Emission Characteristics of NOx During the Combustion of Waste Energetic Materials

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Abstract. A large amount of NOx will be produced during the combustion process of waste energetic materials (EMs), which is extremely harmful to human health and ecological environment, and has become an urgent problem for all countries to solve. In this paper, the NOx emission characteristics of four typical types of waste EMs (double-base propellant, TNT, triple-base propellant and RDX) under different temperature and atmosphere conditions were studied by tube furnace experiment. The results showed that under the condition of nitrogen environment, with the increase of temperature, the combustion reaction of waste EMs was accelerated, NOx emission and nitrogen conversion rate decreased. Under the same experimental conditions, the nitrogen content of waste EMs was not proportional to nitrogen conversion. With the increase of oxygen content, NOx emissions and nitrogen conversion rate increased, which was not conducive to the control of NOx emissions. Therefore, the waste EMs burned in 1000 ℃ and nitrogen environment, the emission of NOx was the lowest. The results of this study provide reliable data support for the realization of green and clean burning of waste EMs.

1 Introduction

With the development of military technology and the updating of weapons and equipment, some major military powers produce thousands or even tens of thousands of tons of energetic materials (EMs) every year [1]. When EMs exceeds their life span, their stability and sensitivity will change greatly, resulting in their safety cannot be guaranteed in the storage process, so it must be dealt with in time to eliminate safety risks [2-3]. Waste EMs disposal industry is one of the most serious sources of pollution in the field of national defence, causing great pressure on the environment. Traditional EMs destruction methods such as open burning [4] will produce a large amount of toxic gas (mainly NOx), which will harm human health and ecological environment. The harm of NOx mainly focuses on the harm to the human body, the production of photochemical smog, acid rain, damage to the ozone layer and so on [5-6]. Therefore, it is very important to establish a green and clean disposal system for waste EMs.

In order to understand the NOx emission characteristics of different types of waste EMs in the combustion process, this paper selects double-base propellant (DP), 2,4,6-trinitrotoluene (TNT), triple-base propellant (TP) and cyclotrimethylenetetranitramine (RDX) as four typical EMs for combustion test in tube furnace.

The NOx emission characteristics of these four EMs under different temperature and atmosphere conditions were studied. This study is helpful to understand the impact of combustion environment on NOx emission of waste EMs, and has a guiding role in disposal of waste EMs and reducing the content of NOx in its combustion exhaust.

2 Experiment

2.1 Experimental materials and preparation

The waste EMs used in the experiment are DP, RDX, TNT and TP, all of which were provided by Luzhou North Chemical Industry Co., LTD. DP is mainly composed of nitrocellulose and nitroglycerin, and TP is mainly composed of nitrocellulose, nitroglycerin and nitroguanidine. The waste EMs were pulverized and dried in the oven at 55 ℃ for 3 days. Finally, the experimental samples with particle size range of 75-150 μm were screened. To prevent moisture absorption, the prepared samples were stored in a dryer for future use. The ultimate analysis of four kinds of waste EMs is listed in Table 1.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Ultimate analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>DP</td>
<td>22.00</td>
</tr>
<tr>
<td>RDX</td>
<td>16.22</td>
</tr>
<tr>
<td>TNT</td>
<td>37.01</td>
</tr>
<tr>
<td>TP</td>
<td>17.51</td>
</tr>
</tbody>
</table>

Table 1 Ultimate analysis of four kinds of waste EMs

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2.2 Experimental equipment and experimental methods

The experimental device is displayed in Figure 1. The system consists of gas cylinder, mass flow controller, electric heating tube furnace, gas filter, buffer tank and gas analyzer (MGA6, Germany). During the experiment, the feed gas is 100% N₂, 10% O₂/90% N₂ and 20% O₂/80% N₂, and the total feed gas is 1 L·min⁻¹, which was controlled by the mass flow controller. The set temperature of the experiment is 600 ℃, 800 ℃ and 1000 ℃ respectively, which is measured by the thermocouple extending into the center of the tube, representing the central temperature of the tube furnace. The total mass of the experimental sample is 50 mg. Repeat the test three times to ensure the accuracy of the experimental results.

The tube and push rod of the tube furnace are made of 310S stainless steel, and the crucible is made of corundum to ensure the safety of waste EMs pyrolysis. The inlet end of the furnace tube is equipped with a thermocouple and circulating water cooling, which can ensure that the inlet end temperature is less than 50 ℃. The crucible containing the sample is placed at the inlet end of the furnace tube before the experiment to prevent the sample from decomposing before entering the center of the furnace. The crucible is connected with the push rod by thread. When the gas indicator on the flue gas analyzer is stable at the set flow concentration, the sample is quickly pushed into the center of the furnace through pushing the pull rod. In order to ensure the gas tightness of the furnace tube in the process of pushing and pulling, the push rod and the plug at the inlet end are connected through the sealing ring. After the experiment, the crucible was pulled out by pulling the rod.

![Figure 1. Experimental system diagram.](image)

2.3 Data analysis

NOₓ emission \(m_{NO_x}\), mg) is determined according to the integral value of the gas release curve in equation (1).

\[
\begin{align*}
   m_{NO_x} &= \int_{t_0}^{t_0+\Delta t} Q \cdot C_{NO_x} \cdot 46 \cdot 10^{-3} \cdot dt / (22.4 \times 60) \\
   \end{align*}
\]

where, \(t_0\) denotes the time when sampling starts, s; \(\Delta t\) denotes the sampling duration, s; \(Q\) denotes the sampling flow, L·min⁻¹; \(C_{NO_x}\) denotes the instantaneous concentration of NOₓ, ppm; 46 refers to the molecular weight of NOₓ (calculated as NO₂), g·mol⁻¹; 22.4 refers to the molar volume of the gas, L·mol⁻¹.

Nitrogen conversion rate (%), calculated according to equation (2)

\[
\eta = \frac{\int_{t_0}^{t_0+\Delta t} Q \cdot C_{NO_x} \cdot 10^3 \cdot dt / (22.4 \times 60) \cdot M \cdot w(N)/14}{C_{N} \cdot m\text{w}}
\]

where, \(M\) denotes the mass of waste EMs used in the experiment, 50 mg; \(w(N)\) denotes the mass fraction of nitrogen in waste EMs, wt%; 14 refers to the molar mass of N, g/mol.

3 Results and discussion

3.1 Effect of temperature on NOₓ emission

The NOₓ emission of different waste EMs is studied in an inert atmosphere (N₂) through a tube furnace to determine the temperature condition with the lowest NOₓ emission. Temperature directly affects the combustion status of EMs and NOₓ emission characteristics. As shown in Figure 2, with the increase of temperature, the peak NOₓ emission concentration of waste EMs decreases. Figure 2(a) shows that the peak NOₓ emission reached 4666 ppm when DP burns at 600 ℃. With the increase of temperature, the NOₓ emission is the least at 1000 ℃, and the peak value is 2716 ppm, which is mainly attributed to the increase of the reaction rate of reducing NOₓ to N₂ by DP pyrolysis releases CO, H₂ and CH₄ with the increase of temperature [7]. As can be seen from Figure 2(b), with the increase of temperature, the peak concentration of NOₓ emission decreases from 3005 ppm to 1048 ppm. The main reason is that with the temperature rises, RDX burns more violently, which accelerates the precipitation of NOₓ.

Meanwhile, high temperature is also conducive to the reduction of NOₓ into N₂. Therefore, NOₓ emissions are reduced.

It can be seen from Figure 2(c) that the NOₓ emission curve of TNT combustion shows a single release peak. The peak of NOₓ emission concentration at 800 ℃ is 1015 ppm, which decreases significantly compared with the peak of NOₓ emission concentration at 600 ℃ of 2530 ppm. When the temperature reaches 1000 ℃, the peak of NOₓ emission concentration is only 375 ppm, mainly because TNT has a high C/O (87.5%). In the nitrogen environment, incomplete combustion generates a large amount of CO, and the temperature rises, increasing the reaction rate of CO and NOₓ, and a large amount of NOₓ is reduced [8]. As can be seen from Figure 2(d), the peak of NOₓ emission from TP combustion at 1000 ℃ is only 172 ppm, mainly because nitroguanidine generates NH₃ at about 598.5 ℃ [9]. However, in N₂ atmosphere, NH₁ reacts slowly with NOₓ when the temperature is lower than 800 ℃. But the combustion is intense when the temperature reaches 1000 ℃, the reduction rate of NH₁ is accelerated, a large amount of NOₓ is reduced by CO and NH₁, and the concentration of NOₓ is greatly reduced. The NOₓ curve of TP combustion presents a bimodal distribution at 800 ℃ because TP combustion generates NOₓ first, when the temperature is higher than 600 ℃, NH₃ begins to reduce NOₓ, but the reaction rate is slow and NOₓ is continuously generated. Therefore, the NOₓ curve of TP combustion presents a bimodal distribution at 800 ℃.
Figure 3 shows that the NOx emissions and nitrogen conversion rates of waste EMs at different temperatures. As figure 3 shown that with the increase of temperature, the NOx emission mass of waste EMs decreases significantly, the NOx emission mass law of DP, TNT and RDX is similar, the NOx mass decreases significantly from 600 °C to 800 °C, and becomes stable from 800 °C to 1000 °C, the lowest levels were 11.73 mg, 2.76 mg and 5.4 mg, respectively. Due to the formation of NH3 in the combustion process of TP, a large amount of NOx is reduced, and the mass of NOx emission decreases significantly.

### 3.2 Effect of atmosphere on NOx emission

By studying the influence of temperature on NOx emission of waste EMs, the NOx emission of waste EMs combustion is minimum at 1000 °C. Then through learning the NOx emission curves of DP, RDX, TNT and TP burning in different atmosphere environment at 1000 °C, to determine the optimal atmosphere environment of waste EMs combustion.

Figure 4 shows that with the increase of oxygen content, the peak concentration of NOx emission increases in RDX, TNT and TP combustion, and the peak area increases, indicating that the increase of oxygen concentration accelerates the combustion reaction. Meanwhile, the reaction of oxygen and carbon weakens the reduction effect of CO on NOx. This illustrates that the increase of oxygen content is not conducive to the control of NOx generated in the combustion process.

Figure 4(a) shows that the NOx emission curves of DP combustion at 10% O2 and 20% O2 basically coincide, and the concentration peak is 3858 ppm and 3703 ppm, respectively. It can be seen from Figure 5 that the mass of NOx generated by DP under 10% O2 and 20% O2 atmosphere is 14.49 mg and 14.31 mg respectively, which is higher than 11.73 mg under N2 atmosphere. It can be concluded that oxygen concentration has no effect on NOx emission from DP combustion, and N2 atmosphere is the best condition for DP combustion. It can be seen from Figure 4(b) that with the increase of oxygen concentration, the amount of NOx generated by RDX combustion increases, and the peak value increases from 1834 ppm of 10% O2 to 2331 ppm of 20% O2. Combined with Figure 5, the mass of NOx released by RDX combustion also increases from 9.29 mg at 10% O2 to 11.69 mg at 20% O2. This is due to the presence of N in RDX is the structure of N-O2. The increase of oxygen concentration promotes the conversion of N to NOx, resulting in an increase in the mass of NOx generation. It can be seen from Figure 4(c) that the NOx generated by TNT combustion is similar to RDX. The curve peak value of NOx generated by TNT combustion at 20% O2 is 1694 ppm, which is higher than the peak value of 1228 ppm at 10% O2. In TNT, N is the structure of C-NO2. With the increase of oxygen concentration, a large amount of C and CO are oxidized to produce CO2 in the combustion process, which reduces the reduction of NOx. Therefore, the mass of NOx generated in 20% O2 atmosphere combustion is 6.61 mg, much higher than 2.76 mg in N2 atmosphere.

As Figure 4(d) shown that the NOx release curve of TP combustion under 10% O2 and 20% O2 atmosphere presents a bimodal feature, with the first release peak being small and the second release peak dominating. This is because NH3 reacts with O2 and CO is also oxidized by oxygen, both weakens the reduction effect. TP is composed of NC, NG and NQ. In NC and NG is O-N2O structure. NH3 is the product of thermal decomposition of NQ. In the process of TP combustion, less NH3 content is released and a large amount of NOx is continuously generated. Therefore, the concentration of NOx decreases first and then increases, showing a bimodal characteristic. As a result, the NOx released increased from 0.46 mg in N2 atmosphere to 3.53 mg in 20% O2 atmosphere.
As shown in Figure 5, with the increase of oxygen concentration, the NOx emission and nitrogen conversion rate of DP remain basically unchanged, while the NOx emission and nitrogen conversion rate of RDX, TNT and TP increase gradually. The NOx generated by TP combustion changes most obviously. When the oxygen concentration increases from 10% to 20%, the NOx emission increases from 1.92 mg to 3.53 mg, and the nitrogen conversion rate increases from 3.52% to 6.49%. This is because the selectivity of NH3 reaction decreases with the increase of oxygen concentration [10-11], NH3 is more likely to undergo oxidation reaction with O2, which reduces its reduction effect on NOx.

In summary, with the increase of oxygen concentration, NOx emission mass of waste EMs combustion showed an increasing trend. Therefore, in practical engineering, the oxygen content in the incinerator can be reduced by ignition methods such as gas burner, electric heating, and the use of graded combustion, so as to reduce the amount of NOx generation.

4 Conclusion

The NOx emission characteristics of waste EMs combustion were studied by tube furnace experiment. The influence of temperature and atmosphere on NOx were obtained. The main conclusions are as follows:

In nitrogen atmosphere, with the increase of temperature, the peak of NOx emission concentration was reduced. At 1000 ℃, the masses of NOx emission from combustion of DP, RDX, TNT and TP were lowest. They were 11.73 mg, 2.76 mg, 0.46 mg and 5.4 mg, respectively. When DP, RDX and TNT burn under 800 ℃, the NOx emission mass tended to be stable, which was similar to the combustion at 1000 ℃. The mass of NOx emission of TP combustion under 1000 ℃ decreases significantly, due to NH3 is generated during TP combustion and NH3 reacts quickly with NOx when the temperature exceeds 800 ℃.

Comparing the nitrogen content and nitrogen conversion rate of different waste EMs, it was found that there was no proportional relationship between the NOx conversion rate and the nitrogen content of waste EMs. With the increase of oxygen concentration, NOx emission peak and NOx emission mass of waste EMs combustion increased. Therefore, increasing oxygen content is not conducive to controlling the generation of NOx.

References

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