Effect of NOx on Ammonia Ignition Delay Times

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***Abstract*—Ammonia is considered a promising renewable energy storage medium that can be used as a clean fuel without producing carbon emissions. Simulation results clearly show that NO2 shortens the ignition delay time of ammonia fuel. However, there is a nonlinear relationship observed in the simulations. It was expected that adding different concentrations of NO2 would linearly decrease the ignition delay time. However, it was found that the ignition delay time drops sharply at a certain amount of NO during the ignition. Analysis of simulation phenomena and data indicates that NO enhances combustion by altering the concentrations of active species OH and O in the system, thereby changing the rates of NH3-NH2 elementary reactions and reducing the ignition delay time. Effect of NO2 on ammonia point, which is related to the concentration of NO2. At lower NO2 concentrations, the drop occurs in the low-temperature range. As the NO2 concentration increases, the temperature point at which the drop occurs shifts to a higher temperature range.**

***Keyword*—Ammonia, Fuel-lean, NOx, Ignition delay times, high pressure**

I. Introduction

With the acceleration of modernization, environmental problems are becoming increasingly serious, therefore, shifting towards a low-carbon energy structure has become a key direction of global energy strategy. Finding renewable and clean energy alternatives to traditional chemical fuels such as coal, oil, and natural gas has become crucial.

Ammonia is considered a promising renewable energy storage medium that can be used as a clean fuel without producing carbon emissions. Due to its carbon free nature, ammonia has attracted widespread attention as a fuel for mixed combustion with coal, which may provide an effective way for the low-carbon transformation of traditional energy sources [1–3].

The Ignition Delay Time (IDT) is a key parameter for measuring combustion characteristics, which is closely related to the realization of stable oxidation combustion and the optimization of fuel efficiency. In addition, IDT is also an important indicator for verifying and developing chemical reaction kinetics models.

In 2015, Mathieu and Petersen [4] proposed that the experimental conditions for the previous study on the ignition delay of ammonia were unclear, and there was a significant deviation between the chemical kinetics model and the experimental results. On the other hand, there is a scarcity of medium and high pressure experimental data on the delay time of ammonia ignition, and this pressure range happens to be the operating pressure range of the engine. Therefore, they filled the gap in this area. In the shock tube, the ignition delay time of ammonia was tested under conditions of pressure of 1.4, 11, and 30 bar, temperature range of 1560–2455 K, and equivalence ratio of 0.5 to 2.0. The experimental results showed that the pressure and equivalence ratio had a significant impact on the ignition delay. Simulation comparative studies have shown that Dagaut *et al.*' s (2008) model can effectively predict the ignition delay data of ammonia gas.

In 2019, Shu *et al.* [5] extended Mathieu and Petersen's research by measuring the ignition delay time data of ammonia in the mid temperature range. On the other hand, they use an ammonia/air mixture, which is closer to the actual application conditions. The specific experimental conditions are: pressure of 20 and 40 bar, temperature range of 1100–1600 K, and equivalence ratio of 0.5 to 2.0. The simulation results indicate that NOX can react with NH2 to generate N2 and H2O within this temperature range, achieving the requirement of NOX emission reduction. During the same period, Pochet *et al.* [6] conducted research on Low-Temperature Combustion (LTC) of ammonia gas and proposed that ammonia gas is difficult to ignite and requires the assistance of accelerators. The research results indicate that adding at least 10% hydrogen can significantly improve the ignition delay time of ammonia gas. The simulation results indicate that the chemical reaction mechanisms related to H2NO and N2HX need to be improved.

In 2020, He *et al.* [7] measured the ignition delay time of NH3/H2/O2 and NH3/O2 mixtures in a fast press machine at equivalence ratios of 0.5 to 2, temperatures of 950 to 1150 K, and pressures of 20 to 60 bar. Experiments have shown that a higher mole fraction of H2 in the fuel mixture increases the reactivity of ammonia, while the effect of equivalence ratio varies with the content of H2. The simulation results indicate that the chemical reaction mechanism cannot predict the ignition delay time of NH3/H2/O2 mixtures well. Hydrogenation promotes the O/H group pool, but has little impact on NOX emissions.

Recently, Dai *et al.* [8–9] measured the ignition delay time of pure ammonia and ammonia hydrogen, ammonia methane, and ammonia dimethyl ether using a fast press under pressure range of 10–75 bar, temperature range of 610–1210 K, and equivalence ratio of 0.5–2. The experimental results show that under lean combustion conditions, the mixing of 5% H2 reduces the ignition delay time of ammonia by 12 times; The mixing of 5% CH4 reduces the ignition delay time of ammonia by 5 times; When the addition amount of DME increases from 2% to 5%, the ignition delay time of ammonia decreases by 10 times. In terms of simulation, they updated the combustion mechanism of ammonia doped hydrogen and constructed the reaction mechanism of ammonia doped DME. According to the analysis of the reaction mechanism, it was

found that the ignition enhancement effect of H2 and CH4 on NH3 is closely related to the formation and decomposition of H2O2. The group pool generated by the "DME pre oxidation" promotes the oxidation of ammonia.

Feng *et al.* [10] studied the auto recognition characteristics of NH3/diesel blended fuel in RCM. The NH3 blending ratio was (10%, 30%, 50%), and the ignition delay was tested under temperature range of 670–910 K, pressure range of 10–20 bar, and equivalence ratio of 0.5 to 1.5. NH3 significantly suppressed the ignition delay of diesel fuel. They constructed a hybrid mechanism to predict the inhibitory effect of NH3 addition, but the simulation of IDT and NTC phenomena was not good. Sensitivity and pathway analysis indicate that NH3+OH ⇒ NH2+H2O and NH2+NO ⇒ N2+H2O are key reactions for accurately predicting IDT.

II. Simulation

There is an important functional module on CHEMKIN's page-the zero dimensional homogenization reactor, which can conduct ignition experiments on different mixed fuels (NH3/NO2 mixed fuel and NH3/NO mixed fuel) under different conditions (NH3 or NO2, NO addition). In the process of this experimental study, the principle of gradual observation was adopted for step-by-step analysis. Firstly, a series of experiments were conducted without additives by changing temperature, pressure, and equivalence ratio. The experimental data were comprehensively analyzed and compared, and then reaction path analysis and sensitivity analysis were carried out to reveal the essential reasons affecting its ignition delay. Then, keeping the concentration of NH3 constant, increasing different amounts of NO and continuously adjusting the concentration of NO, controlling the relationship between temperature, pressure, equivalence ratio, and NO concentration, a series of simulated data were obtained. By comparing and analyzing the experimental data, the influence of NO additives on the ignition delay time of NH3 was explored. In the above experiment, the zero dimensional homogeneous reactor in CHEMKIN can simulate gas ignition and combustion, and the influence of some ancillary processes in the reaction process can be ignored. By analyzing simulated experimental data, the temperature of combustion at different times, the content of different components, and the reaction rate of the elements can be obtained, which points out the direction for exploring the essence of the experiment.

III. Results and Discussion

Figs. 1 and 2 show the ignition delay distribution of different concentrations of NO under equivalent ratios phi = 0.1, pressures of 1.75 to 100 atm.

Through comparative analysis, the ignition delay time of NH3 shows an upward trend with increasing temperature at different NO concentrations. As the concentration of NO additive increases, the ignition delay time of combustion product NH3 gradually decreases. At lower temperatures, due to the lower collision efficiency between molecules, the change in ignition delay time is not significant. As the temperature increases, it is evident that the higher the concentration of NO added, the more significant the decrease in ignition delay time. So the above curve roughly presents a ray pattern distribution, with the lower temperature points as the reference points of the ray, diverging towards the higher temperature areas. When the concentration of additive NO is at 0 ppm, 100 ppm, and 500 ppm, due to the lower concentration of O in the group pool, the effects of the three on the ignition of combustion product NH3 remain basically the same, and the degree of impact on the system is relatively small. When the concentration of NO additive reaches 1000 ppm, the overall effect on the experiment is not significant in the low-temperature region due to the low temperature. However, when the temperature reaches 1600 K, the molecular activity increases, the reaction rate of each module accelerates, and the ignition delay time of NH3 undergoes a significant change, resulting in a significant decrease.

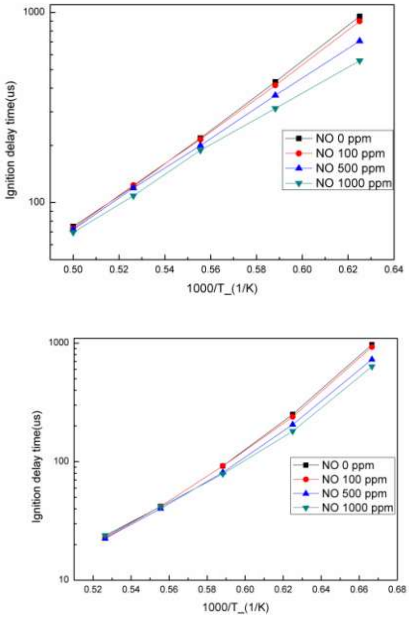

Fig. 1. (a) p=1.75 atm, (b) p=10 atm, phi=0.1, ignition delay time plots for different amounts of NO.

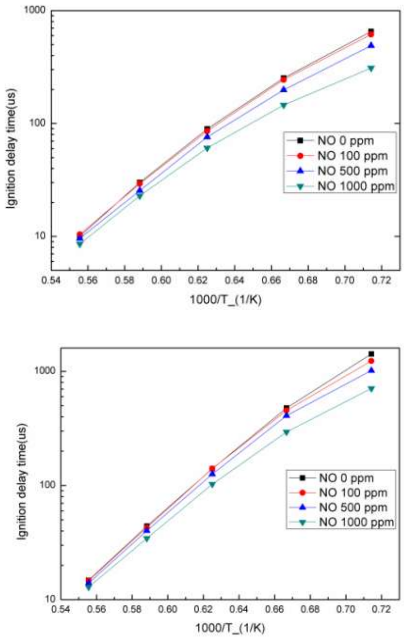

Fig. 2. (a) p=1.75 atm, (b) p=100 atm, phi=0.1, ignition delay time plots for different amounts of NO.

With the increase of system pressure, when the concentration of NO additive is the same, the movement rate between molecules increases when the system pressure is high, resulting in an overall decrease in ignition delay time. At a pressure of p=100 atm, the degree of influence reaches its maximum, and the results of the addition of NO on the combustion of the system also show significant differences. The ignition delay time is significantly shorter at a NO concentration of 1000 ppm compared to experimental results at other concentrations. From this, it can be seen that the additive NO must have a certain significance in the entire reaction process. By changing the elementary reactions inside, it plays a driving role in the combustion reaction of NH3, thereby achieving the effect of shortening the ignition delay time. And when the system pressure is high, the effect is more pronounced.

As shown in Figs. 3 and 4, the chemical reaction pathway analysis of ammonia fuel is shown for pressure p=100 atm, equivalence ratio phi=0.1, temperature T=1400 K, and additive NO concentrations of 0 ppm and 1000 ppm.

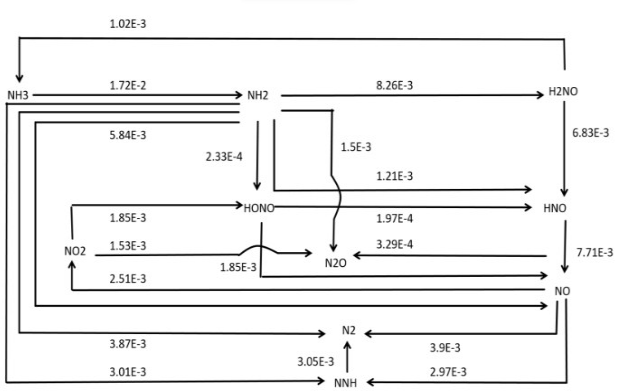

Fig. 3. Reaction pathway analysis of NO 0 ppm, pressure 100 atm, T=1400 K, phi=0.1.

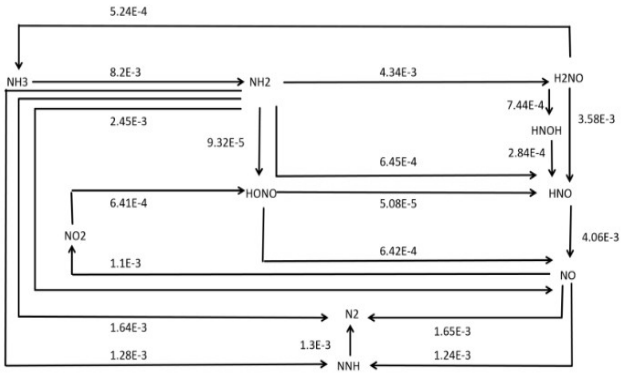

Fig. 4. Reaction pathway analysis of NO 1000 ppm, pressure 100 atm, T=1400 K, phi=0.1.

From the path analysis of the elementary reactions mentioned above, it can be seen that when ammonia fuel ignites and burns without adding NO, the top ten main components that play a significant role are NH3 NH2, H2NO, HONO, HNO, NO, N2, NNH, NO2, HNOH. When the concentration of additive NO is 1000ppm, the top ten main components that play a significant role are NH3 NH2, H2NO, HONO, HNO, NO, N2, NNH, NO2, N2O. Compared to when NO is not added, there is less HNOH and more N2O in the reaction of the basic element. From the simulated experimental data graph, it can be seen that the additive NO has a promoting effect on the ignition delay time of ammonia fuel, and can significantly reduce the ignition delay time in the low temperature range.

When NO is added, the conversion efficiency of NH3-NH2 is 1.72E-2, while the conversion efficiency without NO is 8.2E-3, indicating a significant improvement in the efficiency of the elementary reaction. The main reaction of NH3-NH2 is NH3+OH<=>NH2+H2O. Due to the constant equivalence ratio and equal concentration of ammonia fuel NH3 in both reaction systems. Therefore, in this process, the additive NO changes the rate of NH3-NH2 by altering the concentration of OH groups in the system. And the subsequent series of elementary reactions are accelerated accordingly.

When the additive NO is 1000ppm, the main elementary reaction of N2O is NH+NO<=>N2O+H, NH2 + NO2 <=> N2O + H2O, NH2 + NO2 <=> N2O + H2O. The above three elementary reactions to some extent alter the overall reaction rate and promote the ignition delay time of ammonia fuel.

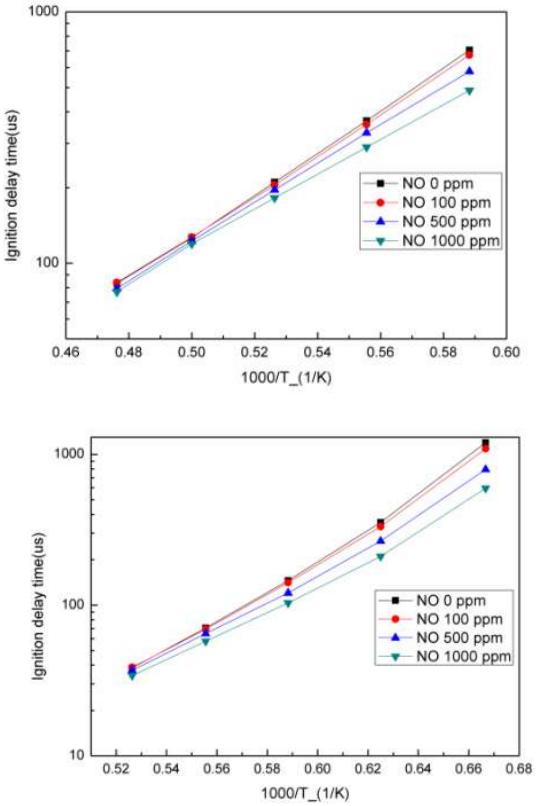

Fig. 5. (a) p=1.75 atm, (b) p=10 atm, phi=0.25, ignition delay time plots for different amounts of NO added.

Figs. 5 and 6 show the simulated experimental data of adding different concentrations of NO under the conditions of equivalence ratio phi=0.25, pressure at 1.75 atm, 10 atm, 50 atm, and 100 atm. When the oxygen concentration decreases, the active molecule O decreases. From the experimental simulation data graph, it can be found that the ignition combustion of NH3 has been inhibited to a certain extent. Under the same pressure and temperature conditions, the ignition delay time has slightly increased compared to phi=0.1. The impact in other aspects is similar to phi=0.1.

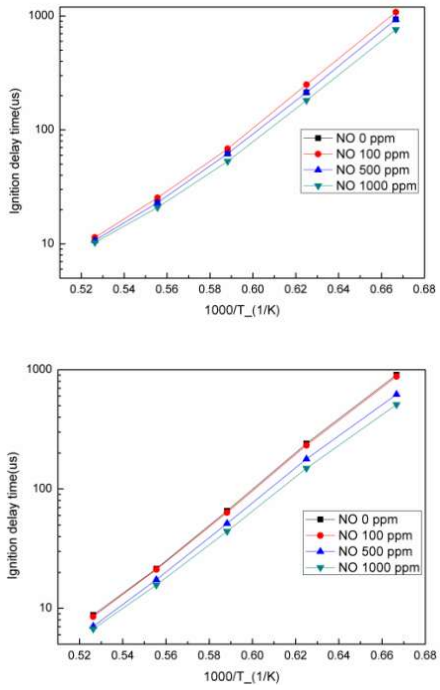

Fig. 6. (a) p=50 atm, (b) p=100 atm, phi=0.25, ignition delay time plots for different amounts of NO added.

As shown in Fig. 7, the experimental data graph shows the changes in ignition delay time of ammonia fuel under the conditions of equivalence ratio phi=0.1, system pressures p=1.75 atm and p=100 atm, and the addition of different concentrations of NO2.

The above two comparison graphs of ignition delay under different pressures are under low pressure and high pressure conditions. It can be seen that the ignition delay time of ammonia fuel under low pressure conditions is negatively correlated with the concentration of NO2 added, that is, the higher the concentration added, the smaller

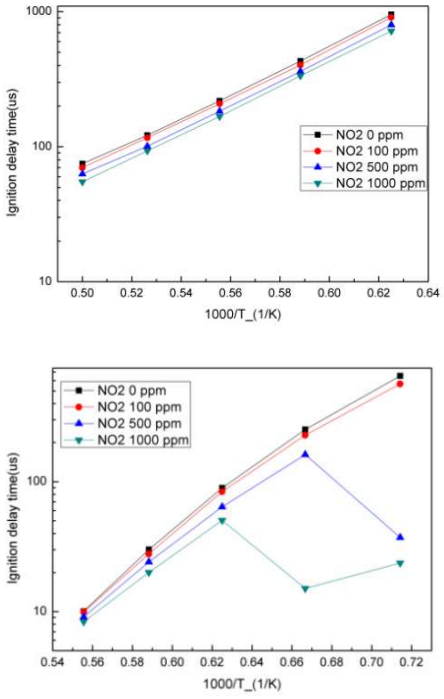

Fig. 7. (a) Ignition delay time plots at 1.75 atm, (b) 100 atm, phi=0.1, with different amounts of NO2.

The ignition delay time. The ignition delay time does not change significantly when the system is under low pressure conditions. When the pressure of the system is increased to a high pressure of 100 atm, there is a significant change in the ignition delay time. The overall correlation remains unchanged and remains consistent with low-pressure conditions, indicating a negative correlation. However, as the concentration of NO2 gradually increases, a sudden change occurs at a certain temperature point, resulting in a sharp decrease in ignition delay time. The temperature point at which a sudden change occurs is generally related to the concentration of NO2, and as the concentration of NO2 increases, this temperature point moves towards the high-temperature zone. But at a concentration of 1000 ppm, the ignition delay time drops sharply and then increases again.

As shown in Figs. 8 and 9, the chemical reaction pathway analysis of ammonia fuel is shown for pressure p=100 atm, equivalence ratio phi=0.1, temperature T=1500 K, and concentrations of additive NO2 at 1000 ppm and 500 ppm.

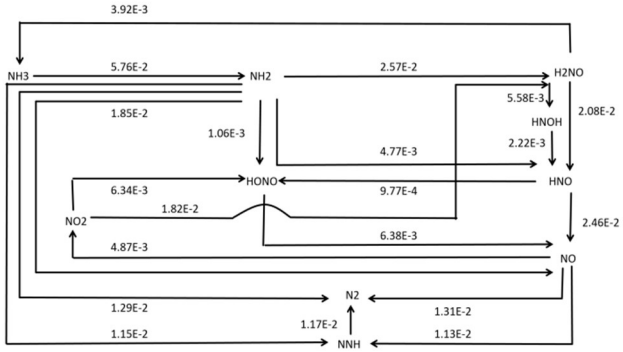

Fig. 8. Reaction path analysis of NO2 1000 ppm pressure 100 atm, T=1500 K, phi=0.1.

From the above reaction pathways, it can be seen that the combustion process of ammonia fuel can be roughly divided into three pathways by NH3-NO. NH3-NH2-HONO-NO, NH3-NH2-HNO–NO, NH3-NH2-H2NO-HNO-NO. The reaction of the third pathway plays a dominant role in the three elementary reaction processes, with an order of magnitude about twice that of the former. When adding NO2 with a concentration of 500 ppm and NO2 with a concentration of 1000 ppm, the latter has a greater impact on the reaction rate of each element. This precisely confirms that when the concentration of the additive NO2 increases to a certain value, the ignition delay time of ammonia fuel decreases sharply. And at the temperature point where a sudden decrease occurs, it gradually moves towards the high temperature range with the increase of NO2 concentration.

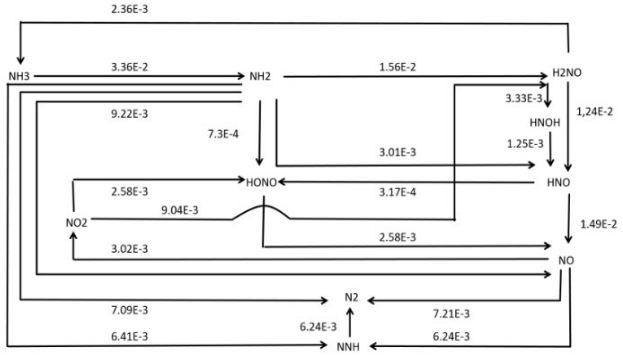

Fig. 9. Reaction path analysis of NO2 500 ppm pressure 100 atm, T=1500 K, phi=0.1.

IV. Conclusions

This paper mainly focuses on the changes in ignition delay time of ammonia fuel when different concentrations of NO and NO_2 are added during combustion. Both can change the ignition delay time, showing a positive correlation. As the concentration increases, the ignition delay time decreases, and the effect area is mostly in the low temperature range, not obvious in the high temperature range. NO and NO2 alter the elementary reaction by changing the groups OH and O in the system. After adding NO2, the ignition delay time will experience a sudden drop at a certain temperature point, and the area of occurrence is also related to the concentration of NO2. When the concentration of NO2 is low, it occurs in the low-temperature range. When the concentration of NO2 increases, the temperature point where a sudden drop occurs moves towards the high temperature range.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Fei Liu wrote the paper; Jing-Xing Wu, Yu-Tao Ma and Xian-Jie Wang conducted the formal analysis and data curation; Yu Song is responsible for funding acquisition and paper validation; all authors had approved the final version.

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