of the experiment is higher than the initial pressure, it indicates the generation of non-condensable gases during the runaway reaction. In this case, if the temperature during the reaction runaway exceeds the boiling point of the liquid phase, it is classified as a mixed release type; otherwise, it is classified as a gas release type. If the system pressure at the end of the experiment equals the initial pressure, it implies that no non-condensable gases were produced during the reaction process, and the release type of the reaction system is classified as vapor release.

From Table 1, it can be inferred that the temperature during the reaction runaway is 50℃, while the boiling point of HDI is 252℃. Therefore, the system is classified as a gas system.

3.2.Release calculation

3.2.1.Calculation of release quantity

The release quantity, which is the total mass of material that needs to be released due to system overpressure, is typically represented by the mass flow rate W. For gas-type safety releases, the DIERS method or the modified method proposed by Leung[5] is commonly used for calculation. The DIERS method is expressed as Equation (3).

$$W = Q_G \frac{m_R}{V} \tag{3}$$

In the equation, m_R represents the mass of reactants, kg; V denotes the volume of the reactor, m³;Q_G stands for the maximum value of gas release, m³/s, as determined by calculation in Equation (4).

$$Q_G = \left[\left(\frac{V_s}{P}\frac{dP}{dt}\right)_m - \left(\frac{V_s}{T}\frac{dT}{dt}\right)_m\right]\frac{m_R}{m_s} \tag{4}$$

In the equation, m_s represents the mass of the test substance, kg. V_s denotes the volume of gas in the test cell, m³. The subscript m indicates that the calculation utilizes data corresponding to the maximum pressure rise rate and temperature rise rate.

Additionally, upon activation of the release device, there will be some material discharged simultaneously with the release, taking into account this loss. Leung proposed a correction for this issue, as shown in Equation (5).

$$W = Q_G \frac{m_R}{V}\frac{1}{(1+\alpha_0)^2} \tag{5}$$

In the equation, α_0 represents the gas content, as determined by calculation in Equation (6).

$$\alpha_0 = 1 - \frac{1}{V}\left(\frac{m}{\rho_f}\right) \tag{6}$$

Calculation of release capacity. The release capacity of gas systems is generally calculated using the Tangren method[6], as shown in Equation (7).

$$G = \sqrt{\frac{P}{v_0}}\frac{\left(\frac{2}{\alpha_0}\left[\left(\frac{1-\alpha_0}{\alpha_0}\right)(1-\eta)-\ln\eta\right]\right)^{0.5}}{\frac{1}{\eta}+\left(\frac{1-\alpha_0}{\alpha_0}\right)} \tag{7}$$

In the above equation,$_{v0}$ represents the specific volume of the reactor; $v_0 = V/m_R$. P denotes the design pressure of the reactor, MPa.η is the critical pressure ratio, calculated using Equation (8):

$$\eta = \left[2.016 + \left(\frac{1-\alpha_0}{2\alpha_0}\right)^{0.7}\right]^{-0.714} \tag{8}$$

The discharge area of the safety release device, represented by the ratio of the discharge quantity to the discharge capacity, is expressed as Equation (10), where A denotes the required discharge area, measured in square meters (m²).

$$A = \frac{W}{G} \tag{10}$$

When manufacturing safety release devices, the production manufacturer also provides the flow coefficient K_v. In this case, the correction of the discharge area is expressed as Equation (11):

$$A = \frac{W}{K_v G} \tag{11}$$

3.2.2.Calculation of discharge area

Selecting a tank volume of 10m^3, approximately containing 8000 kg of HDI material, with a release pressure of 0.25MPa. The design pressure is set as the reference at 0.8MPa for design purposes. The maximum accumulated pressure is set at 0.88MPa.

Table 3 presents the temperature, pressure, and temperature rise rate corresponding to the maximum pressure rise rate obtained from the VSP2 experiment. Substituting these data into the above formula yields the discharge data as shown in Table 4.

Table 3. Required data for safety release calculation

Maximum pressure rise rate/(MPa/min)	Corresponding temperature/(K)	Corresponding pressure/(MPa)	Corresponding temperature rise rate/(K/min)
0.129	433	0.6	5.83

Table 4. Calculation Results of Safety Release Capacity

α_0	Q_G /(m^3·s^{-1})	W(DIERS) /(kg·s^{-1})	W(Leung) /(kg·s^{-1})
0.234	0.061	49.49	32.48

The discharge capacity G calculated from Equation (7) is 21746.84kg·m^{-2}·s^{-1}. Typically, discharge devices have prescribed flow coefficients. Assuming a flow coefficient of 0.8, the final discharge areas under the conditions of a release pressure of 0.25MPa, before and after Leung correction, are respectively 0.0028m^2 and 0.0019m^2.

4.Conclusion

Adiabatic experiment of hexamethylene-diisocyanate was carried out in this paper by means of the bleed size calorimeter VSP2. Through the analysis of the experimental data, it was determined that hexamethylene-diisocyanate belonged to the gas bleed system, and the safe bleed design was carried out based on the experimental data and related bleed theory.

(1) Under adiabatic conditions, the HDI sample involved in this paper can achieve the highest temperature of 232℃, the maximum temperature rise rate of 6.94℃ /min, the maximum pressure of 1.2MPa, the maximum pressure rise rate of 0.129MPa/min, and the adiabatic temperature rise of 182℃; Although according to the severity evaluation criteria of thermal runaway reaction, the severity of thermal runaway reaction is not high (" medium "etc.); However, gas is generated in the runaway process, and the maximum pressure exceeds the design pressure of the reactor, so a drain device needs to be installed.

(2) After full cooling at the end of the reaction, the pressure in the system is higher than the initial pressure, and the temperature cannot reach the boiling point of HDI when the reaction is out of control, so the release system belongs to the type of gas release.

(3) For the reactor with a set volume, the safe discharge calculation was carried out. The modified method of DIERS and Leung method was used to calculate the discharge area and discharge diameter respectively, and the results of the two calculations were different by about 20%.

Since Leung's modified method takes into account the loss of materials, it requires a smaller release area than DIERS method. When conditions permit, the release area calculated by DIERS method is more conservative, and it is safer and more reliable when the reaction is out of control.

References

1. Wang Jinjun, Teng Zhijun, Li Xiaoming, et al (2022) Application Research of Mixed Reactors in Synthesis of HDI by Gas-phase Phosgenation[J]. Polyurethane Industry, 37(04): 28-31.
2. Xiao Wang, Shuang Hu, Xia Yang, et al (2023) Thermal stability and kinetic analysis of isophorone diisocyanate (IPDI), Thermochimica Acta, Volume 727: 179574.
3. Ouyang S M, Ye J C, Chen W C, et al (2024) Taguchi method-based evaluation of thermal hazard of lift-off pyrotechnics under various storage conditions[J]. Journal of Loss Prevention in the Process Industries, 87: 105207.
4. Stoessel F (2021) Thermal safety of chemical processes: risk assessment and process design[M]. John Wiley & Sons.
5. Leung J C (1992) Venting of runaway reactions with gas generation[J]. AIChE journal, 38(5): 723-732.
6. Tangren R F, Dodge C H, Seifert H S (1949) Compressibility effects in two-phase flow[J]. Journal of Applied physics, 20(7): 637-645.