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Research paper

The Preparation and Properties of Low-Nitrogen Nitrocellulose by Alkaline Denitration

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Abstract: Waste high-nitrogen nitrocellulose (NC) has always been disposed of as hazardous material for destruction, and has not been recycled as a resource. The present work describes how waste high-nitrogen NC may be converted to low-nitrogen NC *via* an alkaline denitration reaction between sodium hydrosulfide and the nitrate ester groups, in order to control and reduce the nitrogen content for industrial products.

Scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) and X-ray diffraction (XRD) were used to detected the changes in the surface morphology and chemical structure of the NC samples. TG-DSC tests analyzed the decomposition temperature and the heat released on thermal decomposition, and the explosion heat was obtained by calorimetry.

The results demonstrated that the denitration reaction does not destroy the skeletal structure of NC. Notably, the nitrogen content of NC may be reduced from 12.92 to 10.74%, generating the level for industrial products (N <12%). Moreover, NC samples with different nitrogen contents have similar decomposition trends and decomposition temperatures, but the heat released is gradually decreased and the explosion heat is significantly reduced, and confirms the successful partial

removal of nitrate ester groups from NC. Therefore, the alkaline denitration affords
a potential method for recycling waste high-nitrogen NC.

Keywords: waste, high-nitrogen nitrocellulose, denitration, nitrogen
content, explosion heat, recycling

1   Introduction

Nitrocellulose (NC) is the product of the esterification reaction between cellulose
and nitric acid, and the nitrate ester groups ($-ONO_2$) are the characteristic groups
in the macromolecular chain [1, 2]. Theoretically, the highest nitrogen content
is close to 14.14%. However, in practice, the maximum nitrogen content is
13.8% [3, 4]. Low-nitrogen NC is widely used as industrial products (N <12%),
including photographic films, inks, leathers and various nitro paints. NC is the
main energetic component of single-base, double-base and triple-base propellants
(N >12.5%), which provide the propulsion energy for weapons [5-8]. The danger
level increases with the nitrogen content of NC.

Propellants are mainly used in military situations, and the decomposition
and migration of functional components causes propellants to become
waste ammunition after a period of storage. With the rapid development and
replacement of weapons systems, a lot of waste ammunition is generated
around the world every year [9]. Waste ammunition must be disposed of in time.
Incineration, biodegradation, advanced oxidation and alkaline hydrolysis are
the current disposal methods for waste ammunition [10, 11]. Waste ammunition
is decomposed and destroyed by most of these methods, but they are not
used effectively, resulting in wasted resources. At present, solvent extraction
technology for each component has been widely applied for propellants with NC
as the main component [12]. However, the recycled high-nitrogen NCcannot be
used to prepare military ammunition. Freedman *et al.* [13] reported that the nitro
groups can be removed from NC under denitration conditions, with the nitrogen
content of the original NC being decreased from 13.2 to 12.2%. However,
the biodegradation rate is low and the nitrogen content reduction efficiency
is not high, so it could not be applied industrially. Alkaline hydrolysis is the
most flexible and economical technology for disposing of NC [14]. Knill and
Kennedy [15] outlined the basic degradation pathways of NC for the first time.
Shukla and Hill [16, 17] have used the density functional theory (DFT) to study
the mechanism of alkaline hydrolysis of NC in the gas phase and in bulk aqueous
solution. Christodoulatos *et al.* [18] studied the kinetics of the alkaline hydrolysis

of NC based on experimental data analysis. Alinat *et al.* [19] reported a method for optimizing the denitration yield through experimental design, and the optimal conditions for denitration were found through suitability analysis.

Although the alkaline hydrolysis of NC is delicately designed [2, 3, 8, 14-19]. Furthermore, it can be converted into industrial products when the nitrogen content is reduced. Raeisi and Najafpour [20] reported the alkaline decomposition of waste NC into pure cellulose with 1.5 mol·L⁻¹ sodium hydroxide at 55 °C. However, these researches showed that the high concentration of alkali could completely destroy the skeletal structure of NC [18, 20, 21]. Urbanski [22] and Li *et al.* [23] reported that NC could be hydrolyzed with sodium hydrosulfide (NaHS) without destroying the skeletal structure. Moreover, low-nitrogen NC has extensive industrial applications [24]. Therefore, it is of great significance to be able to resource utilize these energetic materials.

Previous studies have focused on the disposal of waste high-nitrogen NC, and the recovery of NC with a controlled nitrogen content for industrial products by alkaline denitration was rarely studied [25]. In the present work, NaHS was used as the denitration reagent to remove some of the nitrate ester groups from NC. Changes in the surface morphology and chemical structure of the low-nitrogen NC were analyzed by SEM, FT-IR, ¹H NMR and XRD. The decomposition temperature and the heat released by thermal decomposition of NC were systematically analyzed after different reaction times. The nitrogen content was determined by elemental analysis. More importantly, a calorimeter was used to obtain the explosion heat of these specimens. The objective was to convert waste high-nitrogen NC extracted from propellants into industrial products, which has great economic and social benefits that should not be underestimated.

2   Materials and Methods

2.1 Materials

Waste high-nitrogen NC was obtained from Luzhou North Chemical Industry Co., Ltd. (Luzhou, China), and the NC was maintained at a humidity of 30% in the vehicle during transportation. NaHS, absolute ethanol, distilled water, 30% hydrogen peroxide and acetone-d_6 ((CD_3)$_2$CO) were supplied by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China).

2.2 Alkaline denitration of NC

Initially, the waste high-nitrogen NC was dried in a vacuum oven at 60 °C for 12 h. NaHS (2.6 g) was then completely dissolved in absolute ethanol (192 mL)

with stirring. This solution was preheated to a specified temperature in a water bath before being charged into the reactor. Finally, NC (8 g) was added to the NaHS solution, and the reaction was continuously stirred at 40 °C. After the reaction was complete, the mixture was transferred to an ice bath to rapidly cool the reaction medium to room temperature. The denitration time was set at 15 min (1#), 30 min (2#) and 60 min (3#) for comparison.

2.3 Post-processing of the prepared low-nitrogen NC

The denitration reaction could produce sodium nitrate, sodium nitrite, sulfur and sulfides. Initially, distilled water was added to remove the residual sodium hydrosulfide and soluble materials. The samples were then added to 30% hydrogen peroxide solution (40 mL), and the reaction was performed with stirring for 30 min to remove sulfur and sulfides. After this reaction, the samples were isolated by suction filtration. Finally, after washing several times with absolute ethanol and water, the samples were dried in an oven at 60 °C for 12 h.

2.4 Characterisation

Scanning electron microscope (SEM) images were obtained using a Quanta FEG 250 (Zeiss, Germany) to characterize the surface morphology of the NC, with an accelerating voltage for the SEM of 15 kV. Fourier transform infrared spectra (FT-IR) were obtained using a Nicolet 10 (Thermo Scientific, USA) in order to characterize changes in the functional groups. The spectra were recorded in the range from 4000 to 650 cm^{-1} at a spectral resolution of 4 cm^{-1}. The ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an Avance-III 500 MHz (Bruker, Switzerland), $(CD_3)_2CO$ was used as the solvent and tetramethylsilane (TMS) was used as an internal standard. X-ray diffraction (XRD) was carried out using D8 ADVANCE instrument (Bruker, USA) to characterize the crystal structure of the NC. Elemental analysis was performed using a Vario macro cube (Elementar, Germany) to determine the change in the nitrogen content of the NC; each sample was measured three times and the results were averaged. TG-DSC experiments were performed on the samples under an argon atmosphere (20 mL·min^{-1}) at a heating rate of 10 °C·min^{-1} from 50 to 350 °C with an NETZSCH STA 449 C (Netzsch, Germany) analyzer. The explosion heat of the NC was determined using a ZDHW-6W calorimeter (Tianyuan, China). The weight of the sample was 1.000 ±0.005 g for each test, recording in a nitrogen atmosphere. The explosion heat of each sample was measured three times and the results were averaged.

3   Results and Discussion

## 3.1 Recovery of NC with low nitrogen content

In order to reuse waste high-nitrogen NC, it was converted into raw materials, in practice *via* chemical methods. Here, according to the structural characteristics and performance of the NC, the nitrate ester groups were partially removed by alkaline denitration, and the objective of reducing the nitrogen content was achieved. In short, NaHS was used as the denitration reagent, which can convert nitrate ester groups into hydroxyl groups on the NC *via* alkaline hydrolysis (Equation 1):

$$C_6H_7O_2(OH)_{(3-x)}(ONO_2)_x + NaHS \rightarrow C_6H_7O_2(OH)_{(4-x)}(ONO_2)_{(x-1)} + NaNO_2 + S \quad (1)$$

where *x* represents the degree of initial substitution, which is in the range from 2 to 3. It has been determined that the reaction of NC with the alkali reagent is not a simple saponification reaction, which could regenerate cellulose and the alkali metal nitrate [25]. More importantly, the nitrate ester groups are removed from NC through alkaline denitration, and the liberated nitrate reacts with NaHS to form nitrite. This denitration reagent could not damage the skeletal structure of NC, thus leaving the performance unaffected [22, 26]. Subsequently, the reaction time was controlled to adjust the degree of denitration, and NC with different low nitrogen contents was obtained. By partial alkaline denitration with NaHS of the nitrate ester groups of NC and controlling the nitrogen content *via* the reaction time, the resultant NC was modified with controlled nitrogen content and without destroying the skeletal structure, two of the basic requirements for recovery of low-nitrogen NC as industrial products.

3.2 Surface morphology

Figure 1 shows the microstructure of the samples denitrated for 0, 15, 30, and 60 min, respectively. It can be seen that NC is actually a slender fibre, which provides sufficient interface for the alkaline denitration reaction with NaHS. Therefore, the samples are actually suspended in the NaHS solution for a solid-liquid reaction. The nitrate ester groups are removed by alkaline denitration and converted into hydroxyl groups. The surface of the NC becomes slightly rougher when the reaction time is long, but the surface morphology of NC has not changed significantly after denitration.
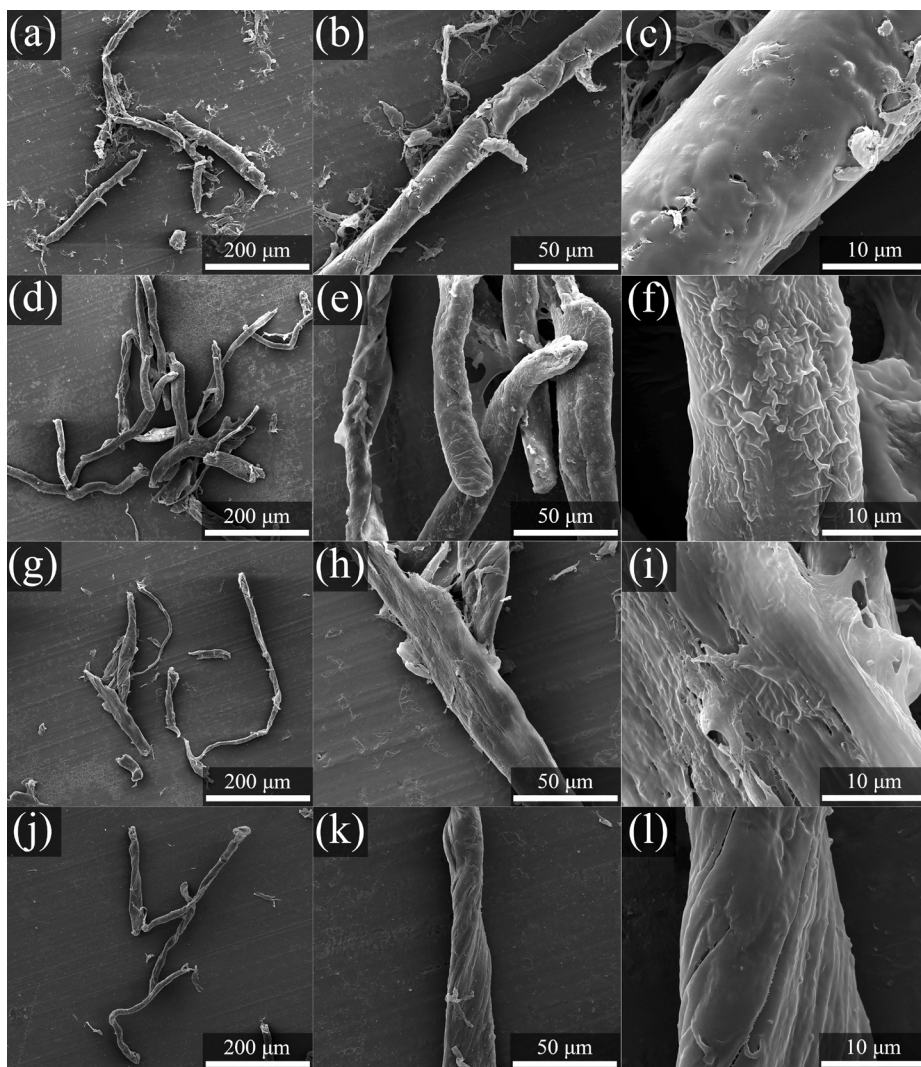
Figure 1. SEM images at different magnifications of the original NC (a-c), and denitrated for 15 min (d-f), 30 min (g-i), and 60 min (j-l)

3.3 Chemical structure

The chemical structure of NC was characterized by FT-IR before and after the denitration reaction. In all of the spectra, the small peak at 2912 cm^{-1} is attributed to the asymmetric stretching vibration of the CH$_2$ group, and the weak peak to the right reflects the symmetric stretching vibration of the CH$_2$ group. The peaks

at 1638 and 1256 cm^{-1} are related to the asymmetric and symmetric stretching vibrations of the $-NO_2$ group, respectively. In addition, the absorption peaks at 836, 746 and 679 cm^{-1} are related to the stretching and twisting vibrations of the $O-NO_2$ group, and correspond to the characteristic peaks of a nitrate ester group [27, 28] (Figure 2(a)). The absorption peaks around 1156 and 1058 cm^{-1} are caused by the asymmetric and symmetric stretching vibrations of the oxygen bridges and ring groups in the molecular structural unit of NC, and are characteristic peaks of cellulose molecules [29]. As shown in Figure 2(b), compared to the original NC, the characteristic peak at 836 cm^{-1} indicates that the intensity of the nitrate ester groups has been significantly reduced when the reaction time is long, and is consistent with the assumption that partial removal of the nitrate ester groups on NC releases nitrate through alkaline denitration [2]. Moreover, a wider O–H group absorption peak appears at 3396 cm^{-1}, the changes in the absorption peaks of the two groups being attributed to alkaline denitration, and corresponds to the conversion of nitrate ester groups of NC into hydroxyl groups. It was also observed that more nitrate ester groups are converted with increased reaction times. By comparison of the spectra, it was found that the absorption peak of the C–O–C group remains basically unchanged, which also proves that the denitration reaction does not cause cleavage of the C–O bond [16, 17].
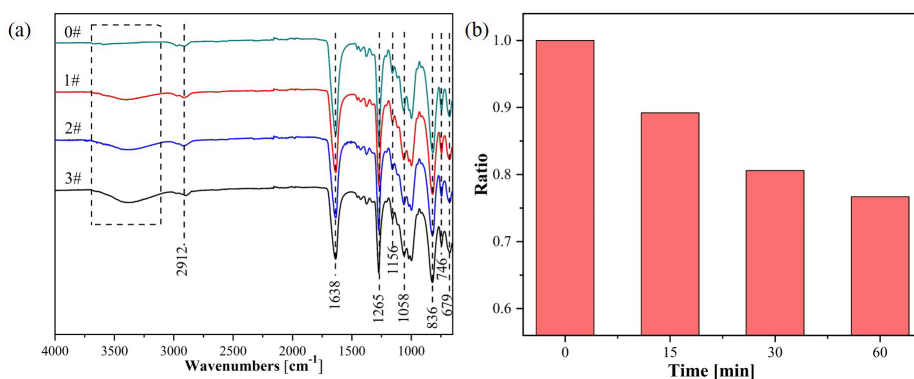
Figure 2 (a) Infrared spectra of four NC samples denitrated for 0 min (0#), 15 min (1#), 30 min (2#), and 60 min (3#), and (b) the ratio of the $O-NO_2$ group's intensity at 836 cm^{-1} compared to the original NC

^{1}H NMR and XRD measurements were subsequently employed to confirm the changes in the structure of the NC. The structural unit of NC is shown in Figure 3(a). Due to the different degrees of substitution, the β-D-glucopyranose

units can be assigned as:
– 2,3,6-trinitro (1a),
– 3,6-dinitro (1b),
– 2,6-dinitro (1c), and
– 6-nitro (1d) substitution.

Figures 3(b) and 3(c) show the ^{1}H NMR results for the original NC (0#) and NC after denitration for 30 min (2#) in $(CD_3)_2CO$, respectively. The internal standard peak of TMS appears at 0.14 ppm, the peaks at 2.05 and 2.85 ppm are due to $(CD_3)_2CO$ solvent and water, respectively, while the peaks at 0.89 and 1.31 ppm are impurity peaks. The ^{1}H NMR peaks at 3.5~6 ppm are due to different degrees of substitution of NC [30]. As shown in Figure 3(d), it can be seen that the ^{1}H NMR peaks of NC have not shifted. Furthermore, as shown in Figure 3(e), the strong XRD peak at about 12.4°, and two distinct diffraction peaks located at 19.9° and 23.9°, correspond to the crystalline domain of NC. More importantly, all of the NC samples have similar trend curves and the reflection peaks hardly shift, so the molecular chain structure of NC has not been changed during the denitration process.
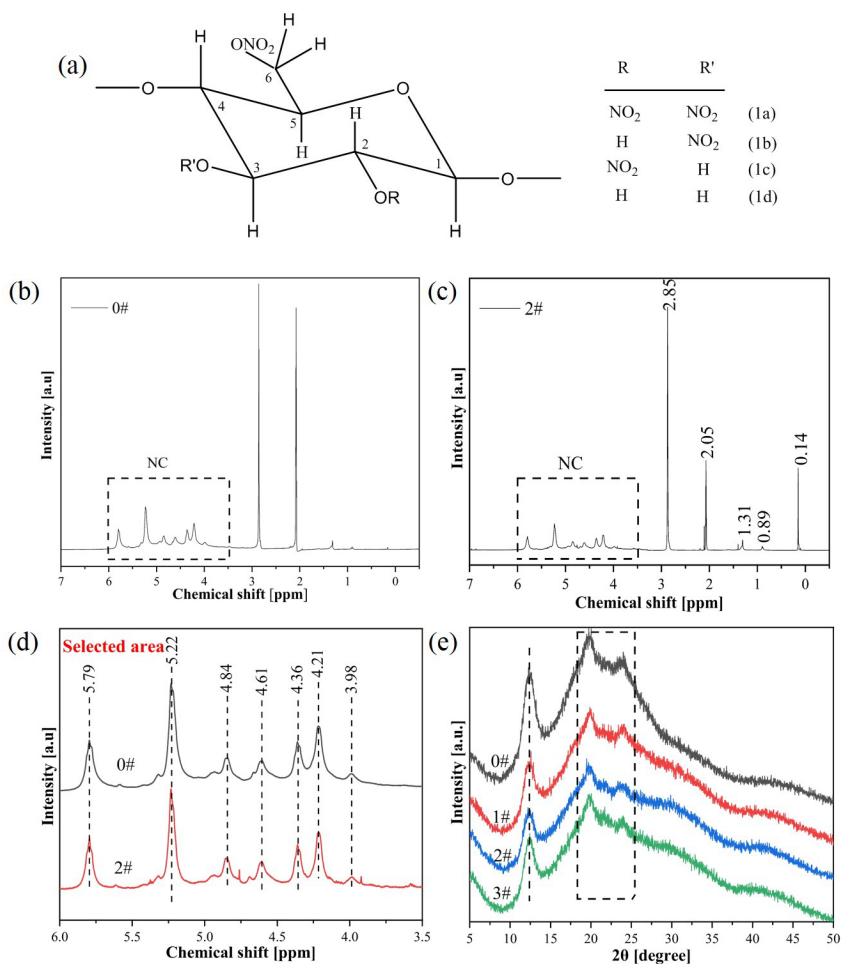
Figure 3. (a) The structural unit of NC, (b, c) ^{1}H NMR spectra of the original NC and denitrated for 30 min (2#) recorded in $(CD_3)_2CO$, (d) enlarge profiles of the selected area in Figures 3(b) and 3(c), (e) XRD diffractograms of four NC samples with different reaction times

3.4 Elemental composition

Different NC samples have a different nitrogen contents, and their solubility and uses are also different [31]. The determination of the nitrogen content is of great significance to the practical applications of an NC sample [32]. A change in the number of nitrate ester groups directly affects the nitrogen content. As shown in Table 1, compared to the original NC, the nitrogen content of the prepared

NC samples decreases significantly over the reaction times. This is because the nitrate ester groups of NC are replaced by hydroxyl groups, and the standards for industrial application are met (N <12%). Moreover, the relative molecular mass of the nitrate ester group is about 62, while the relative molecular mass of the hydroxyl group is about 17. Therefore, the carbon and hydrogen contents become slightly increased, while the oxygen content becomes slightly decreased compared to the original NC, the sulfur content in the denitration product is reduced after disposed by the hydrogen peroxide solution. Moreover, since NC is a high polymer and the standard deviation of the nitrogen content is relatively small in the tests, this indicates that the quality of the prepared low-nitrogen NC is relatively consistent.

Table 1. Elemental content and yield of four NC samples with different reaction times

Sample	N [%]		C [%]	H [%]	O [%]	S [%]	Yield [%]
	Result	Average					
0#	12.88	12.92	24.87	2.58	58.16	0.16	–
	12.95						
	12.92						
1#	11.82	11.78	26.23	2.98	57.84	0.14	78.02
	11.74						
	11.78						
2#	11.18	11.13	27.13	3.20	57.21	0.07	72.65
	11.07						
	11.14						
3#	10.73	10.74	27.43	3.42	57.08	0.07	65.21
	10.82						
	10.68						

Waste high-nitrogen NC is still a hazardous material that could be a threat to humans and the environment because of its physical and chemical properties [33-35]. At present, resource utilization is also a developing trend. Waste high-nitrogen NC was converted into raw materials for industrial products with low nitrogen content, such as bonding agents, celluloid, leathers and various nitro paints. It is also noteworthy that the prepared low-nitrogen NC has a certain recovery yield. In addition, as the nitrogen content of the NC is decreased, safety in storage and use is increased. It enables the recovery of low-nitrogen NC of extremely high value in environmental protection and actual applications.

3.5 Thermal behaviour

The TG curves of four NC samples with different reaction times are shown in Figure 4. It can be seen that the thermal decomposition of NC is very rapid when the temperature is increased to around 200 °C, and the decomposition reaction is completed in a short time. Moreover, NC samples after different reaction times exhibit a similar trend in thermal decomposition to that of the original NC. However, the thermal decomposition of the original NC occurs earlier than that of the other samples, this is because the thermal decomposition of NC breaks the O–NO$_2$ bond as a first step [36-38]. As the denitration process proceeds, the TG mass change in low nitrogen NC is less than that of the original sample. In order to clearly express the degree of change in the TG curves, the weight loss of the original NC is calculated to be 89.50%. After 60 min of the denitration reaction, the weight loss of the low-nitrogen NC has decreased to 80.75%. Compared to the original sample, the partial removal of the nitrate ester groups reduces the oxygen content of the NC, therefore the thermal decomposition of the low-nitrogen NC may be incomplete.
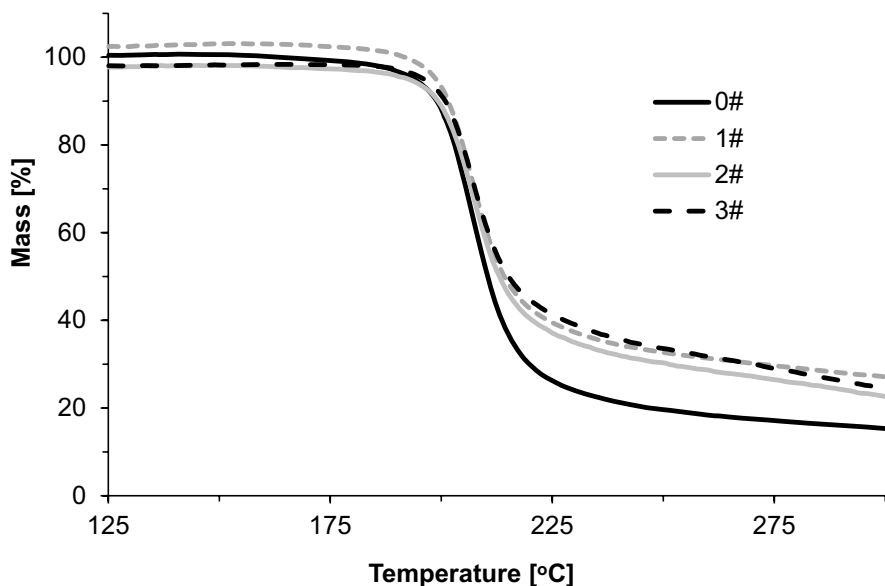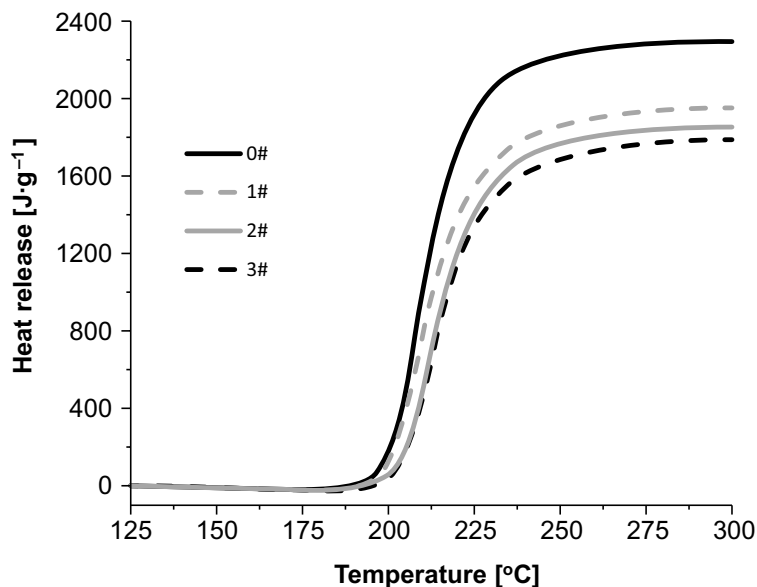

Figure 4. TG curves of four NC samples with different reaction times

The heat release rates recorded by DSC are presented in Figure 5. It is observed that all of the NC samples have similar trend curves, exothermic peaks and close decomposition temperatures, including the initial decomposition

temperature T_i and the maximum decomposition temperature T_m. The maximum decomposition temperature T_m of the samples is hardly affected by the denitration. In addition, the peak of heat release rate Q_P of NC is gradually decreased. The curves of heat release of the four NC samples with different reaction times are plotted in Figure 6. All samples reach maximum heat release at 300 °C, which means that the four samples have all been completely decomposed before 300°C. However, the heat release ΔH_d of NC further decreases with the denitration reaction times, and the maximum heat release being reduced by 21.99%. This is mainly because of the fact that the nitrate ester group is the main exothermic group in NC, and as its content is decreased, the heat released is also decreased. The results of these non-isothermal tests, corresponding to Figures 5 and 6, are summarized in Table 2. The decomposition temperature of the samples increased slightly with increased denitration time, which may indicate improved thermal stability and safety for storage of low nitrogen content NC.
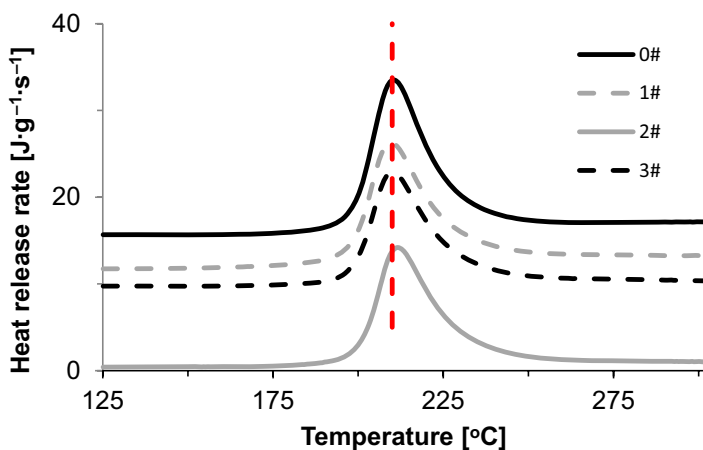
Figure 5.   DSC curves of four NC samples with different reaction times (red dashed vertical line at 210 ºC)

Figure 6. Heat release *versus* temperature of four NC samples with different reaction times

Table 2. Results of DSC tests of four NC samples with different reaction times

Sample	T_i [°C]	T_m [°C]	Q_p [J·(g·s)$^{-1}$]	ΔH_d [J·g^{-1}]
0#	183.6	210.4	18.1	2293.6
1#	183.9	210.1	14.5	1958.0
2#	184.5	210.9	13.8	1853.6
3#	184.7	210.9	13.1	1789.1

3.6 Energetic performance

The explosion heat is the heat released by unit mass of NC burning under a nitrogen atmosphere and is used to detect energy changes in energetic materials [39]. The content of nitrate ester groups is the main parameter that affects the explosion heat of NC. Therefore, the completion of NC denitration was verified by comparing the explosion heat. The explosion heat of NC was measured calorimetrically, and the energy change of the samples after denitration was recorded. As shown in Figure 7, the explosion heat of the original NC was 4290 ±25 J·g^{-1}. After 15 min of denitration, a significant decrease in the explosion heat was observed. The explosion heat of this sample had changed to 3476 ±23 J·g^{-1}, a reduction of 18.97%. This is mainly due to some of the

nitrate groups on the NC being replaced by hydroxyl groups, and the energy of a nitrate group is much higher than that of a hydroxyl group. Over the denitration reaction times, the explosion heat of the prepared low-nitrogen NC samples was reduced to 3210 ± 29 and 2962 ± 24 J·g^{-1}, respectively, a reduction by a maximum of 30.96%. It was found that the energy of the NC was changed in line with the progress of the reaction, which reflects, to a certain extent, the orderly progress of the denitration reaction. It could be predicted that complete denitration of NC might be achieved to regenerated cellulose when the reaction time is long, but that is not the objective. These results also confirm the conclusion that the nitrogen content of the prepared NC is gradually decreased.
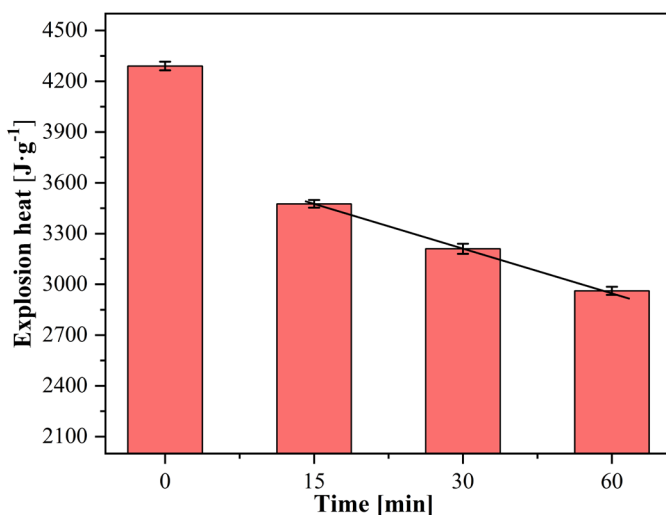
Figure 7.   Explosion heat of four NC samples with different reaction times

4   Conclusions

In order to realize the re-use of waste high-nitrogen NC, low-nitrogen NC was obtained by alkaline denitration with sodium hydrosulfide. The results from FT-IR, SEM, ^{1}H NMR and XRD confirm that the skeletal structure of NC is not damaged, while denitration with sodium hydrosulfide is relatively milder than sodium hydroxide. Therefore, waste high-nitrogen NC can be processed on a large scale. The nitrogen content of the NC can be controlled and reduced from 12.92 to 10.74% through control of the experimental parameters, reaching the level for industrial products (N <12%). Furthermore, the TG-DSC experiments

demonstrated that NC samples with different nitrogen contents have similar decomposition trends and decomposition temperatures, but the heat released is obviously different, and the maximum heat released is reduced by 21.99%. The energy change of the four samples was also determined using a calorimeter, and showed that the explosion heat was decreased from 4290 $\pm$25 to 2962 $\pm$24 J·g^{-1}, due to partial removal of the nitrate ester groups. It is anticipated that alkaline denitration could become a superior candidate for resource disposal and utilization of waste high-nitrogen NC.

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