Effect of Acid Concentration on Thermal Stability of nitrocellulose (NC) for Civil Use

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Abstract. The effect of acid concentration in nitrocellulose (NC) on thermal stability of NC for civil use was studied using differential scanning calorimeter (DSC). The thermal explosion temperature (Tb) and kinetic parameters of NC thermal decomposition were calculated using different methods based on the thermal decomposition behaviors of NC in high pressure-gold plated stainless steel crucible at different heating rates. The results show that acid content in NC reduces the stability of NC remarkably, including reducing the characteristic decomposition temperature such as peak temperature (Tp), onset temperature (Tonset), initial temperature (T0) and critical temperature of thermal explosion (Tb). The big difference between NC with different acid content is that the relative quantity of activation energy and the change trend of activation energy. The most interesting thing is that NC with more acid content has the lower characteristic temperature but higher calculated activation energy.

Keywords: Nitrocellulose for civil use, thermal stability, thermal decomposition, differential scanning calorimeter, high pressure crucible.

1. Introduction
Nitrocellulose (NC) is a kind of material which has been used widely in military domain and civil field, such as, it’s a main part of gun propellant and rocket propellant, and having huge demand in coating or printing ink industry [1]. The main difference between NC for military use and civil use is the nitrogen content, with the property of intending to decompose more easily as nitrogen content increases. NC is a material with self-accelerating decomposition property which can cause self-igniting due to heat accumulation in the center of NC package. Thereby, special precautions such as sealing package, adulterating water or solvent into NC have been required to take by law to make sure the safety in transportation or warehouse. However, catastrophic tragedy caused by thermal decomposition and ignition of NC happened in August 12, 2015 at Tianjin port in China. Thermal stability of NC has been a great interest for explosive chemist and safety process engineer since 1950[2-7]. Recently, effects of a lot of factors, such as thermal history [8], water [9,10], inorganic salts[11], heating rate[12], nitrate content[13], particle size[14] and solvents[15], on thermal decomposition of NC have been reported, and the calculation of characteristic parameters on thermal safety of NC through non-isothermal DSC[16,17] curves were conducted. Katoh,K [18] studied the decomposition and ignition of NC in the presence of sulfuric acid using accelerating rate calorimeter (ARC)and hand-built ignition testing equipment. It was reported that thermal stability decreases as the sulfuric acid content increases to
certain amount. However, to the best of our knowledge, the quantitative characterization of acid content’s influence on thermal stability of NC hasn’t been reported. In the light of the influence of acid on catalytic decomposition of NC, we studied the thermal behaviors of NC with different nitric acid concentration, and presented quantitative results on characteristic parameters of thermal decomposition of NC for civil use.

2. Experimental section

2.1. Sample
The No.1 NC with acid content 0.095 mass%, and nitrogen content 11.9 mass%, was provided by Sichuan Northern Nitrocellulose Ltd, and the No.2 NC with nitrogen content 11.9 mass%, and acid content 0.338 mass% was prepared in Xi’an Chemistry Research Institute based on the No.1 NC. All samples were heated in oven at 50°C to remove organic solvent before thermal analysis tests.

2.2. Experimental apparatus and conditions
Differential scanning calorimeter (DSC) experiments were carried out on Q200 (TA company) at heating rate 1K/min~8K/min from room temperature to around 573K in high pressure sealed crucible (gold-plated) with volume of 27μl and maximum pressure 100bar. Sample mass is about 0.1mg.

3. Results and discussions

3.1. Experiment results
Typical DSC curves of NC are presented in Fig.1.

![Figure 1. Typical DSC curves for NC with different acid content](image_url)

Note: No.1 and No.3 denote different NC with 0.095% and 0.338% acid content, the number 1 and 2 denote the heating rate.

It can be seen from the fig.1, the DSC curve moves toward the high temperature region and the peak temperature increases as the heating rate increases for the same sample, which is the same as normal results reported [13]. The big difference is that the DSC curve can be divided into two parts, which is to say, the NC decomposes in two macroscopic processes, and the first one is the main process. The other point which should be paid attention to is that the second process is weak at low heating rate such as 1K/min in this study, and as the heating rate increases, the second process becomes more significant. This phenomenon can be attributed to the different experimental condition. In this study, the high-
pressure sealed crucible was used, which can prohibit the volatilization of gas products and initiate secondary reactions. Another point we can see is that as the acid content increases, the second exothermic process becomes more obviously, which indicates that the acid content influences the second exothermic process. Maybe the gas products or mole ratio of gas products changed as acid content changes, but without further qualitative and quantitative results by mass spectrum or light spectrum, no definite explanation can be given.

The characteristic parameters of DSC curve for NC with different acid content are showed in table 1.

### Table 1. Values of characteristic parameters of DSC curves

| Sample number | T₀ (K) | T_onset (K) | T_p (K) | Q (J/g) |
|---------------|--------|-------------|---------|---------|
| No.1-1        | 423.9  | 435.7       | 444.9   | 1887    |
| No.1-2        | 437.4  | 450.2       | 462.8   | 1961    |
| No.1-4        | 449.0  | 462.7       | 478.1   | 2071    |
| No.1-8        | 453.7  | 467.7       | 484.3   | 1846    |
| No.3-1        | 362.8  | 381.3       | 394.9   | 1664    |
| No.3-2        | 369.3  | 387.8       | 405.9   | 2228    |
| No.3-4        | 374.9  | 393.4       | 415.4   | 1754    |
| No.3-8        | 377.1  | 395.6       | 419.2   | 2256    |

Note: T₀, initial temperature deviates from the base line; Tonset, extrapolated onset temperature; Tp, peak temperature; Q, heat released during the whole decomposition process.

It can be seen from tab.1 that the T₀, Tp, Tonset increase as the heating rate increases, which is the same as the normal results of DSC experiment. The characteristic temperature parameters such as T₀, Tp and Tonset decrease significantly as acid content increases at the same heating rate.

### 3.2. Decomposition kinetics

From the fig 1 we can see that the DSC curve is asymmetric and the shape of DSC curve is related to the heating rate because of the second decomposition process. It will incur big error if we calculate the kinetic three factors using data in whole decomposition temperature span, so we use temperature data between T₀ to Tp to calculate activation energy. It was assumed by Ozawa method that the reaction degree is the same at peak temperature for the same sample at different heating rate, hence, it’s reasonable and rational to calculate the kinetic parameters using data from t₀ to Tp, which means that the point of reaction degree \( \alpha =1 \) corresponds to the point at peak temperate. The calculated results of activation energy and correlation coefficient for No.1 and No.3 NC using Flynn-Wall-Ozawa method were given in fig2, and fig3.

From fig2 and fig3 we can see the value for R² is more than 0.95, and decreases as the reaction degree increases. The big difference of activation energy change between No.1 and No.3 NC is that the activation energy decreases monotonously for No.1 NC, on the other hand, the activation energy for No.3 NC increase in the first stage and decrease monotonously as reaction goes. Another point we should pay attention to is that the highest value of activation energy for No.1 NC is 103.6 KJ/mol, and the lowest value is 89.7 KJ/mol, on the other hand, the highest value for No.3 NC is 157.8 KJ/mol, and the lowest value is 104.2 KJ/mol which is even bigger than the highest value for No.1 NC. This is the first time to observe this phenomenon that the one with higher activation energy has lower characteristic decomposition temperature, which indicates that the relative sequence for characteristic temperature of DSC curves isn’t directly related to the relative sequence for activation energy.
To confirm the correctness of kinetic parameters calculation by Flynn-Wall-Ozawa method, the kinetic parameters were calculated using Kissinger method, and the results were listed in table 2.

Table 2. The kinetic parameters for NC calculated using Kissinger method

| Sample number | E_e (J/mol) | E_p (J/mol) | E_0 (J/mol) | ln(A_e/s⁻¹) | ln(A_p/s⁻¹) | ln(A_0/s⁻¹) |
|---------------|-------------|-------------|-------------|-------------|-------------|-------------|
| No.1          | 96342.7     | 81551.3     | 97883.0     | 14.3        | 9.7         | 15.6        |
| No.3          | 165182.1    | 104006.2    | 150745.8    | 40.1        | 19.6        | 38.1        |

Notes: E, lnA denote the activation energy and pre-exponential factor; subscript e, p, 0 mean Tonset, Tp and T0 were used to calculate kinetic parameters.

Activation energy calculated using Kissinger method follows the same change trend as that calculated using Flynn-Wall-Ozawa method, the activation energy of No.1 NC decreases from 97.8 KJ/mol at T0 point to 81.5 KJ/mol at Tp point, but the activation energy of No.3 NC increases from 150.7KJ/mol at T0 point to 165.1 KJ/mol at Te point, and then decreases to 104.0 KJ/mol at Tp point. Based on the above results obtained through two methods, it’s safe to say the activation energy changes in the whole decomposition process of NC, and it’s hard to find a simple mechanism function such as the first order reaction or first order autocatalytic reaction to describe this process.
3.3. Thermal safety
The critical temperature of thermal explosion (Tb) can be calculated from Eq.1 [19].

\[ \text{Tb} = \frac{\text{E}_0 - \sqrt{\text{E}_0^2 - 4\text{E}_0\text{RT}_p}}{2\text{R}} \]  \hspace{1cm} (1)

Where R is the gas constant (8.314J·mol\(^{-1}\)·K\(^{-1}\)),\( \text{E}_0 \) is the value of activation energy obtained by Ozawa’s method. \( \text{T}_p \) is the peak temperature when the heating rate \( \beta \rightarrow 0 \). The peak temperature of NC at different heating rate was showed in fig4.

![Figure 4. Peak temperature of NC at different heating rate](image)

It was fitted by exponential function, and the fitting equation for No.1 and No.3 NC are \( \text{T}_p = -72.08739 \times \exp(\beta / -1.69314) + 484.9230 \) and \( \text{T}_p = -44.68639 \times \exp(\beta / -1.68969) + 419.6045 \), respectively. By extrapolating the equation to \( x = 0 \), the peak temperature \( \text{T}_p \) are obtained 412.8K for No.1 and 373.9K for No.3, respectively.

The average value of activation energy calculated using Ozawa’s method for No.1 and No.3 NC are 102161.1J/mol and 140041.5 J/mol respectively. The Tb obtained by substituting the activation energy and \( \text{T}_p \) data into Eq.1 are 427.7K for No.1 and 382.5 K for No.3 NC respectively.

4. Conclusion
Acid content in NC has significant influence on thermal decomposition of NC, especially on characteristic temperature such as initial temperature (\( \text{T}_0 \)), onset temperature (\( \text{T}_{\text{onset}} \)), and peak temperature (\( \text{T}_p \)).

NC with lower acid content has higher characteristic temperature but lower activation energy. Acid content in NC can reduce the critical temperature of thermal explosion (Tb) of NC. For No.1 NC with 0.095% acid content the Tb is 427.7K, and 382.5K for No.3 NC with 0.338% acid content.

For the safety in transportation process or storage of NC, it’s important to maintain the good sealing of the package to avoid the solvent vaporization which can increase the acid concentration and further lead to catastrophic accident.

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