

A COMPARISON OF THERMAL DECOMPOSITION ENERGY AND NITROGEN CONTENT OF NITROCELLULOSE IN NON-FAT PROCESS OF LINTERS BY DSC AND EA

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Investigations of nitrogen content and thermal decomposition activation energy (E_a) of two different kinds of nitrocellulose (NC) products, NMNC and MNC from the non-fat and original processes of linters, respectively, were discussed. In this study, differential scanning calorimetry (DSC) and element analyzer (EA) are used, for the above two chemicals, along with the same nitration condition in use of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) mixing acid. E_a was calculated by our induced model. According to our experimental results, the nitrogen content of NMNC/MNC was 11.71 and 11.55 mass%, in a low nitrogen content condition of mixing acid. The E_a parameters were 319.91 (NMNC) and 347.27 (MNC) kJ mol^{-1} , individually. They indicated that the non-fat process of a linter made a higher degree of stability than the others. This research also presents an efficient and accurate model of the thermal decomposition property evaluation for non-fat process of linters. The outcome is believed to be very useful for helping to understand, and be applied as, an inherently safer design during relevant NC manufacturing processes.

Keywords: activation energy (E_a), DSC, element analyzer (EA), nitrocellulose (NC), nitrogen content

Introduction

We attempted to understand the influence of a linter's non-fattening process on synthetic nitrocellulose. The process is conducted through nitration in the same condition to compare the result of nitrocellulose with different nitrogen content (non-fatted linter and un-non-fatted linter). Furthermore, a process of refining NC to remove sulfate ester was also developed [1–3].

The investigations of nitrogen content and thermal decomposition activation energy (E_a) of two different kinds of nitrocellulose (NC) products are discussed via element analyzer (EA) and differential scanning calorimeter (DSC), respectively.

We used differential scanning calorimetry (DSC) to analyze the thermal decomposition of nitrocellulose and then applied the Arrhenius equation to calculate the mathematical model of activation energy. We then obtained the E_a of NC according to the methods of Regnier, Chang, Brill, Lou, Chu, Zheng-Wang and Lin [4–11]. This was to understand the differences between non-fatted and un-non-fatted linter as well as the differences between synthetic nitrocellulose. We anticipated further understanding the effect of a linter's non-fattening process on nitrocellulose's thermal decomposition [2, 10, 12–16].

Introduction to cellulose

Cellulose is a natural polymer in which there are repeated units with three hydroxyl groups and all can be nitrated. The molecular structure of the cellulose is shown in Fig. 1 [12].

Currently, we have two materials to make nitrocellulose: linter and wood pulp. In terms of military applications, linter is mainly the material of nitrocellulose [12]. Cellulose usually contains fat, pectin, dust, protein, sand and other alloys [12]. The typical components of cotton are listed in Table 1 [12].

Though linter contains fewer alloys than cotton, it still affects the nitration process. Therefore, it needs non-fattening before being nitrated [13]. Ordinary cellulose is usually less acid-resisting but alkali-proof. Therefore, the de-fattening process is conducted in alkali solution [14, 15].

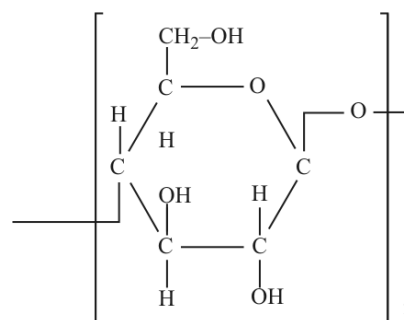


Fig. 1 Molecular structure of the cellulose [12]

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Table 1 Typical components of cotton

Chemical components	Range/mass%	Standard/mass%
Cellulose	88–96	94
Protein	1.1–1.9	1.3
Pectin	0.7–1.2	0.9
Dust	0.7–1.6	1.2
Wax	0.4–1.0	0.6
Organic acid	0.5–1.0	0.8
Carbohydrate		0.3
Pigment		trace
Others		0.9

Cellulose's nitration and its mixed acid composition

The mixed nitric-sulfuric acid ratio is about 2.5 to 3. Owing to the significant impact of acid to nitration action, insufficiently mixed nitric-sulfuric acid was very susceptible to influence by the water produced in the nitration [1]. The conditions to make nitrocellulose with different nitrogen contents are displayed in Table 2 [1].

Nitrocellulose refinement

Nitrocellulose refinement is a very complicated process. Finding an effective way to eliminate trace amounts of acid to acquire more stable nitrocellulose is the key to this study. For nitration agent using sulfuric and nitric acid as the mixed acid, the mass ratio between sulfuric and nitric acid is ca. 3:1. Hence, there will be a reaction between the un-nitrated cellulose and hydroxyl groups and then become sulfurate ester ($-\text{OSO}_3\text{H}$).

Since too much sulfurate ester in nitrocellulose affects its stability; there will be a risk of in spontaneous combustion in long-term storage. Modern industrial processing is to boil it in thin nitric acid solution [2]. After this process, the nitrocellulose is boiled in carbonate calcium to neutralize the trace amount of acid. However, it cannot make sulfurate ester in more stable state [1–3].

Table 2 Conditions to produce nitrocellulose with different nitrogen content

Component of mixed acid (specific mass)	Mixed acid's mass ratio/%	Mass ratio of mixed acid and linter	Reaction time/min	Nitrogen/mass%
Nitric acid (1.4)	40.57			
Thick sulfuric acid (1.84)	57.41	60:1	45	11.5–12.5
Water	2.02			
Fumed nitric acid (1.5)	26.00			
Thick sulfuric acid (1.84)	64.60	60:1	20	13.2–13.6
Water	9.40			

Thermal decomposition of NC

The thermal decomposition activity is the same as ordinary nitrate ester. It can be expressed by the Arrhenius equation as shown in Eq. (1) [4–11]:

$$r = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where r is the decomposition rate; E_a is the activation energy of thermal decomposition (kJ mol^{-1}); T is the absolute temperature (K); R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and A is the frequency factor. In essence Eq. (1) was used to calculate and analyze the activation energy of thermal decomposition [4–11].

Experimental

Materials

- Mexican linter from domestic arsenal.
- Israeli linter from domestic arsenal.

Methods

Instruments available for this study are listed as follows:

- Electrical oven: Risen universal oven.
- Differential scanning calorimetry (DSC): Netzsch DSC 200, Germany.
- Element analysis (EA): PerkinElmer Model 2400 CHN.

Refining the linter (process as shown below)

- Extracting Mexican linter (eight hours) with chloroform in Soxhlets extractor.
- A continuous extraction (eight hours) with methyl alcohol.
- De-fattening with sodium hydroxide with the normality of 1 N at the temperature between 85–90°C for four hours.
- Boiling de-fatted Mexican linter in de-ionized water for four hours.
- Flushing Mexican linter with de-ionized water until it was chemically neutral.

- Using hydrochloric acid (with the normality of 0.5 N for one hour stirred) to neutralize the reaction.
- Flushing with de-ionized water until there was no more trace acid.

Production of low nitrogen-content nitrocellulose (the process is shown below)

- Poured 12 mL of de-ionized water in a 500 mL double neck flask and the ice-bathed at 10°C.
- Slowly poured 200 mL of sulfuric acid (1.84) into the flask.
- Gradually dropped 186 mL of nitric acid (1.40) into the flask with the temperature below 10°C and then waited until the temperature returned to room temperature.

Refining the nitrocellulose (the process is shown below)

- Boiled the initial nitrated product in a 500 mL 50 mass% acetic acid solution at 85–90°C for an hour.
- Filtered with clean water four times.
- Boiled in a 500 mL 2 mass% sodium bicarbonate solution at 85–90°C for ten minutes.
- Boiled with 500 mL water three times (six hours for the first time, two hours for the second time, and one hour for the last time) at the temperature 85–90°C.
- EA analyses of the refined products are in Table 3.

Table 3 EA analyses of NMNC and MNC

Sample	NMNC			MNC		
	Element	C%	H%	N%	C%	H%
1	27.3	2.72	11.67	27.3	2.8	11.61
2	27.31	2.73	11.74	27.46	2.79	11.48
N mass%	11.71			11.55		

The average nitrogen content N mass% was calculated with the root mean square

Operating procedures of DSC

Mexican, Israeli and refined linters

Scanning rate of 5°C min⁻¹. We intentionally used nitrogen as the carrier gas. Its flow rate was 10 mL min⁻¹, and then heating from 50 to 500°C.

NMNC, MNC

Scanning rate of 5°C min⁻¹. We intentionally used nitrogen as the carrier gas. Its flow rate was 10 mL min⁻¹, and then heating from 50 to 280°C.

Results and discussion

Discussion on linter refinement

The linter used in industrial production usually has been refined, that is, the non-fating process. However, linter produced in this process is usually made through alkali boiling, which does not ensure purifying the linter. This study thus had to make a second refinement.

We used organic solvent (chloroform and methyl alcohol) to extract the organic impurities. We first eliminated the linter's outer protective material and then boiled it in alkali solution (sodium hydroxide) to completely eliminate the impurities in the linter. In addition to better understanding the effect of the refined linter, we further analyzed the difference between the raw and the refined linter and realized their influence on nitrocellulose. We obtained Fig. 2 after analyzing the Mexican linter, Israeli linter, and refined Mexican linter with DSC.

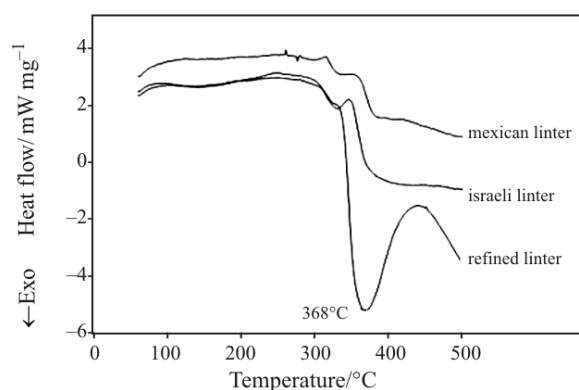


Fig. 2 DSC thermal curves of Mexican, Israeli and refined linters with scanning rate of 5°C min⁻¹

We observed a significant exothermic peak of refined Mexican linter at 368°C. For un-refined Mexican linter and Israeli linter, though, there was a deviation from the baseline. We cannot see as prominent exothermic peak as that of refined Mexican linter. We could thus infer that trace impurities influenced the excursion of thermal decomposition.

A nitrogen content comparison between NMNC and MNC

Under the same nitration conditions (temperature, time duration and mixed acid), we compared the nitrogen content of unrefined Mexican linters and refined Mexican linter after the nitration process. The results are as given in Table 4.

We could see that the refined Mexican linter had higher nitrogen content. This revealed the fact that incomplete refinement could affect the nitration.

Table 4 Comparison of nitrogen content between NMNC and MNC

Sample	Mexican linter	Refined Mexican linter
Mass of mixed acid/g	640	640
Mass of linter/g	10	10
Mixed acid: linter (mass ratio)	64: 1	64: 1
Reaction time period/min	45	45
Reaction temperature/°C	28–32	28–32
Nitrogen content/mass%	11.55	11.71

Thermal decomposition E_a comparison between NMNC and MNC

This study examined NMNC and MNC with DSC, acquired some thermodynamic parameters, and then modified the Arrhenius equation to fit the activation energy of nitrocellulose on decomposition [4–11].

To facilitate the model development, we first set T_0 and T_f are onset temperature and final temperature for runaway excursion. Meanwhile, Q_0 and Q_t are total heat of decomposition and time of the exothermic reaction heat released by decomposed materials.

We could calculate the conversion rate α on the basis of DSC curve.

$$\alpha = \frac{Q_t}{Q_0} = \frac{mC_p(T_f - T)}{mC_p(T_f - T_0)} = \frac{(T_f - T)}{(T_f - T_0)} \quad (2)$$

where m and C_p are sample mass and sample heat capacity, then

$$1 - \alpha = 1 - \frac{(T_f - T)}{(T_f - T_0)} = \frac{(T - T_0)}{(T_f - T_0)} \quad (3)$$

Based on the Arrhenius equation:

$$-r_A = -\frac{dC_A}{dt} = kC_A^n = A \exp\left(-\frac{E_a}{RT}\right) C_A^n \quad (4)$$

where r_A is the reaction ratio; C_A is the sample concentration; k is a reaction ratio constant; n is reaction order.

Let

$$C_{A0} = \frac{\rho}{M} \quad (5)$$

where ρ is sample density; M is the molecular mass; and C_{A0} is the concentration before the sample was examined:

$$C_A = C_{A0}(1 - \alpha) \quad (6)$$

By combining Eq. (3) with Eq. (6) to substitute Eqs (4), (7) could be expressed as follows:

$$\begin{aligned} -\frac{dC_A}{dt} &= AC_{A0}^n (1 - \alpha)^n \exp\left(-\frac{E_a}{RT}\right) = \\ &= AC_{A0}^n \left(1 - \frac{T_f - T}{T_f - T_0}\right)^n \exp\left(-\frac{E_a}{RT}\right) \\ AC_{A0}^n \left(1 - \frac{T_f - T}{T_f - T_0}\right)^n \exp\left(-\frac{E_a}{RT}\right) &= \\ &= AC_{A0}^n \left(1 - \frac{T - T_0}{T_f - T_0}\right)^n \exp\left(-\frac{E_a}{RT}\right) \end{aligned} \quad (7)$$

As obtained from the non-isothermal curve, heat of decomposition varies with the reaction rate.

Therefore Eq. (8) can be presented as follows:

$$Q_t = Q_0 - (r_A) \quad (8)$$

Substituting Eq. (7) into (8),

$$\begin{aligned} Q_t = Q_0 - (r_A) &= Q_0 \left(-\frac{dC_A}{dt}\right) = \\ &= AQ_0 C_{A0}^n \left(\frac{T - T_0}{T_f - T_0}\right)^n \exp\left(-\frac{E_a}{RT}\right) \end{aligned} \quad (9)$$

Dividing $\left(\frac{T - T_0}{T_f - T_0}\right)^n$ on both sides of Eq. (9), and

then taking the natural logarithm on both sides, we have Eq. (10):

$$\ln \left[\frac{Q_t}{\left(\frac{T - T_0}{T_f - T_0}\right)^n} \right] = \ln AQ_0 C_{A0}^n - \frac{E_a}{RT} \quad (10)$$

The values of $\ln[Q_t/(T - T_0/T_f - T_0)^n]$ vs. $1/T$ are indicated in Figs 3 and 4.

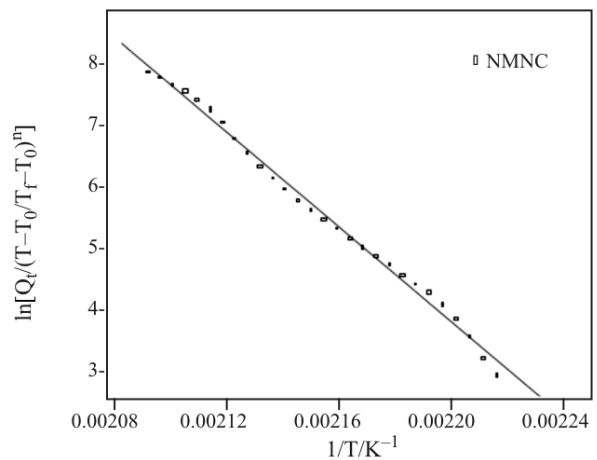


Fig. 3 Activation energy analysis for NMNC with scanning rate of 5°C min⁻¹ by DSC

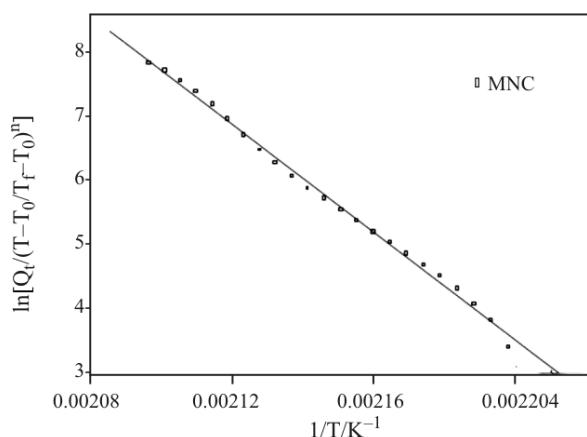


Fig. 4 Activation energy analysis for MNC with scanning rate of $5^{\circ}\text{C min}^{-1}$ by DSC

Table 5 Thermal decomposition E_a comparison between NMNC and MNC

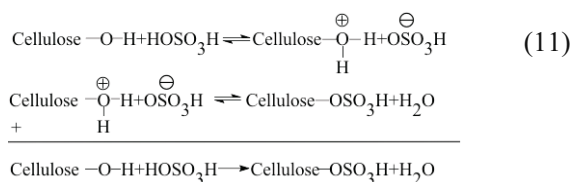
Sample	NMNC	MNC
Reaction order/ n	1.46	1.22
Activation energy $E_a/\text{kJ mol}^{-1}$	319.9	347.27
Linear/ R^2	0.99715	0.99824

We obtained the best straight line by substituting the appropriate reaction order n along with the heat of decomposition from slope = $-E_a R^{-1}$.

From Table 5, we can see that MNC had a higher thermal decomposition E_a than NMNC, which means it did not decompose as easily as NMNC. The main reason was that un-refined MNC still contained some impurities which might affect its nitration. This again proved the difference between the refined and un-refined linters.

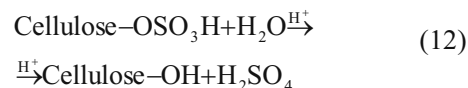
Nitrocellulose's refining process

In terms of the mixed acid used in the nitration process, sulfuric acid shared the greatest percentage because it is the dehydrating agent; the sulfurate ester ($-\text{OSO}_3\text{H}$) was inevitable. The reaction mechanism can be depicted as Eq. (11) [16]:

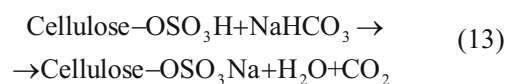


In addition to lowering nitrogen content in the nitrocellulose, too much sulfurate ester also deteriorated the stability and thus jeopardized the long-term storage

safety. Sulfurate ester should be decreased through the refining process. This study used 50 mass% acetic acid solution as the catalyst to catalyze the sulfurate ester into hydroxyl group. This eliminated the residues of sulfurate ester derivatives [2]. The reaction equation can be represented by Eq. (12):



To completely eliminate sulfurate ester, we used 2 mass% sodium carbonate solution after the acid catalysis was used to neutralize the sulfurate ester residues. This process produced ionized sodium sulfurate groups, which were a stable base, to thoroughly eliminate the unstable factors of sulfurate ester to nitrocellulose. Consequently, the reaction equation can be followed by Eq. (13) [1]:



Alkali boiling in industrial production has been used to get rid of the acid residues in nitrocellulose, but it fails to effectively eliminate the unstable factors. The greatest difference between the refining process in this study and that in industrial process is that we effectively eliminated the sulfurate ester, which significantly reduced the risk of long-term storage [2].

Fortunately, to date, many excellent researches focused on thermal analysis have been conducted and proposed by scientists all around the world [17–27]. Therefore, we sincerely hope this study can help the relevant plants or processes for avoid accidents.

Conclusions

Based on the linter refinement of nitrocellulose, we made a complete thermal decomposition analysis of low nitrogen content nitrocellulose to understand the refined linters' influence on the nitrocellulose production process. We thus reached the following conclusions:

- Nitrocellulose made from refined linter has high nitrogen content when under the same process condition (mass, temperature, nitration agent, and time duration).
- Re-refined nitrocellulose have better thermal decomposition effect.
- More stable sodium sulfurate groups, which are produced when sulfurate ester is neutralized with sodium carbonate, effectively eliminate the sulfurate ester, which reduces the risk of long-term storage.

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Nomenclature

A	frequency factor/ $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
C_A	sample concentration/ mol L^{-1}
C_p	heat capacity/ $\text{J kg}^{-1} \text{K}^{-1}$
E_a	activation energy/ kJ mol^{-1}
k	rate constant/ $\text{mol L}^{-1} \text{s}^{-1}$
M	molecular mass/ g mol^{-1}
m	sample mass/ g
n	reaction order, dimensionless
Q_0	total enthalpy of heat decomposition/ kJ kg^{-1}
Q_t	enthalpy for composed exothermal/ kJ kg^{-1}
R	gas constant/ $8.31415 \text{ J K}^{-1} \text{ mol}^{-1}$
r	the reaction rate/ g s^{-1}
T	absolute temperature/ K
T_0	onset temperature/ K
T_f	final temperature/ K
t	time/ s
α	conversion rate/ g s^{-1}
ρ	sample density/ g L^{-1} .

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