



Ignition enhancement of ethylene/air by NO_x addition

Guo Peng, Chen Zheng *

State Key Laboratory for Turbulence and Complex Systems, College of Engineering, Peking University, Beijing 100871, China

Received 12 April 2012; revised 12 May 2012; accepted 6 July 2012

Available online 2 May 2013

KEYWORDS

Ethylene/air;
Ignition enhancement;
 NO_x addition;
Reaction path analysis;
Sensitivity analysis

Abstract Recently, non-equilibrium plasma assisted combustion (PAC) has been found to be promising in reducing the ignition delay time in hypersonic propulsion system. NO_x produced by non-equilibrium plasma can react with intermediates during the fuel oxidation process and thereby has influence on the combustion process. In this study, the effects of NO_x addition on the ignition process of both the homogeneous ethylene/air mixtures and the non-premixed diffusion layer are examined numerically. The detailed chemistry for ethylene oxidization together with the NO_x sub-mechanism is included in the simulation. Reaction path analysis and sensitivity analysis are conducted to give a mechanistic interpretation for the ignition enhancement by NO_x addition. It is found that for both the homogenous and non-premixed ignition processes at normal and elevated pressures, NO_2 addition has little influence on the ignition delay time while NO addition can significantly promote the ignition process. The ignition enhancement is found to be caused by the promotion in hydroxyl radical production which quickly oxidizes ethylene. The promotion in hydroxyl radical production by NO addition is achieved in two ways: one is the direct production of OH through the reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$, and the other is the indirect production of OH through the reactions $\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$ and $\text{C}_2\text{H}_4 + \text{O} = \text{C}_2\text{H}_3 + \text{OH}$. Moreover, it is found that similar to the homogeneous ignition process, the acceleration of the diffusion layer ignition is also controlled by the reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$.

© 2013 Production and hosting by Elsevier Ltd. on behalf of CSAA & BUAA.

1. Introduction

In scramjet engines for hypersonic aircraft, the combustion resistance time is usually within a few mini-seconds. In order to achieve efficient propulsion, fuel vaporization, mixing between fuel and air, ignition, and complete combustion

should happen within such a short period. Therefore, ignition and combustion enhancement is of critical importance for the development of hypersonic propulsion system.

Recently, non-equilibrium plasma assisted combustion (PAC) has been found to be promising in reducing the ignition delay time and enhancing the flame stabilization and propagation in hypersonic propulsion system.^{1–3} The ignition delay time can be greatly reduced with the help of non-equilibrium plasma by increasing both the local temperature and the radical concentration.^{4–7} In the literature, there have been extensive studies on PAC. For examples, Ombrello et al. found that NO_x generated by non-equilibrium plasma can significantly reduce the ignition delay time of methane;^{6,7} Takita et al. numerically investigated the influence of adding radicals

* Corresponding author. Tel.: +86 10 62757532.

E-mail addresses: guop@pku.edu.cn (P. Guo), cz@pku.edu.cn (Z. Chen).

Peer review under responsibility of Editorial Committee of CJA.



Production and hosting by Elsevier

(H, O, OH) on the ignition process of hydrogen and methane, and the results^{8,9} showed that adding radicals can accelerate the chain initial reactions as well as the chain branching reactions, thus reducing the ignition delay time. However, most of the previous studies only demonstrated the performance of non-equilibrium plasma in combustion enhancement. In order to give a mechanistic interpretation for the underlying mechanisms of PAC, further research based on simulations including detailed chemistry and reaction path analysis is required.

The objectives of this study are to assess the effects of NO_x addition (which can be produced by non-equilibrium plasma⁶⁻⁹) on the ignition of the ethylene/air mixtures and to interpret the chemical kinetics involved in the ignition enhancement by NO_x addition. Ethylene is chosen as the fuel because it is the main product of the thermal dissociation of the large hydrocarbon fuels which are widely used as the propulsion energy source. In the following text, the numerical models and specifications are presented first. Then, the effects of NO_x addition on the homogeneous and the non-premixed diffusion layer ignition processes are assessed, and the chemical kinetics involved in the ignition enhancement is discussed. Finally, the main conclusions are summarized.

2. Numerical methods and specifications

In order to assess the kinetic effects of NO_x addition on the ignition of the premixed ethylene/air mixture, the homogeneous ignition process at constant pressure is simulated. The governing equations for the temperature T and the mass fraction of the k th species Y_k are

$$\frac{dT}{dt} = - \frac{\sum_{k=1}^n (h_k \omega_k W_k)}{\rho c_p} \quad (1)$$

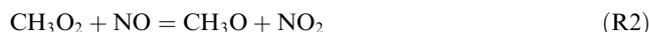
$$\frac{dY_k}{dt} = \frac{\omega_k W_k}{\rho} \quad \text{for } k = 1, 2, \dots, n \quad (2)$$

where t , ρ , c_p , h_k , ω_k , W_k and n denote, respectively, the time, density, specific heat at constant pressure, enthalpy, production rate and molecular weight of k th species, and the total number of species. The chemical reaction rates and the thermal properties under different conditions (temperature, pressure, and composition) are calculated using the CHEMKIN package.¹⁰ The ordinary differential Eqs. (1) and (2) are integrated implicitly using the VODE solver.¹¹

The homogenous ignition process is purely controlled by chemical kinetics in which there are no mass and heat transport. However, in practical PAC process, the ignition is also affected by mixing of fuel and air as well as heat conduction. In order to assess the ignition enhancement in circumstances where transport processes happen, we study the non-premixed ignition process in a diffusion layer configuration.¹² The in-house code A-SURF is employed to simulate the non-premixed ignition process in the diffusion layer between the static cold fuel and hot air. A-SURF solves the conservation equations of one-dimensional, compressible, multi-component, reactive flow using the finite volume method. The CHEMKIN package¹⁰ is incorporated into A-SURF to calculate the temperature- and component-dependent thermodynamic and transport properties as well as the chemical reaction rates. A-SURF has been successfully used in our previous studies.¹³⁻¹⁷ The details on the governing equations, numerical

schemes, and code validation can be found in Refs.^{13,14} and thereby are not repeated here. In the simulation, the computational domain is 20 cm. A multi-level, dynamically adaptive mesh with the minimum mesh size of 4 μm is used to accurately and efficiently resolve the ignition kernel development. The diffusion layer between the cold fuel ($T = 300$ K) and the hot air ($T = 1100$ K) is located at the middle of the computational domain (i.e. $x = 10$ cm). When the fuel and the air diffuse into each other, the ignition kernel is developed and the local temperature rapidly increases. By changing the amount of NO_x in the hot air side, the effects of NO_x addition on the non-premixed ignition of ethylene/air can be assessed.

The detailed reaction mechanism for ethylene oxidation is employed in this work and it is primarily the USC-Mech II,^{18,19} which consists of 111 species and 784 elementary reactions. This mechanism was demonstrated to be able to accurately predict the ignition process of ethylene/air mixtures when the initial temperature is above 1000 K.¹⁸ The NO_x related elementary reactions are not included in USC-Mech II. In order to investigate the kinetic effects of NO_x addition, the NO_x sub-mechanism is obtained from the GRI-Mech 3.0²⁰ by deleting other reactions not related to species containing nitrogen and it is added into the USC-Mech II. Moreover, as suggested by Takita et al.⁹ and Luo et al.,²¹ the following low temperature NO_x chemistry²²⁻²⁴ is added into the detailed mechanism:



3. Results and discussion

3.1. Effects of NO_x addition on homogeneous ignition process

There are many different ways to define the ignition delay time, τ , in the literature. In this study, the definition of ignition delay time is based on the evolution of the temperature as a function of time, $T(t)$, and τ is the time at which the peak value of the rate in the change of the temperature (dT/dt) occurs (which corresponds to the maximum heat release rate). It is also acceptable to define the ignition delay time as the time when the temperature reaches certain degree above the initial temperature T_u , e.g. $T_u + \Delta T$, or as the sudden rise in the OH* concentration, where OH* represents the excited electronic state of OH radical as commonly used in shock-tube experiments. As demonstrated in our previous study,²⁵ the ignition delay times determined in these three ways are very close. Therefore, different definitions of the ignition delay times can be used interchangeably since they are quantitatively similar.

Fig. 1 demonstrates the effects of NO_x addition on the ignition delay time of the stoichiometric ethylene/air mixtures at different initial temperatures and pressures p . It is seen that at both atmospheric and elevated pressures (10^5 and 10^6 Pa), NO addition in the amount of 0.5% vol. can reduce the ignition delay time by one order of magnitude when the initial temperature is in the range of 1000–1200 K. Compared to NO, NO₂ addition is shown to have much weaker influence on the ignition delay time. Therefore, NO is much more effective than NO₂ in terms of ignition enhancement for ethylene/

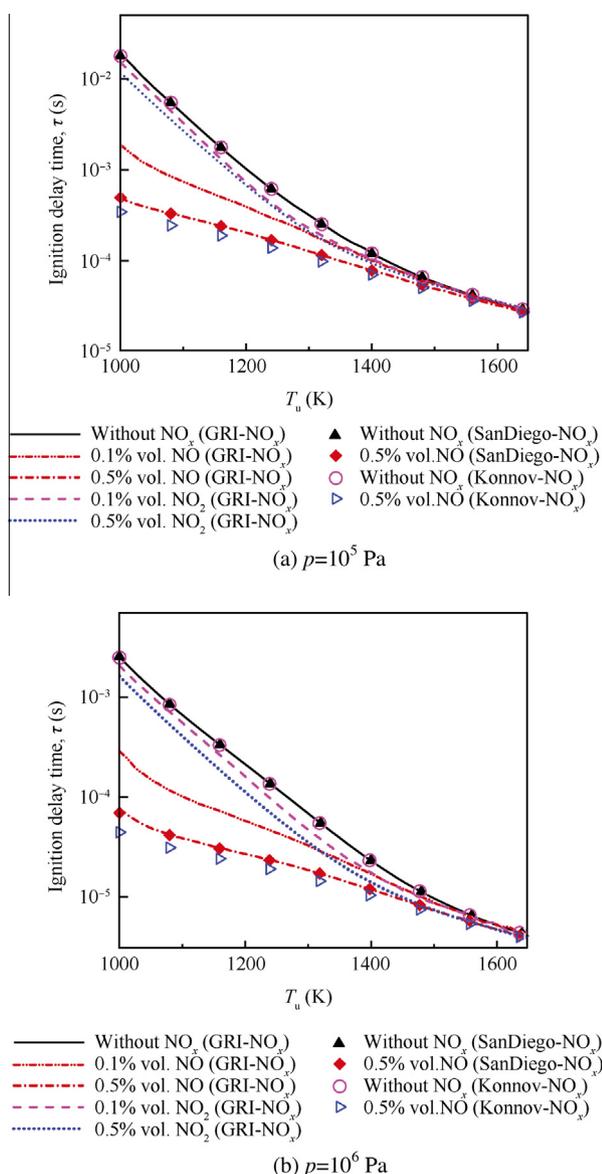


Fig. 1 Change of ignition delay time of stoichiometric ethylene/air/ NO_x mixture with initial temperature at different pressures.

air mixtures. Moreover, Fig. 1 indicates that the ignition enhancement by NO addition decreases with the initial temperature. It is seen that when the initial temperature is above 1400 K, the ignition happens within 10^{-4} s and NO_x addition has little influence on the ignition delay time.

There are different reaction mechanisms for NO_x available in the literature. To ensure that our conclusions do not depend on the NO_x sub-mechanism, the calculations are repeated and compared based on the USC-Mech II mechanism integrating with two other NO_x sub-mechanisms from, respectively, the SanDiego-Mech 2005²⁶ and the Konnov's mechanism.²⁷ As shown in Fig. 1, the results from these different mechanisms agree quite well with each other. This demonstrates the validity of the kinetic model used in the present work. Therefore, in the following only the NO_x sub-mechanism obtained from the GRI-Mech 3.0²⁰ is used in simulation.

Fig. 2 shows the change of the ignition delay time with the amount of NO_x addition. Similar to the results in Fig. 1, NO_2

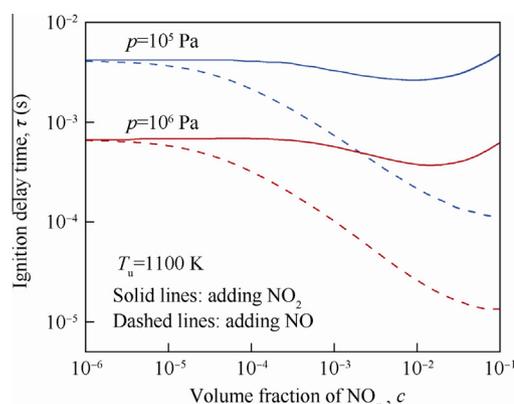


Fig. 2 Effects of NO_x addition on the ignition delay time of stoichiometric ethylene/air/ NO_x mixture initially at $T_u = 1100$ K.

addition is shown to have little influence on the ignition delay time, while NO addition is able to significantly promote the ignition process and to reduce the ignition delay time by more than one order of magnitude. Moreover, unlike the initial temperature which greatly affects the ignition enhancement at a given amount of NO addition (as shown in Fig. 1), the pressure is shown in Fig. 2 to have little influence: the reduction in the ignition delay time at a given amount of NO addition at normal pressure (10^5 Pa) is nearly the same as that at elevated pressure (10^6 Pa).

It is observed in Fig. 2 that too much NO_x addition can prohibit the ignition process resulting in longer ignition delay time, especially for NO_2 addition. In practical PAC process, the NO_x concentration is usually within several thousand ppm⁶. Therefore, according to Fig. 2, the ignition process should be always enhanced by NO_x produced by non-equilibrium plasma.

3.2. Effects of NO_x addition on non-premixed ignition process

The non-premixed ignition occurs in a diffusion layer between the static cold fuel ($T = 300$ K) and hot air ($T = 1100$ K). Fig. 3(a) shows the evolution of the temperature distribution during the non-premixed ignition process without any NO_x addition. The initial ($t = 0$ ms) temperature and the composition concentration distributions are in the form of a step-function with the discontinuity located at $x = 10.0$ cm. After the contact of the hot air with the cold fuel, heat conduction and mass diffusion occur and a mixing layer is developed. Meanwhile, chemical reactions take place during the mixing process. Since the reaction rate is more sensitive to the temperature than to the concentrations of the reactants, the ignition kernel is first found in the hot air side, as shown in Fig. 3(a). Moreover, it is observed in Fig. 3(a) that the ignition kernel propagates towards the cold fuel side. This is due to the facts that the small amount of fuel diffused into the hot air can be consumed in the ignition kernel, and that there is more fuel diffused into the air side at the position closer to the initial contact surface ($x = 10.0$ cm).

The evolution of the maximum temperature during the non-premixed ignition process with different amounts of NO addition is plotted in Fig. 3(b). It is seen that the non-premixed ignition process is also strongly affected by NO addition. Similar to the homogeneous ignition process, the non-premixed

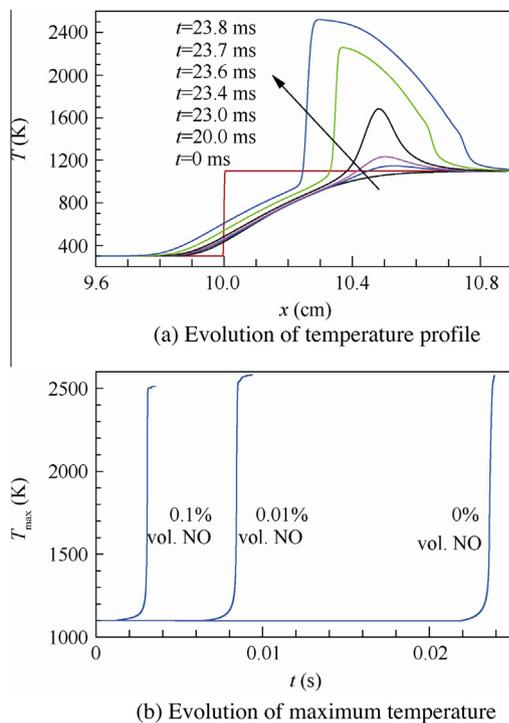


Fig. 3 Evolution of temperature profile and the maximum temperature during non-premixed ignition process in a diffusion layer configuration.

ignition delay time is defined as the time when the peak value of the rate in the change of the maximum temperature (dT_{\max}/dt) occurs.

Fig. 4 demonstrates the effects of NO_x addition on the non-premixed ignition delay time in a diffusion layer configuration. Similar to the results in Fig. 2 for the homogeneous ignition process, Fig. 4 indicates that NO addition can greatly promote the non-premixed ignition process and reduce the ignition delay time by more than one order of magnitude. Unlike NO, adding NO₂ is shown to have little influence on the non-premixed ignition delay time. It is noted that the ignition delay time of the non-premixed ignition process is much larger (by a factor around ten) than that of the homogeneous ignition

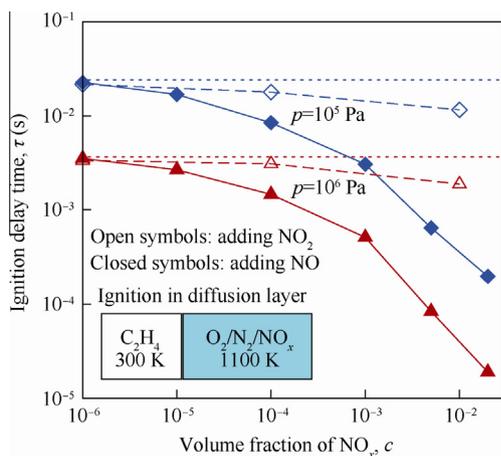


Fig. 4 Effects of NO_x addition on the non-premixed ignition delay time in a diffusion layer configuration.

process, which can be observed by the comparison between Figs. 4 and 2. This is due to the facts that the cold fuel and hot air need to mix with each other by heat and mass diffusion in the non-premixed ignition process, and that the average temperature in the non-premixed ignition process is lower than the homogeneous ignition process (which is 1100 K in Fig. 2).

In order to explain the change of the ignition delay time with NO addition observed in Figs. 1–4, reaction path analysis and sensitivity analysis are conducted in the next subsection based on the homogeneous system to understand the kinetics involved in the ignition enhancement.

3.3. Chemical kinetics involved in ignition enhancement

Chemical reaction path analysis is conducted for the homogeneous ignition process of stoichiometric ethylene/air mixture at $T_u = 1100$ K and $p = 10^5$ Pa without and with 0.1% vol. NO addition. Fig. 5 shows the evolution of the molar fraction of major radicals (OH, O, HO₂, and C₂H₃) as well as NO and NO₂ during the homogeneous ignition process. The evolution of the molar fraction of H radical is close to that of O radical and thereby is not shown in Fig. 5 for clear demonstration. It is seen that with 0.1% vol. NO addition, the radical pool is much more easily generated and thereby the ignition process is greatly accelerated. Without NO addition, the OH and O radicals can be built up only after $t > 10^{-3}$ s. However, with 0.1% vol. NO addition, the OH and O radicals can be generated much earlier which results in the reduction of the ignition delay time. Moreover, it is observed in Fig. 5(b) that NO is converted into NO₂ during an initial period. As will be explained later, this process in fact plays an essential role in promoting the ignition process.

It is well-known that in the homogeneous ignition process of the ethylene/air mixture, the ethylene is first oxidized to

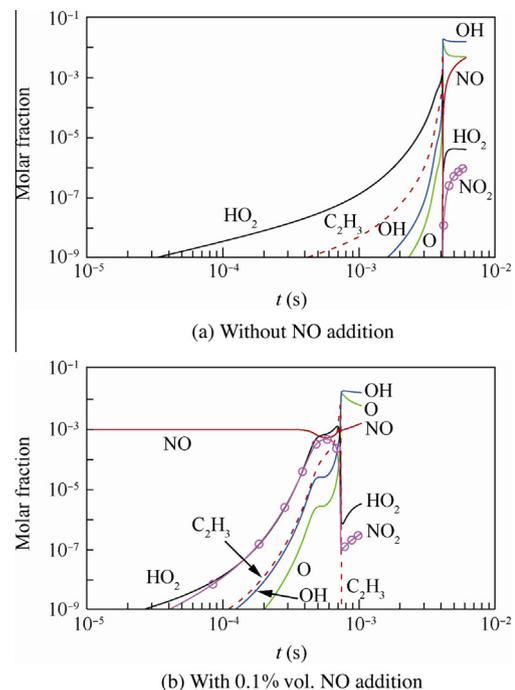


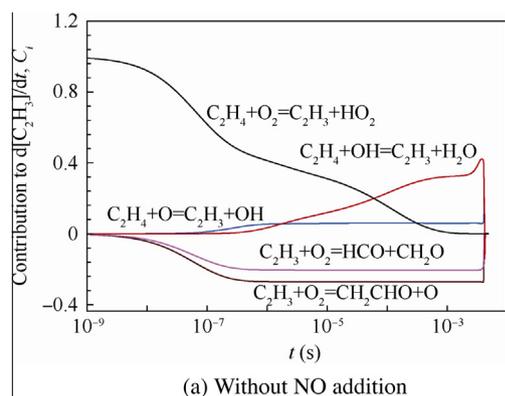
Fig. 5 Evolution of molar fractions of different species during homogeneous ignition process of stoichiometric ethylene/air mixture.

ethenyl (C_2H_3) through the reaction $C_2H_4 + O_2 = C_2H_3 + HO_2$. The rates of this reaction and the C_2H_3 oxidation reactions basically control the ignition process.²⁸ Therefore, we first investigate the generation path of C_2H_3 with and without NO addition. We introduce the following definition of the contribution of the i th reaction to the concentration change of a certain intermediate species^{29,30}

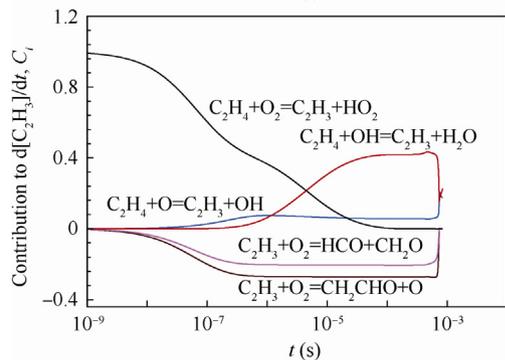
$$C_i = f_i / \sum_{i=1}^m (|f_i|) \quad (3)$$

where f_i represents the rate of change in the concentration of the considered species due to the i th reaction, and m is the total number of elementary reactions. Therefore, the positive (negative) value of C_i indicates that the considered species is generated (consumed) by the i th reaction. It is noted that the values of C_i at different time cannot be directly compared since the reaction rates (and so do the numerator and denominator in Eq. (3)) change greatly with time in the ignition process. Only the comparison between values of C_i for different reactions at the same time is meaningful.

The major reactions related to the production and consumption of C_2H_3 during the ignition process of atmospheric ethylene/air mixtures at initial temperature $T_u = 1000$ K are plotted in Fig. 6. It is seen that without NO addition, C_2H_3 is mainly produced by the reaction between C_2H_4 and O_2 at $t < 6 \times 10^{-5}$ s, after C_2H_4 is mainly oxidized by hydroxyl radical OH through the reaction $C_2H_4 + OH = C_2H_3 + H_2O$. However, with 0.1% vol. NO addition, the reaction between



(a) Without NO addition



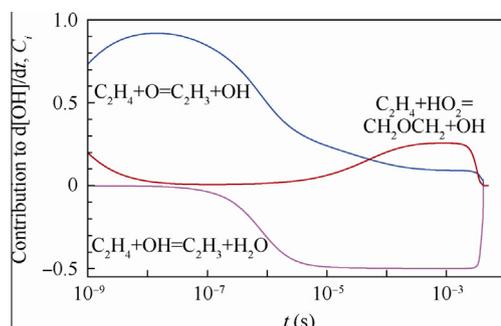
(b) With 0.1% vol. NO addition

Fig. 6 Major reactions related to the production ($C_i > 0$) and consumption ($C_i < 0$) of C_2H_3 in the homogeneous ignition process of stoichiometric ethylene/air mixture.

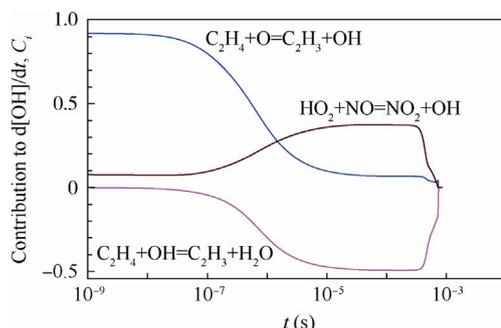
C_2H_4 and OH is greatly advanced and becomes dominant in the oxidation of C_2H_4 when $t > 4 \times 10^{-6}$ s. Therefore, the ignition enhancement by NO addition is mainly due to the earlier appearance of OH radical which greatly accelerates the oxidation of C_2H_4 . Moreover, the comparison between Fig. 6(a) and (b) indicates that NO addition has little influence on the further oxidation path of C_2H_3 .

Since the appearance of OH radical can greatly accelerate the oxidation of C_2H_4 , we investigate the reaction path of OH radical and the results are presented in Fig. 7. It is seen that without NO addition, OH is mainly produced through the reaction $C_2H_4 + O = C_2H_3 + OH$ at a very small reaction rate due to the extremely low concentration of O radical (see Fig. 5). However, with 0.1% vol. NO addition, as shown in Fig. 7(b), the OH radical can be generated through the reaction $HO_2 + NO = NO_2 + OH$ at a much faster reaction rate since the concentration of HO_2 is several orders higher than that of O radical (see Fig. 5). Therefore, NO addition can greatly enhance the production of OH radical via the reaction $HO_2 + NO = NO_2 + OH$, in which HO_2 is mainly produced by the reaction $C_2H_4 + O_2 = C_2H_3 + HO_2$ as demonstrated in Fig. 6. Similar analysis have been done to study contributions to OH accumulation at the same conditions, and the results, as shown in Fig. 7, demonstrated that the main consumption path of OH radical is to oxidize C_2H_4 through the reaction $C_2H_4 + OH = C_2H_3 + H_2O$.

Fig. 8 demonstrates the main generation and consumption reactions of oxygen radical O during the ignition process of atmospheric ethylene/air mixtures at initial temperature $T_u = 1000$ K with and without NO addition. When NO is not added, Fig. 8(a) indicates that O radical is mainly produced by the reaction $C_2H_3 + O_2 = CH_2CHO + O$. When



(a) Without NO addition



(b) With 0.1% vol. NO addition

Fig. 7 Major reactions related to the production ($C_i > 0$) and consumption ($C_i < 0$) of OH in the homogeneous ignition process of stoichiometric ethylene/air mixture.

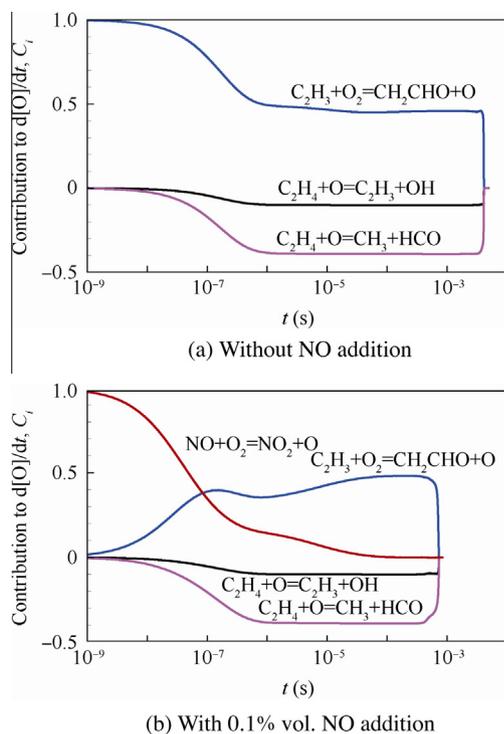


Fig. 8 Major reactions related to the production ($C_i > 0$) and consumption ($C_i < 0$) of O in the homogeneous ignition process of stoichiometric ethylene/air mixture.

0.1% vol. NO is added, Fig. 8(b) shows that before $t = 10^{-7}$ s, O radical is mainly produced by the reaction $\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$, which is much faster than the reaction $\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{CHO} + \text{O}$ since the concentration of NO is much higher than that of C_2H_3 (see Fig. 5). Therefore, with the appearance of NO, O radical can be quickly produced through the reaction $\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$, after which O radical reacts with C_2H_4 to produce OH through the reaction $\text{C}_2\text{H}_4 + \text{O} = \text{C}_2\text{H}_3 + \text{OH}$.

The reaction rates of ethenyl involved reactions during the ignition process of atmospheric ethylene/air mixtures at initial temperature $T_u = 1000$ K are plotted in Fig. 9. The solid lines denote results with 0.1% vol. NO addition while the dashed lines without NO addition. The reaction rate of $\text{C}_2\text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_3 + \text{HO}_2$ is expanded ten times and this reaction is shown to be the chain initiation reaction in the ignition process without NO addition. When NO is added, a great amount of OH generated through the reaction $\text{NO} + \text{HO}_2 = \text{OH} + \text{NO}_2$ can participate in the fast reaction $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$, and thereby accelerates the oxidation of ethylene molecule. The O radical is shown to oxidize C_2H_4 through the reactions $\text{C}_2\text{H}_4 + \text{O} = \text{C}_2\text{H}_3 + \text{OH}$ and $\text{C}_2\text{H}_4 + \text{O} = \text{CH}_3 + \text{HCO}$.

Therefore, according to the results shown in Figs. 6–9, the ignition enhancement by NO addition is caused by the promotion in OH radical production which quickly oxidizes C_2H_4 through the reaction $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$ (see Fig. 6). The promotion in OH production by NO addition is achieved in two ways: one is the direct production of OH through the reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$ (see Fig. 7), and the other is the indirect production of OH through the reactions $\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$ and $\text{C}_2\text{H}_4 + \text{O} = \text{C}_2\text{H}_3 + \text{OH}$ (see Fig. 8).

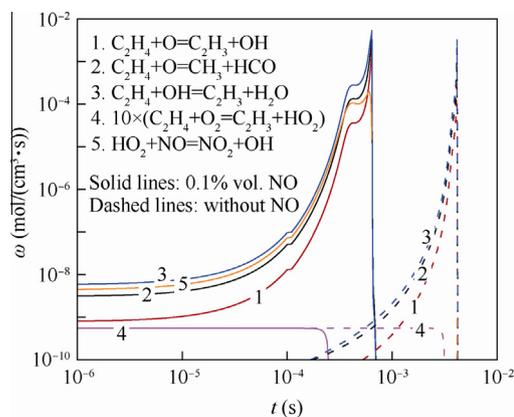


Fig. 9 Reaction rates of ethenyl involved elemental reactions in homogeneous ignition process of stoichiometric ethylene/air mixture without and with 0.1% vol. NO addition.

In order to further reveal the elementary reactions involved in the ignition enhancement by NO addition, sensitivity analysis is conducted for the homogeneous ignition process of atmospheric ethylene/air mixtures at initial temperature $T_u = 1000$ K with and without 0.1% vol. NO addition. The logarithmic sensitivities of different reactions are compared in Fig. 10.

It is observed that without NO addition, the ignition delay time is mainly affected by the reactions involved in the oxidation of C_2H_4 and C_2H_3 by HO_2 and O_2 , respectively. However, in the case of 0.1% vol. NO addition, the sensitivity of these reactions is reduced indicating that the ignition process is affected by other elementary reactions. This is consistent with the results shown in Figs. 6–9. Moreover, Fig. 10 indicates that the elementary reactions $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$ and $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$ strongly influence the homogeneous ignition process when 0.1% vol. NO is added into the mixture. This further validates the conclusion that the ignition enhancement by NO addition is caused by the promotion in OH radical production (through reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$) which quickly oxidizes C_2H_4 (through reaction $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$).

Fig. 11 shows the change of the normalized ignition delay time with NO addition for the homogeneous and diffusion

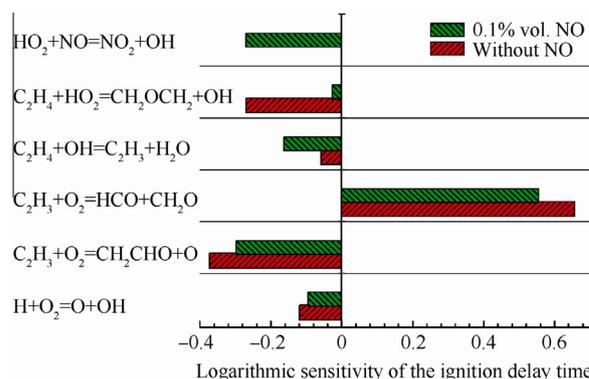


Fig. 10 Logarithmic sensitivity analysis on ignition delay time of stoichiometric ethylene/air mixture without and with 0.1% vol. NO addition.

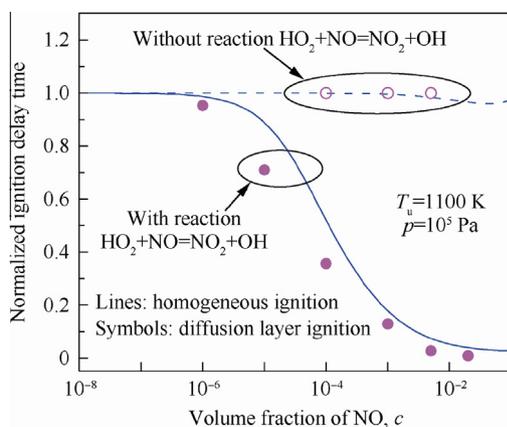


Fig. 11 Effects of the reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$ on normalized ignition delay time, $\tau(c)/\tau(c=0)$, for both homogeneous and diffusion layer systems.

layer systems. The normalized ignition delay time is defined as $\tau(c)/\tau(c=0)$, the inverse of which is the speed-up in ignition caused by NO addition. It is seen that the change of the normalized ignition delay time with the volume fraction of NO is similar for both systems. Therefore, the non-premixed ignition process is also enhanced by NO_x related elementary reactions. Furthermore, Fig. 11 demonstrates the effects of the most important enhancement reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$ on the normalized ignition delay time of the homogeneous and diffusion layer systems. When reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$ is frozen, the normalized ignition delay times of both the homogeneous and the diffusion layer systems are close to 1.0, which indicates that the ignition cannot be promoted by NO addition. Therefore, similar to the homogeneous ignition process, the acceleration of the diffusion layer ignition is also controlled by the reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$.

4. Conclusions

- (1) It is found that NO_2 addition has little influence on the ignition delay time, while NO addition can significantly promote the ignition process.
- (2) For the homogeneous ignition process, it is shown that the ignition enhancement by NO addition decreases with the initial temperature and that NO addition has little influence on the ignition delay time when the initial temperature is above 1400 K. For the non-premixed ignition process, the ignition delay time is much longer than that of the homogeneous ignition process. Nevertheless, for both the homogeneous and non-premixed ignition processes, the ignition delay time can be reduced by more than one order of magnitude when a certain amount of NO is added.
- (3) Reaction path analysis and sensitivity analysis are conducted for the homogeneous ignition process without and with 0.1% vol. NO addition and it is found that the ignition enhancement by NO addition is caused by the promotion in OH radical production which quickly oxidizes C_2H_4 through the reaction $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$. The promotion in OH production by NO addition is achieved in two ways: one is the direct

production of OH through the reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$, and the other is the indirect production of OH through the reactions $\text{NO} + \text{O}_2 = \text{NO}_2 + \text{O}$ and $\text{C}_2\text{H}_4 + \text{O} = \text{C}_2\text{H}_3 + \text{OH}$. Furthermore, we demonstrate that similar to the homogeneous ignition process, the acceleration of the diffusion layer ignition is also controlled by the reaction $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$.

Acknowledgements

The author would like to thank Beijing Municipal Natural Science Foundation (Grant No. 3102016); National Natural Science Foundation of China (Grant Nos. 50976003, 51136005) for funding this work.

References

1. Starikovskii AY. Plasma supported combustion. *Proc Combust Inst* 2005;**30**(2):2405–17.
2. Starikovskaia SM. Plasma assisted ignition and combustion. *J Phys D Appl Phys* 2006;**39**(16):R265.
3. Sun W, Uddi M, Ombrello T, Won SH, Carter C, Ju Y. Effects of non-equilibrium plasma discharge on counterflow diffusion flame extinction. *Proc Combust Inst* 2011;**33**(2):3211–8.
4. Takita K. Ignition and flame-holding by oxygen, nitrogen and argon plasma torches in supersonic airflow. *Combust Flame* 2002;**128**(3):301–13.
5. Liu JB, Ronney PD, Wang F, Lee LC, Gundersen M. Transient plasma ignition for lean burn applications. In: *41st AIAA aerospace sciences meeting and exhibit*; 2003 Jan 6–9; Reno, Nevada; 2003.
6. Ombrello T, Qin X, Ju YG, Gangoli S, Gutsol A, Fridman A. Non-equilibrium plasma discharge: characterization and effect on ignition. In: *44th AIAA aerospace sciences meeting and exhibit*; 2006 Jan 9–12; Reno, Nevada; 2006.
7. Ombrello T, Ju Y, Gangoli S, Gutsol A, Fridman A. Ignition enhancement using magnetic gliding arc. In: *45th AIAA aerospace sciences meeting and exhibit*; 2007 Jan 8–11; Reno, Nevada; 2007.
8. Takita K, Ju Y. Effect of radical addition on extinction limits of H_2 and CH_4 flames. In: *44th AIAA aerospace sciences meeting and exhibit*; 2006 Jan 9–12; Reno, Nevada; 2006.
9. Takita K, Abe N, Masuya G, Ju Y. Ignition enhancement by addition of NO and NO_2 from a N_2/O_2 plasma torch in a supersonic flow. *Proc Combust Inst* 2007;**31**(2):2489–96.
10. Kee RJ, Rupley FM, Miller JA. CHEMKIN-II: a Fortran package for the analysis of gas-phase chemical kinetics. Technical report. Livermore(CA): Sandia National Laboratory; 1989 Sep. Report No.: SAND-89-8009. Contract No.: AC04-76DR00789.
11. Brown PN, Byrne GD, Hindmarsh AC. VODE: a variable coefficient ODE solver. *SIAM J Sci Stat Comput* 1989;**10**(5):1038–51.
12. Knikkerr R, Dauplain A, Cuenot B, Poinot T. Comparison of computational methodologies for ignition of diffusion layers. *Combust Sci Technol* 2003;**175**(10):1783–806.
13. Chen Z, Burke MP, Ju Y. Effects of Lewis number and ignition energy on the determination of laminar flame speed using propagating spherical flames. *Proc Combust Inst* 2009;**32**(1):1253–60.
14. Chen Z. Effects of radiation and compression on propagating spherical flames of methane/air mixtures near the lean flammability limit. *Combust Flame* 2010;**157**(12):2267–76.
15. Chen Z, Burke MP, Ju Y. On the critical flame radius and minimum ignition energy for spherical flame initiation. *Proc Combust Inst* 2011;**33**(1):1219–26.

16. Zhang H, Chen Z. Spherical flame initiation and propagation with thermally sensitive intermediate kinetics. *Combust Flame* 2011;**158**(8): 1520–31.
17. Zhang W, Chen Z, Kong W. Effects of diluents on the ignition of premixed H₂/air mixtures. *Combust Flame* 2011;**159**(1):151–60.
18. Wang H, You XQ, Joshi AV, Davis SG, Laskin A, Egolfopoulos F, et al. USC Mech Version II. High-temperature combustion reaction model of H₂/CO/C1–C4 compounds. *Links* 2007, http://ignis.usc.edu/jet_fuel_mech/dodecane_simplified_mech.txt.
19. Sheen DA, You X, Wang H, Løvås T. Spectral uncertainty quantification, propagation and optimization of a detailed kinetic model for ethylene combustion. *Proc Combust Inst* 2009;**32**(1): 535–42.
20. Smith GP, Golden DM, Frenklach M, et al. GRI-Mech 3.0; 1999. Available from: http://www.me.berkeley.edu/gri_mech.
21. Luo Z, Lu T, Liu J. A reduced mechanism for ethylene/methane mixtures with excessive NO enrichment. *Combust Flame* 2011;**158**(7): 1245–54.
22. Bromly J, Barnes F, Muris S, You X, Haynes B. Kinetic and thermodynamic sensitivity analysis of the NO-sensitized oxidation of methane. *Combust Sci Technol* 1996;**115**(4–6):259–96.
23. Tan Y, Fotache C, Law C. Effects of NO on the ignition of hydrogen and hydrocarbons by heated counterflowing air. *Combust Flame* 1999;**119**(3):346–55.
24. Amano T, Dryer FL. Effect of dimethyl ether, NO_x, and ethane on CH₄ oxidation: high pressure, intermediate-temperature experiments and modeling. *Symp(Int) Combust* 1998;**27**(1):397–404.
25. Zhao Z, Chen Z, Chen S. Correlations for the ignition delay times of hydrogen/air mixtures. *Chin Sci Bull* 2011;**56**(2):215–21.
26. Saxena P, Williams FA. Testing a small detailed chemical-kinetic mechanism for the combustion of hydrogen and carbon monoxide. *Combust Flame* 2006;**145**(1–2):316–23.
27. Coppens F, De Ruyck J, Konnov A. The effects of composition on burning velocity and nitric oxide formation in laminar premixed flames of CH₄ + H₂ + O₂ + N₂. *Combust Flame* 2007;**149**(4): 409–17.
28. Faravelli T, Frassoldati A, Ranzi E. Kinetic modeling of the interactions between NO and hydrocarbons in the oxidation of hydrocarbons at low temperatures. *Combust Flame* 2003;**132**(1–2): 188–207.
29. Guo P, Chen Z. Effects of O₃ on the ignition of CH₄/air mixtures. *J Eng Thermophys* 2011;**32**(12):2160–3 [Chinese].
30. Guo P, Chen Z. Effects of NO_x on the ignition of methane/air mixtures. *Chin J Combust Sci Technol* 2010;**16**(5):472–6 [Chinese].

Guo Peng is a graduate student at College of Engineering, Peking University, China. His main research concerns on plasma assisted combustion.

Chen Zheng is a professor and Ph.D. supervisor at College of Engineering, Peking University, China. He received the Ph.D. degree from Princeton University in 2008. His main research interests include combustion and propulsion, alternative and surrogate fuels, fire safety, flame dynamics, chemical kinetics and mechanism reduction, and multi-scale modeling.