Process optimization and thermal risk analysis for 1,3,5-trihydroxy-2,4,6-trinitrobenzenen synthesis

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Abstract. 1,3,5-Trihydroxy-2,4,6-trinitrobenzene (TNPG) is an important precursor material for high-performance explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). In this work, TNPG was synthesized by nitration of phloroglucinol (PG) using the nitrating agent of ammonium nitrate (AN) and sulfuric acid (H2SO4) mixture. The reaction rate and thermodynamics of the nitration reaction was studied. On the basis of a series of reaction calorimetry experiments and thermal stability tests, the feeding sequence and reaction temperature were optimized. The feed sequence of dosing PG/H2SO4 solution into the AN/H2SO4 solution is better than the opposite feed sequence. The best reaction temperature is at 5°C. The highest yield of ~93% TNPG was obtained. In addition, the thermal risk analysis revealed that the thermal risk at the optimal operating condition was low.

1. Introduction
1,3,5-Trihydroxy-2,4,6-trinitrobenzenen, also named trinitrophloroglucinol (TNPG), is an important intermediate for synthesis of the high-energy explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [1]. TNPG has strong combustion or explosive properties with various metals salt, leading TNPG to be an important explosive [2-6]. There are many options of nitrating agents for the synthesis of TNPG using phloroglucinol (PG) as the raw material [7], such as: NaNO2, N2O5, HNO3/H2SO4, AN/H2SO4.

Stephen Velarde uses NaNO2 as the nitrating agent to synthesize TNPG [8]. The exotherm are stable and the process scale-up is convenient, but the yield is only 70%-72%; Ma employed N2O5 to nitrate phloroglucinol for synthesis of TNPG, which overcame the problem of chlorine impurities in the traditional TATB synthesis [9]. Also, nitration by N2O5 nitrating agent have other advantages: (1) faster nitration rate; (2) high yield and product purity; (3) great controllabiliy of the reaction temperature. However, there still exist problems needed to be resolved during the processes of storage, preparation, and scale-up; Nicholas used mixed nitric and sulfuric acid as nitrating agent to synthesize TNPG [10]. After adding HNO3 to H2SO4, it is equivalent to diluting HNO3, which reduces the oxidation ability and corrosiveness of HNO3 and reduces the possibility of side reactions. However, this method will generate a large amount of acid smoke, which is harmful to the environment; Zhang selected HNO3/H2SO4, KNO3/H2SO4, AN/H2SO4 as the nitrating system and investigated the influence of different acid environments on the reaction. The results shown that when AN/H2SO4 is used as the nitrating agent, the reaction yield is the highest, and no gas is generated during the reaction, and the waste acid after the reaction is easy to handle. However, the thermal safety characteristics of the process have not been reported in detail [1].

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From Fig.1, synthesis of TNPG by nitration of PG will undergo three consecutive nitration stages. It is well known that nitration processes are strongly exothermic. Besides, the intermediate and target products may present hazardous thermal decomposition events. Thus, it is necessary to evaluate the thermal risk for this synthesis process. Chen[11] ever investigated the decomposition behaviors of TNPG by TG-DTG and DSC. Recently, Wu[12] determined the decomposition kinetics of TNPG using DSC techniques. To the best of our knowledge, no more literatures were reported to study the process safety problems about synthesis of TNPG.

Fig.1. Synthesis Route for TNPG by Nitration of PG

In this article, the AN/H2SO4 nitration system will be used to synthesize TNPG. Reaction calorimetry tests were carried out on different process conditions, and the best reaction conditions were determined. The thermal risk analysis for the optimized reaction condition will be studied using accelerating rate calorimeter(ARC) and DSC. In the last part, the safety verification of the process is carried out.

2. Experimental section

2.1. Materials.
Concentrated sulfuric acid of 98% was purchased from Shanghai Pharmaceutical Reagent Company of China Pharmaceutical Group; Phloroglucinol with purity higher than 99% was purchased from Maclean Biochemical Technology Co. in Shanghai, Ltd. A.R; 2-Nitroresorcinol (purity ≥99%) was purchased from Maclean Biochemical Technology Co. in Shanghai, Ltd. A.R; Ammonium nitrate, L.P.

2.2. Equipments

2.2.1. Reaction Calorimeter (RC1e). The reaction calorimeter (RC1e) produced by Swiss METTLER TOLEDO is equipped with a 0.5L reactor, a temperature probe, a calibration heater and a feed pump. The temperature, feed rate, reaction heat flow and heat transfer data of the reaction are on-line monitored using RC1e. All RC1e experiments were conducted in isothermal mode, which means the reaction temperature was kept constant by adjusting the jacket temperature [13,14].

2.2.2. Differential scanning calorimetry (DSC). Differential scanning calorimetry (DSC) is a widely used thermal analysis tool to study the thermal stability of hazardous chemicals [15-19]. Differential scanning calorimeter DSC 1 was manufactured by Swiss METTLER TOLEDO. In this work, the thermal stability of the TNPG and product solution was quantitatively tested by DSC in the dynamic mode. The sample was sealed in a high-pressure gold crucible (30 μL) with gold-plated pads. All DSC tests were conducted under N2 atmosphere.

2.2.3. Adiabatic calorimetry. Accelerating Rate Calorimeter (ARC) is a commonly used calorimeter to study the thermal performance of materials through temperature and pressure under adiabatic conditions [20, 21]. The ARC used in this article is produced by the British THT company, the experimental temperature range is 0°C- 500°C, the pressure range is 0MPa-17MPa. the heating-waiting-search (HWS) mode is used for the experiment, and the thermal correction factor $\Phi$ is used for the data to be corrected. The expression of $\Phi$ is

$$\Phi = \frac{m_{cell}C_p,cell+m_{p}C_p,s}{m_{s}C_p,s}$$  \hspace{1cm} (1)

where $m$ represents mass (g). $C_p$ represents the specific heat capacity (J·g-1·K-1). The subscripts of cell and s are the sample container and sample, respectively.
2.2.4. 500MHz NMR. \(^1\)H NMR and \(^{13}\)C NMR spectra were obtained using a Bruker Avance III 500 MHz spectrometer. The chemical shifts (\(\delta\)) are reported in parts per million downfield from tetramethylsilane as an internal standard. To conduct the NMR analysis, the products obtained from RC1e experiments were dissolved in dimethyl sulfoxide (DMSO) as the solvent.

2.3. Synthesis of TNPG
All the synthesis experiments were conducted in RC1e (see Table 1). The synthesis procedure of TNPG is as follows: (1) PG/H\(_2\)SO\(_4\) and AN/H\(_2\)SO\(_4\) solutions were prepared first in the beaker beforehand; (2) added the appropriate amount of PG/H\(_2\)SO\(_4\) or AN/H\(_2\)SO\(_4\) solutions into the reactor and controlled the temperature at the set values; (3) added the other solution into the reactor at a constant feed rate through the feed pump; (4) After the reaction was over, took the reaction solution and poured it into ice. Then filtered and washed the precipitated solid products with ice water and dried it at 45°C for 10h. The operation procedure is shown in Fig.2.

| Run | T (°C) | Initially charged mixture | Mass of initially charged mixture(g) | dosed mixture | Mass of dosed mixture(g) | t\(_{\text{dos}}\) (min) | Mole ratio of PG to AN |
|-----|--------|---------------------------|---------------------------------|--------------|-------------------------|----------------|----------------------|
| 1   | 5      | PG/H\(_2\)SO\(_4\)       | 10/276                          | AN/H\(_2\)SO\(_4\)     | 19.6/184               | 30             | 1:3.1                |
| 2   | 5      | AN/H\(_2\)SO\(_4\)       | 19.6/276                        | PG/H\(_2\)SO\(_4\)     | 10/184                 | 30             | 1:3.1                |
| 3   | 10     | AN/H\(_2\)SO\(_4\)       | 19.6/276                        | PG/H\(_2\)SO\(_4\)     | 10/184                 | 30             | 1:3.1                |
| 4   | 15     | AN/H\(_2\)SO\(_4\)       | 19.6/276                        | PG/H\(_2\)SO\(_4\)     | 10/184                 | 30             | 1:3.1                |
| 5   | 20     | AN/H\(_2\)SO\(_4\)       | 19.6/276                        | PG/H\(_2\)SO\(_4\)     | 10/184                 | 30             | 1:3.1                |

Fig.2. Operation procedure for TNPG synthesis

3. Results and discussion

3.1. Process optimization

3.1.1. Optimization of feeding sequence. In order to study the influence of the feeding sequence on the synthesis reaction, run 1 and run 2 were carried out. In run 1, the PG/H\(_2\)SO\(_4\) solution was first added to the reactor, and then the AN/H\(_2\)SO\(_4\) solution was added to the reactor at a constant feeding rate. The molar ratio of AN to PG is 3:1:1. The experimental heat flow curve is shown in Figure 3. After adding AN/H\(_2\)SO\(_4\) solution, the heat flow quickly stabilized at about 20W. Interestingly, at \(~2\)eq AN, the heat flow drops sharply to about 6W. At the end of the feeding period, the heat flow dropped sharply again, which was attributed to the completion of PG in the reactor. The small peak at about 155 minutes corresponds to the crystallization of TNPG. In run 2, the AN/H\(_2\)SO\(_4\) solution was first loaded into the reactor, and then the PG/H\(_2\)SO\(_4\) solution was metered into the AN/H\(_2\)SO\(_4\) solution at the same feeding time. The experimental heat flow curve of run 2 is shown in Figure 4.
Compared with the heat flow profile of run 1 in Fig.3, one can see that the heat release rate for run 2 are smoother, which is beneficial to temperature control. In addition, by integrating the heat flow curves for runs 1 and 2, the heat conversion at the dosing endpoint of runs 1 and 4 are 88.72% and 95.78%, respectively. This result implies that the feeding sequence employed in run 4 will take less time to reach the reaction completion, which is better in the term of the production efficiency.

We also compare the color of the reaction mixture at the endpoint of dosing period for runs 1 and 2, as shown in Fig.5. It is found that the reaction mixture color for run 1 is obviously deeper than that of run 2. This can be interpreted as follows: the exposure time of PG to air in run 1 were longer than that in run 2 and, as a result, more phenolic hydroxyl groups were oxidized resulting into deep red color. This interpretation was also evidenced by higher yield of TNPG in run 2. The yield of TNPG for runs 1 and 2 are 88% and 93%, respectively.

In the light of the above comparisons, the feeding sequence in run 2 is considered better than that in run 1. Therefore, this feeding sequence was employed in the following runs.

3.1.2. Optimization of reaction temperature. In order to select the suitable reaction temperature for the synthesis reaction, more experiments were carried out at different temperatures, namely, runs 3-5. Except for the reaction temperature, the rest operating conditions in runs 3-5 were the same as that in run 2. The heat flow curves of the RC1e experiment for runs 3-5 are shown in Fig 6-8. For all the heat flow profiles in runs 3-5, the exothermic signal sharply decreased to about zero after the addition of PG/H₂SO₄ solution stopped, indicating that the accumulation of unreacted PG in the reactor can be neglected over the whole process.

The total heat generated (Qtot) by the reactions was obtained by integrating the heat flow profiles and summarized in Table 3.

\[
Q_{\text{tot}} = \int q \, dt
\]  

(2)
Where $q_r$ is the heat release rate by the reaction.

Fig.6. Heat flow profile for run 3

![Fig.6. Heat flow profile for run 3](image)

Fig.7. Heat flow profile for run 4

![Fig.7. Heat flow profile for run 4](image)

Fig.8. Heat flow profile for run 5

![Fig.8. Heat flow profile for run 5](image)

Obviously, as the reaction temperature increased, more heat were released by the reaction. Nevertheless, as shown in Table 2, the yield decreased with the reaction temperature increasing. This phenomenon can be interpreted by that increasing reaction temperature will facilitate the side reactions. This interpretation was further confirmed by the deeper color of the solid product at higher reaction temperature in Fig.9.

Table 2 Experimental data at different reaction temperatures

| Temp(°C) | $Q_{tot}$ (kJ) | Thermal conversion at the dosing endpoint (%) | yield (%) |
|----------|---------------|---------------------------------------------|-----------|
| 5        | 25.66         | 99.96                                       | 93        |
| 10       | 25.70         | 95.60                                       | 85        |
| 15       | 28.34         | 96.22                                       | 81        |
| 20       | 30.86         | 99.75                                       | 76        |
Based on the above results, we identified the operating conditions in run 2 as the optimal operating conditions. In the following part, we will conduct thermal risk analysis for this run in detail.

3.2. Thermal risk analysis

Before conducting the thermal risk analysis for run 2, we first performed the $^1$H-NMR, $^{13}$C-NMR tests on the solid product. The $^1$H-NMR and $^{13}$C-NMR results were shown in Fig. 10. The solid product was identified as the desirable TNPG and the content of the side product could be neglected.

3.2.1. Maximum Temperature of the Synthesis Reaction (MTSR).

The concept of maximum temperature of the synthesis reaction (MTSR) has been widely used to characterize the severity of the exothermic reaction [14, 22-24]. The calculation formula of MTSR is

$$MTSR = T_p + X_{ac,max} \Delta T_{ad}$$

Where $T_p$ is the process temperature, $X_{ac,max}$ is the maximum accumulation of the unreacted reactants, and $\Delta T_{ad}$ is the adiabatic temperature rise of the exothermic reaction. $\Delta T_{ad}$ can be calculated by

$$\Delta T_{ad} = \frac{Q_{tot}}{mc_p}$$

Where $m$ is the mass of the whole reaction mixture added into the reactor, $C_p$ is the specific heat capacity of the reaction mixture.

Combined with the parameters obtained from the RC1e experiment, $\Delta T_{ad}$ was calculated to be 35.50K. The thermal conversion at the end of feeding period was 95.78%. Accordingly, the value of $X_{ac,max}$ was calculated to be 4.22%. Substituting $\Delta T_{ad}$ and $X_{ac,max}$ gave the MTSR of 6.50°C.
3.2.2. Thermal risk of the second decomposition. In order to study thermal risk of the second decomposition, ARC test was carried out on the product liquid. The test temperature range was 50°C - 400°C, the temperature rise step was 5K/min, the waiting time was 10min, and the test sample ball was: HC, mass 14.434g. Sample mass is 0.420g, Φ=8.217. The test results are as shown in Fig 11, the initial exotherm temperature is about 115°C. According to formula 5, the corrected relationship between temperature with TMRad is linearly fitted (Formula 5) [25,26]
\[
\ln(TMRad) = \frac{E}{R} \left(\frac{1}{T}\right) - \ln A
\]
where TMRad (time to maximum rate under adiabatic condition), E represents the apparent activation energy, A represents the pre-exponential factor.

The results are shown in Fig 12, and the fitting equation can be obtained as \( \ln(TMRad) = \frac{11806.120}{T} - 26.427 \). When TMRad=24h, it is obtained that T=80°C, when the maximum temperature rise rate is 24h, the corresponding initial decomposition temperature is TD24=80°C.

3.2.3. Risk assessment. With respect to exothermic reactions, once a cooling failure occurs, the temperature will rise from Tp to MTSR. It is necessary to check whether further temperature rise caused by the secondary decomposition reaction will occur [20, 27]. This can be determined by comparing MTSR with TD24. In addition to the three temperature parameters Tp, MTSR, and TD24, the maximum temperature for technical reason (MTT) is also an important parameter. According to the order of these four parameters, the risk degree of chemical reaction can be divided into 5 levels (Fig 13).
For this reaction, the solvent is H₂SO₄ and the reaction is operated at the normal pressure, so MTT is the boiling point of concentrated sulfuric acid, that is, MTT=338°C, Tₚ=5°C, Tₑ₂₄=80°C, MTSR=6.5°C, so the thermal runaway risk level of this process is level 2.

4. Conclusion
In summary, the AN/H₂SO₄ nitrating agent was employed to nitrate PG for synthesis of TNPG in this work. The reaction process has been optimized in the terms of feed sequence and reaction temperature. It is found that the feeding sequence of addition PG/H₂SO₄ solution is better than the opposite feeding sequence. The optimal reaction temperature was optimized at 5°C. At the optimal operating condition, the desirable TNPG yield reach up to 93% and the obtained TNPG is highly pure. In addition, thermal risk analysis was conducted for the optimized process conditions. The Tₑ₂₄ of the final reaction product was calculated to be 80°C, much higher than the MTSR value (6.5°C). The results show that the danger level of this reaction is 2. In the case of cooling failure, as long as the addition is stopped immediately, no secondary decomposition will occur.

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