Study on the effect of ethanol content on the fire risk of nitrocellulose

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Abstract. Obtaining the burning properties of nitrocellulose with different ethanol contents is necessary to reduce the possibility of nitrocellulose accidents in the process of handing, storage and usage. In this study, the effect of humectant content on the burning properties of NC was tested by the ISO 5660 Cone Calorimeter Test. It was noted that the amount of the ethanol content had little effect on the ignition time of nitrocellulose mixture. Both the maximum mass loss rate and the average mass loss rate of the sample decreased with an increasing ethanol content and gradually closed to fixed values. Also, it was concluded that the peak heat release rate of the sample was mainly contributed by the nitrocellulose component.

1. Introduction

Nitrocellulose (NC) is a typical industrial ingredient and is widely used in both military and civilian industries [1, 2]. NC is usually kept wet in water or an alcohol humectant. Once exposed to dry conditions, NC is shock sensitive and can ignite spontaneously and explode when exposed to heat, flames, ignition sources, sunlight or oxidizing agents (such as perchlorates, peroxides, permanganates, chlorates, nitrates, chlorine, bromine and fluorine) [3, 4]. Defining the effect of the ethanol content on the burning behaviors of NC can improve our understanding of the potential dangers of NC products in the storage and transportation process, and optimize the content of product components. The burning behaviors of NC-humectant mixtures have been investigated by a few researchers. Based on the measurement of ISO 5660 Cone Calorimeter, recent studies [5, 6] found that the fire hazard of NC-humectant mixtures satisfies NC-isopropanol > NC-ethanol > NC-water. Liu et al. [7] experimentally examined the heat release rate (HRR) of NC-isopropanol and NC-ethanol and proposed a simplified method to predict the HRR of industrial NC according to flame height. Furthermore, a sequence of experiments on NC-isopropanol mixture with eight consecutive bulk densities was performed by Liu et al. [8], and it was concluded that, with increasing bulk densities, the fuel regression rate in the quasi-steady burning stage exhibit two distinctive stages: constant stage and decreasing stage. However, the above studies focused only on the burning behaviors of NC with a fixed humectant content and scarce work concerning the effect of different humectant contents on the behaviors of NC-humectant fire. In order to fill the gap in this field and raise awareness of NC products, it is necessary to carry out the present study.

NC can be preserved with the addition of ethanol, while with the loss of ethanol, the spontaneous ignition of NC will be inevitably triggered to cause uncontrollable fire or explosion, which has been asserted to be primary causes for the disastrous explosion in Tianjin Port in China on August 12, 2015.
This disaster resulted in 165 deaths, 8 missing persons, 798 injuries and CNY 6.866 billion direct economic loss [9, 10]. To provide basic knowledge for fire behaviors of NC-ethanol mixtures with different ethanol contents, an attempt was made in the present study to perform fire tests on NC-ethanol mixtures by means of ISO 5660 Cone Calorimeter.

2. Experiments
In this work, the samples were prepared by mixing different mass of ethanol into pure NC (11.96 % N). Table 1 shows the weight of each element in the samples. The total mass of each sample is 10.0 ± 0.2 g.

| Samples | No. | Ethanol content/wt.% | NC (wt.)/g | Ethanol (wt.)/g |
|---------|-----|----------------------|------------|-----------------|
| NC-10   | 1   | 10                   | 9.0        | 1.0             |
| NC-20   | 2   | 20                   | 8.0        | 2.0             |
| NC-30   | 3   | 30                   | 7.0        | 3.0             |
| NC-40   | 4   | 40                   | 6.0        | 4.0             |
| NC-50   | 5   | 50                   | 5.0        | 5.0             |

The ISO 5660 Cone Calorimeter Test [11] has proven to be an effective measurement method to assess the fire risk of NC mixtures. [12] A schematic view of the ISO 5660 Cone Calorimeter is shown in Figure 1. In the present study, a series of experiments was performed using the Cone Calorimeter provided by City university of Hong Kong. Before the start of the experiment, different masses of ethanol and pure NC were thoroughly mixed according to the ratios shown in Table 1. As presented in Figure 2 (a), the sample was wrapped in aluminum foil and placed in a steel square pan that was 100 mm wide and 20 mm high. The experiments were performed in a uniform radiant heat flux of 5 kW/m² over the sample surface. The CO and CO₂ produced after the burning of the sample is recorded by the data acquisition system after passing through soot filter and water filter. As shown in Figure 2 (b), there is basically no combustion residue for each sample. Fire risk parameters, such as ignition time t_ig and HRR of the NC with different ethanol content were recorded.

Figure 1. The configuration of the cone calorimeter.
3. Results and Analysis

3.1. Ignition time

The $t_{ig}$ of the sample as a function of ethanol content is plotted in Figure 3. It can be seen that the amount of the ethanol content has little effect on the ignition time $t_{ig}$ of the sample and the $t_{ig}$ fluctuates around 21.7 s. This phenomenon is most likely attributed to that $t_{ig}$ mainly depends on the volatile properties of treated materials and ignition would occur when the fuel vapor concentration around the electrical spark reaches the combustion limit. [13] As indicated in previous researches [6, 14] and Figure 4 [13, 15], the amount of ethanol volatilized is greater than the amount of decomposition products of NC under 5 kW/m$^2$ external radiant heat flux, thus the $t_{ig}$ of NC-ethanol mixture is dominated by ethanol.

![Figure 3. Ignition time of samples as a function of ethanol content under external radiant heat flux of 5 kW/m$^2$.](image-url)
3.2. Burning process
The mass loss rate (MLR) curves of NC-ethanol mixtures are plotted in Figure 5. The burning period increased, while the peak value of the MLR decreased with an increasing ethanol content. The maximum MLR $\dot{m}_{\text{max}}$ and average MLR $\dot{m}_{\text{ave}}$ of samples are analyzed and plotted in Figure 6. It can be seen from Figure 6 that both $\dot{m}_{\text{max}}$ and $\dot{m}_{\text{ave}}$ decreased with the increase of ethanol content and approached fixed values.

Figure 4. The heat transfer and ignition of NC-ethanol under external radiant heat flux.

Figure 5. Mass loss rate of NC-ethanol mixture with different ethanol contents.
The HRR histories of samples with varying ethanol contents, as measured by the cone calorimeter, are shown in Figure 7. The HRR histories had the same trend as the burning rate. For the NC mixture fire, the total MLR of the mixture can be expressed as:

\[ \dot{m} = \dot{m}_1 + \dot{m}_2 \]  

(1)

where \(\Delta h_1\) and \(\Delta h_2\) are the effective combustion heats of ethanol component and NC component, respectively. The values of \(\Delta h_1\) and \(\Delta h_2\) are 29.68 kJ/g and 4.17 kJ/g, respectively. [14, 16, 7]

Then, the HRR of NC-ethanol mixtures can be expressed as:

\[
\dot{m}_1 = \left( \dot{q} - \Delta h_1 \cdot \dot{m} \right) / \left( \Delta h_1 - \Delta h_2 \right)
\]

\[
\dot{m}_2 = \left( \dot{q} - \Delta h_1 \cdot \dot{m} \right) / \left( \Delta h_2 - \Delta h_1 \right)
\]  

(2)

Based on the measured MLR and HRR data, MLR corresponding to each component of the mixtures can be calculated. The above method was applied to the NC-ethanol mixture with 30 % ethanol content. The result is shown in Figure 8. For NC-ethanol mixture with 30 % ethanol content, the MLR of NC agreed well with the total MLR mixture. Therefore, it can be inferred that for mixtures with an ethanol content of less than 30 %, the MLR was mainly contributed by NC.
content under an external radiant heat flux of 5 kW/m².

Figure 8. The calculated MLRs of ethanol component and NC component in the NC-ethanol mixture.

4. Conclusions
In order to investigate the effect of ethanol content of NC-ethanol mixture on its burning behaviors, a series of experiments on NC-ethanol mixture with five consecutive ethanol content were carried out in the present study. Primary measurements of ignition time, MLR and HRR were analyzed and discussed in detail. The major conclusions are drawn as follows.
The ignition time of NC-ethanol mixture containing different ethanol contents (10 % - 50 %) fluctuated around 21.7 s, and the ignition time was mainly dominated by ethanol which is volatile and has a lower ignition point. Both \( \dot{m}_{\text{max}} \) and \( \dot{m}_{\text{ave}} \) of samples decreased with the increasing ethanol content. For samples with an ethanol content of less than 30%, the peak of MLR was mainly contributed by NC.
This study only focused on the effect of ethanol content on the burning characteristics of NC. It is well known that water and isopropanol are also commonly used as humectants for NC. It is also necessary to study the effects of different isopropanol content and different water content on the fire risk of NC in future work. In addition, only the fire risk of small-scale samples is concerned in the present study. NC products are generally stored in large-scale barrels and are more dangerous in the event of a burning accident. Therefore, large-scale NC burning is worthy of study in the future.

5. References
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Acknowledgments

This research was supported by the National Key R&D program of China (No. 2016YFC0802500) and a grant from the Research Grant Council of the Hong Kong Special Administrative Region, China (contract grant number CityU 11301015).