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COMPARATIVE STUDY ON THE IMPACT OF ETHANE/ETHYLENE/ACETYLENE ADDITION ON IGNITION OF FUEL-RICH N-DECANE/AIR FLAME

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The ignition of heavy hydrocarbon at high altitude regions is difficult as the air is very thin so that the fuel/air is ignited under ultimately fuel-rich condition. To simulate and improve the ignition of heavy hydrocarbon (n-decane) at high altitude regions, the effects of ethane/ethylene/acetylene addition on ignition of fuel-rich n-decane/air mixtures are studied and compared numerically in the present study. Our research found that the addition of C_2H_6 *inhibits the ignition when the starting ignition temperature* (T_0) *<1150 K and promotes the ignition when* T_0 *>1150 K.* C_2H_4 *addition affects little on the ignition when* $T_0 = 1000$ *K and promotes the ignition when* T_0 *>1000 K. The addition of* C_2H_2 *promotes the ignition at all considered temperatures. The ignition delay with ethane, ethylene and acetylene additions at various equivalence ratio and different pressure conditions indicate that the order of promoting auto-ignition from intense to weak are* C_2H_2, C_2H_4 *and* C_2H_6. *Our findings would be a useful guidance to promote the ignition of real jet at high altitude regions by adding* C_2H_2 *to the real jet fuel n-decane. The results also provided a way for the efficient ignition of motor and had great significance in the safe production of oil industry.*

Keywords: Ignition delay, n-Decane, Ethane addition, Ethylene addition, Acetylene addition

1. Introduction

At the high altitude regions (>4500 m), the air is very thin and the oxygen is lacking [1]. In this condition, the mass flow rate of air decreases rapidly during the start-up process of power systems, such as micro gas turbine, lean blowout detection method, etc [2-4]. Therefore, ignition becomes difficult at high altitude regions, a problem that must be overcome. It has been reported that active species addition to the fuel/air mixtures can influence the ignition characteristics [5].

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Recently, the issues of ignition were widely considered experimentally. An et al. found that hydrogen addition to n-heptane promotes significantly the ignition delay, as hydrogen consumes radical species [6]. Mathieu et al. [7] found that NO_2 addition promotes ignition delay through $NO+HO_2=NO_2+OH$. Deng et al. [8] investigated NO_2 addition on ignition of ethane by a stainless steel shock tube.

A lot of numerical works have been done for the problem of ignition. Wang et al. investigated the effect of the addition of hydrogen to the CH_4 ignition in HCCI engine [9]. Hu et al. [10] studied numerically and found that H_2 addition delays the ignition of DME HCCI engines. Li et al. [11] studied numerically and found that the addition of H_2 may promote the burning rate and decrease ignition delays in NH_3 mixtures. Frolov et al. [12] studied numerically and found that H_2 addition enhances ignition at temperature large than 1050 K and inhibits ignition less than 1050 K. Li et al. [13] studied numerically and found that H_2 addition may largely reduce the minimum ignition energy. In the present study, the base fuel n-decane in real jet is chosen in the numerical calculation [14].

In addition, the safety issues and difficult storage prevent the wide application of hydrogen as additive. Compared with heavy hydrocarbons, the chemical property of gaseous hydrocarbons is very active. Therefore, the addition of gaseous hydrocarbons, such as methane and ethane, may promote the ignition of heavy hydrocarbons. Ravi et al. [15] compared the additions of ethane and ethylene on laminar flame speed. However, the comparative study of the impact on the ignition of ethane, ethylene and acetylene additional n-decane/air fuels has not been investigated.

The goal of this paper is to study and compare the influences of ethane, ethylene and acetylene additions to n-decane/air mixtures. The ignition delays of n-decane/air fuels with addition and without adding three species at equivalence ratios, the temperatures and pressures of 1.1-2.0, 1000-1550 K and 1-50 atm are calculated.

2. Methods

The simulations are performed using zero-dimensional closed homogeneous reactor model. This model assumes that the mixtures are homogeneous in a closed reactor. Zero-dimensional closed homogeneous reactor model also amuses that the combustion occurs at a reactor with fix reactor volume, spherical shape, closed and adiabatic system. In this model, the ignition time of hydrocarbon/air mixture can be calculated via Monte Carlo procedure [16] hooked in CHEMKIN II software. In the present work, the problem type of constraining pressure and solving energy equation was chosen with constant volume adiabatically. The temperature response curve was shown in Fig. 1 at the equivalence ratio of 1.5, T_0=1000 k and P=20 atm. The temperature first remains unchanged and steeply increase at one moment. The definition of ignition delay time is the time of 400K increment starting from the initial temperature shown in Fig. 1. Our choice of 400 K temperature rise was used by Hui et al. [17] and Gribi et al. [18].

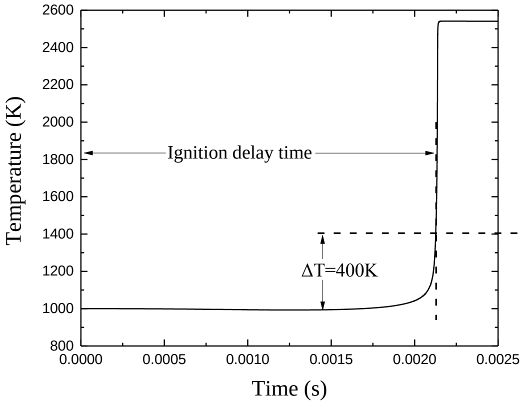


Fig. 1. Temperature response curve of n-decane/air mixture at the equivalence ratio of 1.5, T_0=1000 k and P=20 atm.

The model of chemical kinetics by Naik et al. [19] was used in the simulations of the present work. This model was designed to simulate properties of combustion for base fuels of real jet with 597 species and 3854 reactions. The reported calculation of jet fuels with this model agreed well to relative experimental investigation, shown in Fig. 2 [20-22]. Therefore, using this model in this study can achieve reasonable results.

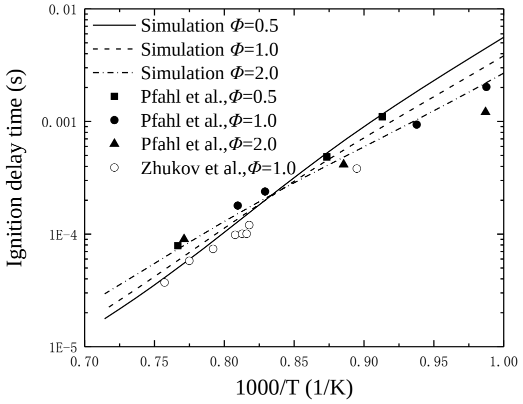


Fig. 2. Comparison between the calculated ignition delays of n-decane/air mixtures with the reported experimental results

In this investigation, ethane, ethylene and acetylene are added to the base fuel respectively. We found the fuel blend equivalence ratio Φ_F and addition ratio R [23] to describe the amount of addition shown as:

$$\phi_F = \frac{C_{BF} / \left[C_A - C_{Add} / \left(C_{add} / C_A \right)_{st} \right]}{\left(C_{add} / C_A \right)_{st}} \tag{1}$$

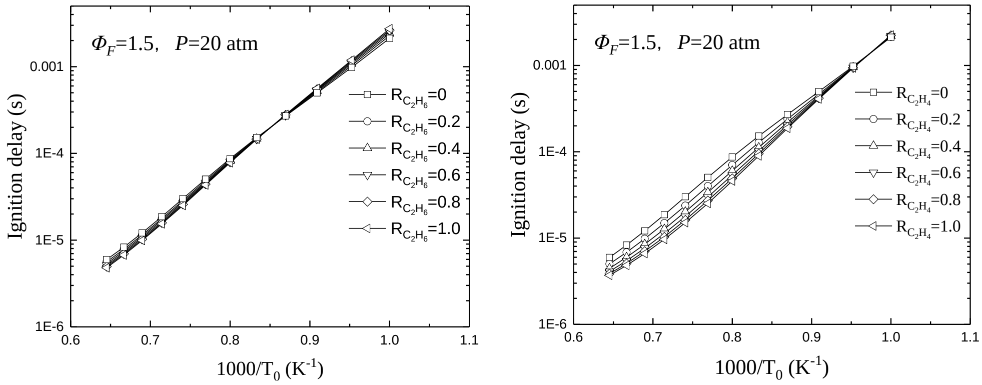
$$R = \frac{C_{Add} + C_{Add} / \left(C_{add} / C_A \right)_{st}}{C_{BF} + \left[C_A - C_{Add} / \left(C_{add} / C_A \right)_{st} \right]} \tag{2}$$

where C_A is the molar fractions of air, C_{Add} is the mole fraction of added ethane, ethylene or acetylene, C_{BF} is the molar fractions of base fuel and the stoichiometric condition is shown as *st*. As the ignition of aircraft engine running at high altitude regions is a fuel-rich, high temperature and pressure process, equivalence ratio and initial temperature are set in the ranges of 1.1-2.0, 1000-1500 K and 20 atm. The addition ratio is set as 0-1. The ignition delay is calculated under different conditions, and the important reactions that are responsible for ignition are identified by the sensitivity analysis.

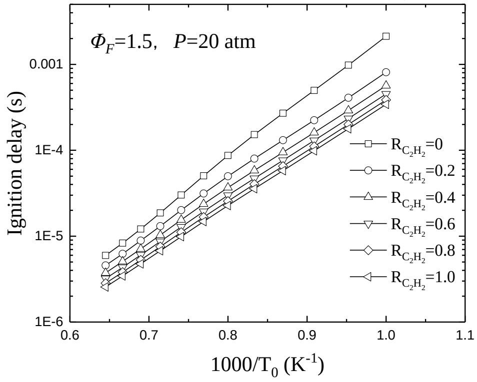
3. Results

3.1 Ignition delays with addition of C_2H_6, C_2H_4 and C_2H_2 under varied temperature

Ignition delay times with various temperature T_0=1000-1550 K is shown in Fig. 3 at Φ_F= 1.5 and P=20 atm. For the addition of C_2H_6, the ignition delay increases when T_0<1150 K, and decreases when T_0>1150 K with the increase of addition ratio. This means that C_2H_6 addition has a negative effect on auto-ignition when T_0<1150 K, and auto-ignition would be enhanced when T_0>1150 K. For the addition of C_2H_4, ignition delay times are similar at T_0=1000 K at various addition ratios. When the temperature increases, the ignition delay times go to diverge for the mixture at different addition ratios. This indicates that the addition of C_2H_4 promotes auto-ignition at higher temperature. For C_2H_2 addition, the increase of addition ratio leads to the reduction of ignition delay for all temperatures calculated in this study. This indicates that auto-ignition would be enhanced for C_2H_2 addition at all temperature conditions calculated. It can be concluded from Fig. 3 that the order of promoting auto-ignition from intense to weak is C_2H_2, C_2H_4, C_2H_6.



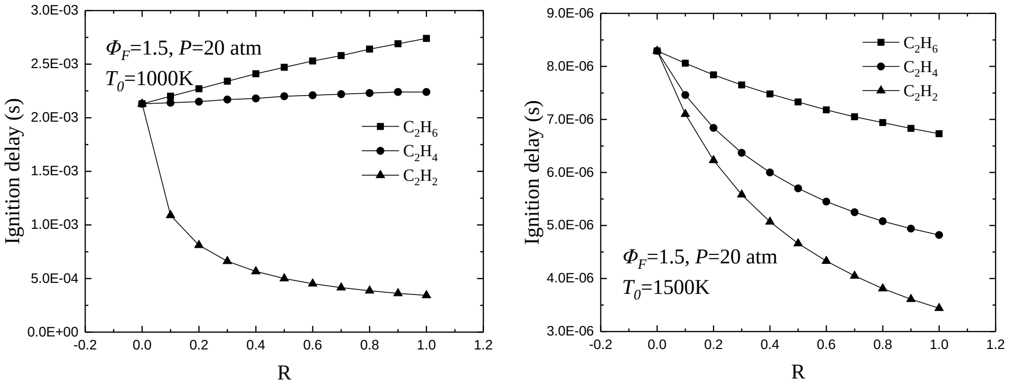
(a) Addition of C_2H_6 (b) Addition of C_2H_4



(c) Addition of C_2H_2

Fig. 3. Ignition delays of systems with addition of (a) C_2H_6, (b) C_2H_4 and (c) C_2H_2 at Φ_F= 1.5 and P=20 atm in different initial temperatures.

To further study the different effect of adding C_2H_6, C_2H_4 and C_2H_2 at different initial temperature, the ignition delays of n-decane/air mixtures in R=0-1 and T_0=1000-1500 K are plotted in Fig. 4. At initial temperature of 1000 K, ignition delay increases linearly with increasing the C_2H_6 addition ratio, remains nearly unchanged with increasing the C_2H_4 addition ratio and decreases exponentially with increasing the C_2H_2 addition ratio. However, the ignition delay time with addition of C_2H_6, C_2H_4 or C_2H_2 decreases when addition ratio increases at 1500 K. The order of enhancing auto-ignition from intense to weak is C_2H_2, C_2H_4 and C_2H_6.



(a) T_0=1000 K (b) T_0=1500 K

Fig. 4. Ignition delays of systems with addition of C_2H_6, C_2H_4 and C_2H_2 at Φ_F= 1.5, P=20 atm and (a) T_0=1000K and (b) T_0=1500K in different addition ratios.

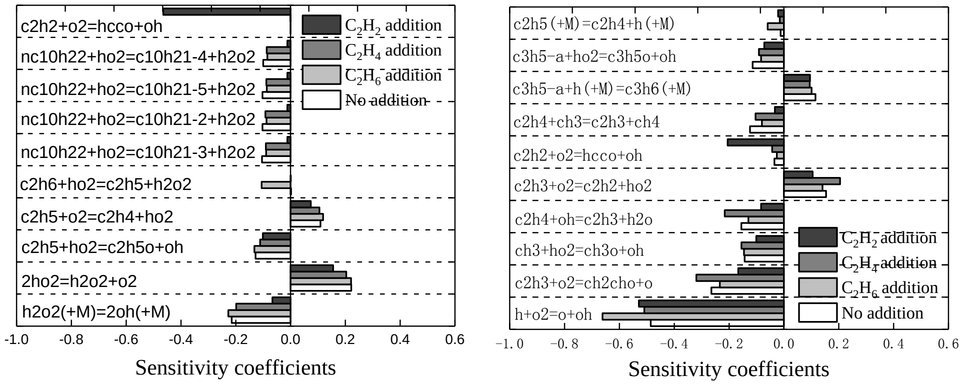
To identification of the dominant reactions after adding C_2H_6, C_2H_4 and C_2H_2 on ignition at different initial temperature, a brute force sensitivity analysis [24] is considered with definition of the sensitivity coefficient as:

$$S_i = \frac{\tau(2k_i) - \tau(0.5k_i)}{2k_i - 0.5k_i} \cdot \frac{k_i}{\tau(k_i)} = \frac{\tau(2k_i) - \tau(0.5k_i)}{1.5\tau(k_i)} \tag{3}$$

where k_i is the rate coefficient of reaction, $\tau(k_i)$ is the relative ignition delay to k_i. The positive sensitivity indicates the effect of increasing the ignition delay when increasing the corresponding reaction rate coefficient, while the negative sensitivity means the inverse impact.

The sensitivity coefficients for n-decane/air mixtures with C_2H_6, C_2H_4 and C_2H_2 additions are shown in Fig. 5 at Φ_F=1.5, P=20 atm and R=1.0 with two initial temperatures of 1000 K and 1500 K. For T_0=1000 K, H_2O_2(+M)=2OH(+M) is shown to be the most sensitive reaction to enhance ignition. The addition of C_2H_2 enhances $C_2H_2+O_2$=HCCO+OH greatly, which has a promoting effect on ignition. Therefore, the ignition delay time is reducd with C_2H_2 addition.

For T_0=1500 K, H+O_2=O+OH is the most sensitive for enhancing ignition. The addition of C_2H_6 promotes C_2H_5(+M)=C_2H_4+H(+M) to increase the production of H atom, which further promotes H+O_2=O+OH. The addition of C_2H_4 promotes C_2H_4+OH=$C_2H_3+H_2O$, which further promotes $C_2H_3+O_2$=CH_2CHO+O. These two reactions promote auto-ignition with C_2H_4 addition and C_2H_4 addition leads to the ignition delay enhancement. The addition of C_2H_2 promotes $C_2H_2+O_2$=HCCO+OH which is same with that at T_0=1000 K, and promotes ignition of the mixtures.



(a) T_0=1000 K

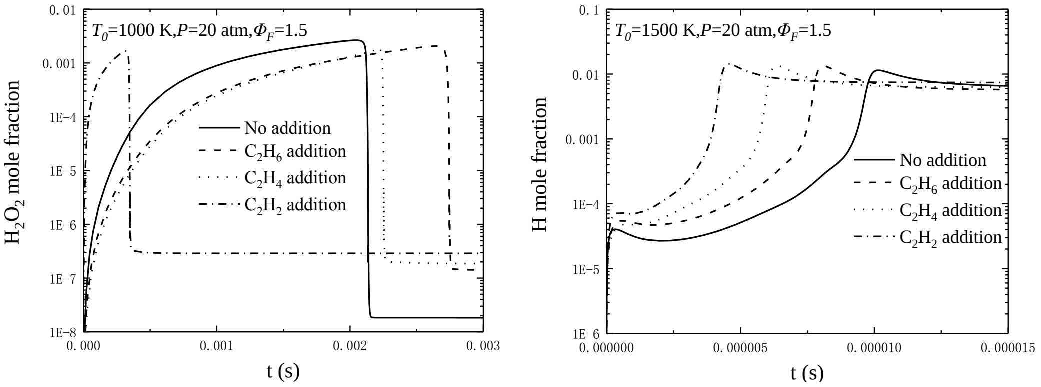
(b) T_0=1500 K

Fig. 5. Ignition delays of systems with addition of C_2H_6, C_2H_4 and C_2H_2 at Φ_F=1.5, P=20 atm and (a) T_0=1000K / (b) T_0=1500K in different addition ratios.

It can be found from above results the most sensitive process for ignition is shown as H_2O_2(+M)=2OH(+M) at T_0<1150 K and H+O_2=O+OH at T_0>1150 K. Therefore, the mole fractions of H_2O_2 and H atom are important for ignition for the conditions of T_0<1150 K and T_0>1150 K, respectively. Fig. 6 shows the mole fraction of H_2O_2 for T_0=1000 K and H atom for T_0=1500 K during ignition period at P=20 atm and Φ_F=1.5.

At T_0=1000 K, the mole fraction of H_2O_2 increases and decreases sharply when the mixtures are ignited. This reveals that at T_0=1000 K, H_2O_2 is accumulated until a certain value where H_2O_2 decomposes rapidly through H_2O_2(+M)=2OH(+M) to led to ignition. The addition of C_2H_2 accelerates the accumulation of H_2O_2, while the addition of C_2H_6 and C_2H_4 decelerates the accumulation of H_2O_2. Therefore, the addition of C_2H_2 (T_0=1000 K) decreases the ignition delay, while the addition of C_2H_6 increases the ignition delay.

At T_0=1500 K, each addition of C_2H_6, C_2H_4 and C_2H_2 accelerates the accumulation of H atom. H radical is accumulated to a certain value where the mixtures are ignited through H+O_2=O+OH. Therefore, each addition of C_2H_6, C_2H_4 and C_2H_2 decreases the ignition delay time at T_0=1500 K. In addition, the addition of C_2H_2 accelerates H radical the most and the addition of C_2H_6 accelerates H radical the least, which results in that the order of promoting ignition from intense to weak is C_2H_2, C_2H_4 and C_2H_6.



(a) H_2O_2 fraction (b) H fraction

Fig. 6. Fraction of (a) H_2O_2 for T_0=1000 K / (b) H atom for T_0=1500 K during ignition period at P=20 atm and Φ_F=1.5.

In general, when T_0<1150 K, the addition of C_2H_6 inhibits the ignition by decelerating the accumulation of H_2O_2, and the addition of C_2H_2 promotes the ignition by accelerates the accumulation of H_2O_2. When T_0>1150 K, each addition of C_2H_6, C_2H_4 and C_2H_2 promotes the ignition by accelerating the accumulation of H atom. In addition, addition of C_2H_4 promotes $C_2H_4+OH=C_2H_3+H_2O$ and $C_2H_3+O_2=CH_2CHO+O$, and the addition of C_2H_2 promotes $C_2H_2+O_2=HCCO+OH$. These threes reactions all have effects of promoting au-ignition.

3.2 Ignition delays with addition of C_2H_6, C_2H_4 and C_2H_2 under varied equivalence ratio

Ignition delay times varied with Φ_F is shown in Fig. 7. Only conditions of $\Phi_F \geq 1.1$ are considered herein because the present study focus on the fuel-rich combustion. It means that ignition delay time changes linearly with equivalence ratio at fuel-rich condition. This indicates that ignition becomes difficult in fuel-rich condition. The slopes with different added species differ from each other. The slopes of conditions with addition of C_2H_6, C_2H_4 and C_2H_2 are all smaller than that without addition. This indicates that the addition of C_2H_6, C_2H_4 and C_2H_2 inhibits the availability of equivalence ratio on auto-ignition. The slope with addition of C_2H_4 is smaller than that with addition of C_2H_2, although the ignition delay time with adding C_2H_4 is larger than that with adding C_2H_2. In addition, the order of promoting auto-ignition from intense to weak is C_2H_2, C_2H_4 and C_2H_6 for all equivalence ratios studied.

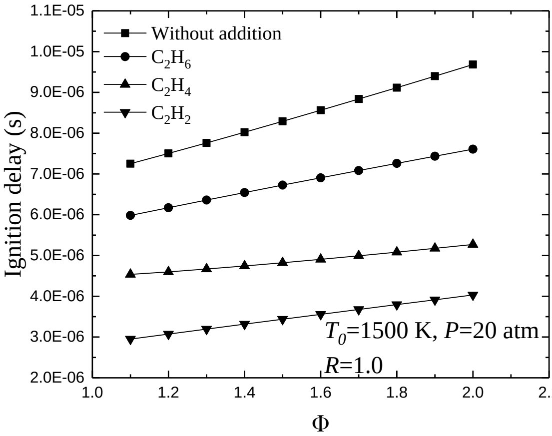
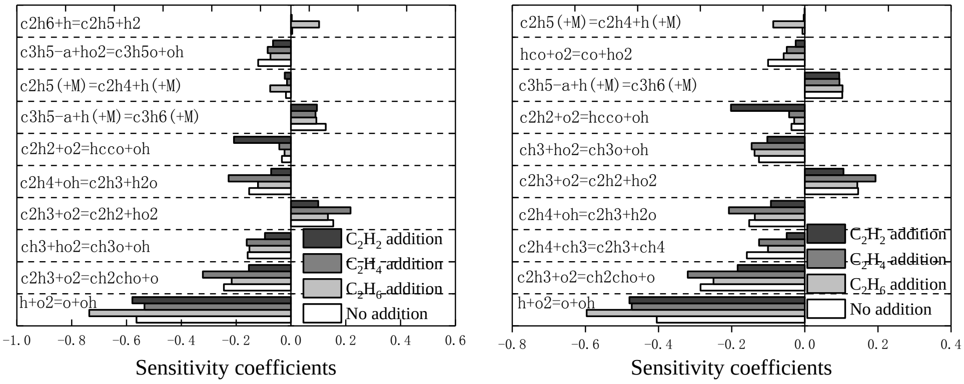


Fig. 7. Ignition delays of systems without addition and with addition of C_2H_6, C_2H_4 and C_2H_2 at T_0= 1500K, P=20 atm and R=1.0 in different equivalence ratios.

The sensitivity coefficients for *n*-decane/air mixtures with of C_2H_6, C_2H_4 and C_2H_2 additions is shown in Fig. 8 at T_0=1500 K, P=20 atm and R=1.0 with two equivalence ratios of 1.1 and 2.0. For Φ_F=1.1, the addition of C_2H_6 promotes the reaction of C_2H_6+H= C_2H_5+H_2 to increase C_2H_5 production. The increased C_2H_5 promotes the reaction of C_2H_5(+M)=C_2H_4+H(+M) to increase the production of H atom. The increased H atom promotes the reaction of H+O_2=O+OH. Therefore, the ignition delay is predicted to be decreased with addition of C_2H_6. C_2H_4 addition promotes the reaction of C_2H_4+OH=C_2H_3+H_2O which increases the production of C_2H_3. The production of C_2H_3 promotes the reactions of C_2H_3 +O_2=CH_2CHO+O and C_2H_3+O_2=C_2H_2+HO_2. The reactions of C_2H_4+OH=C_2H_3 +H_2O and C_2H_3+O_2=CH_2CHO+O promote auto-ignition with addition of C_2H_4. The addition of C_2H_2 promotes the ignition through the reaction of C_2H_2+O_2=HCCO+OH.

For Φ_F=2.0, the effect mechanism of addition of C_2H_6, C_2H_4 and C_2H_2 on ignition delay is similar with that at Φ_F=1.1. The addition of C_2H_6 promotes the ignition via the reactions of H+O_2=O+OH and C_2H_5(+M)=C_2H_4+H(+M). The addition of C_2H_4 promotes the ignition via the reactions of C_2H_4+OH=C_2H_3+H_2O and C_2H_3+O_2=CH_2CHO+O. C_2H_2 addition promotes the ignition through the reaction of C_2H_2+O_2=HCCO+OH.

In general, for fuel-rich condition, the addition of C_2H_6 promotes the ignition by promoting H+O_2=O+OH and C_2H_5(+M)=C_2H_4+H(+M). C_2H_4 addition promotes the ignition by promoting C_2H_4+OH=C_2H_3+H_2O and C_2H_3 +O_2=CH_2CHO+O. The addition of C_2H_2 promotes the ignition by promoting C_2H_2+O_2=HCCO+OH.



(a) Φ_F=1.1 (b) Φ_F=2.0

Fig. 8. Sensitivity coefficients of systems without addition and with addition of C_2H_6, C_2H_4 and C_2H_2 at T_0=1500 K, P=20 atm, R=1.0 and (a) Φ_F= 1.1 and (b) Φ_F= 2.0.

3.3 Ignition delays with addition of C_2H_6, C_2H_4 and C_2H_2 under varied pressure

Ignition delay times variation with the pressure were shown in Fig. 9. As predicted from Fig. 8, ignition delays increase with decreasing the pressure for all conditions. This reveals that ignition is easier than that at high pressure. The variation trends of ignition delay time with pressure without addition and with addition of C_2H_6, C_2H_4 and C_2H_2 are similar. The variation trend is steep when P<10 atm and is near flat when P>20 atm. The order of promoting auto-ignition from intense to weak is C_2H_2, C_2H_4 and C_2H_6 for all pressures studied. However, the diversity of the ignition delay time with different added species is very large at normal pressure, and decreases with the increase of pressure.

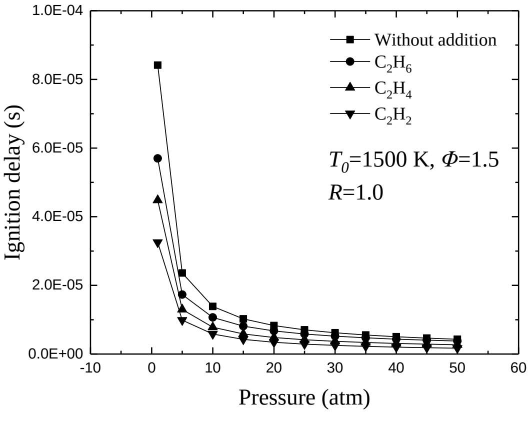
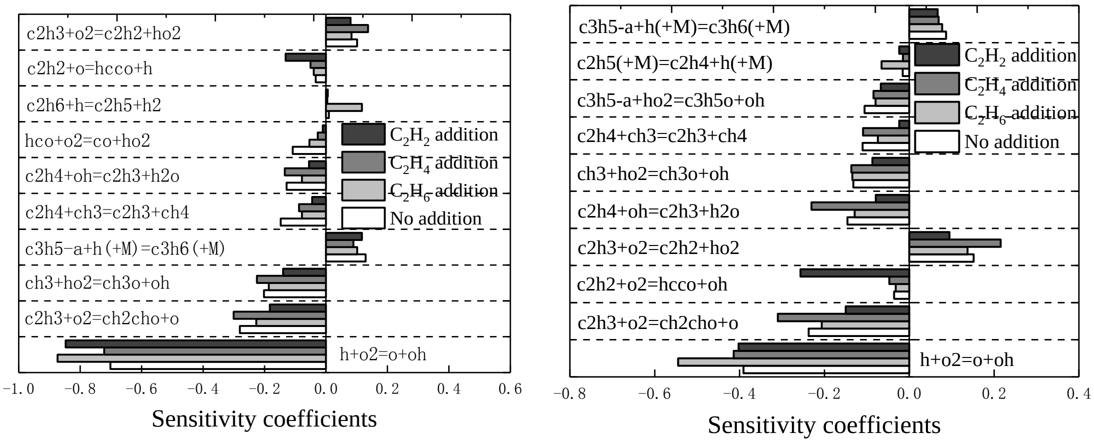


Fig. 9. Ignition delays of systems without addition and with addition of C_2H_6, C_2H_4 and C_2H_2 at T_0=1500K, Φ_F= 1.5 and R=1.0 as a function of pressure.

Fig. 10 shows the sensitivity coefficients for n-decane/air mixtures with the addition of C_2H_6, C_2H_4 and C_2H_2 at T_0=1500 K, Φ_F=1.5 and R=1.0 with two pressures of 1 atm and 50 atm. For P=1 atm, the addition of C_2H_6 promotes the reaction of C_2H_6+H=C_2H_5+H_2, which promotes the reaction of C_2H_5(+M)=C_2H_4+H(+M). The increased H atom promotes the reaction of H+O_2=O+OH. As a result, the ignition is increased with addition of C_2H_6. The addition of C_2H_4 promotes the reaction of C_2H_4+OH=C_2H_3+H_2O and C_2H_3 +O_2=CH_2CHO+O, and reduces ignition delay time eventually. C_2H_2 addition promotes the reaction of C_2H_2+O=HCCO+H. For P=50 atm, the addition of C_2H_6 promotes the ignition through the reactions of C_2H_5(+M)=C_2H_4+H(+M) and H+O_2=O+OH. The addition of C_2H_4 promotes the ignition through the reaction of C_2H_4+OH=C_2H_3+H_2O and C_2H_3+O_2=CH_2CHO+O. The addition of C_2H_2 promotes the ignition through the reaction of C_2H_2+O_2=HCCO+OH.

In general, for all pressure conditions calculated, the addition of C_2H_6 promotes the ignition by promoting H+O_2=O+OH. The addition of C_2H_4 promotes the ignition by promoting C_2H_4+OH=C_2H_3+H_2O and C_2H_3+O_2=CH_2CHO+O. The addition of C_2H_2 promotes the ignition by promoting C_2H_2+O_2=HCCO+OH.



(a) P=1 atm (b) P=50 atm

Fig. 10. Ignition delays of systems without addition and with addition of C_2H_6, C_2H_4 and C_2H_2 at T_0=1500K, Φ_F=1.5 and R=1.0 as a function of pressure.

3.4 Comparison with other additions of fuel-rich n-decane/air mixtures

H_2 [17] and H_2O_2 [18] and α-methylnaphthalene [25] additions of n-decane/air mixtures were reported to shorten the ignition delay times. Our results show a similar tendency to the previous investigations (H_2, H_2O_2 and α-methylnaphthalene additions [17,18,25]) of ignition delay time varying with equivalence ratio and addition ratio. Compared with H_2, H_2O_2 and α-methylnaphthalene additions, C_2H_2 addition shows more efficient under low pressure. C_2H_6 (3.2×10^{-3}s, 1000K, 10 atm), C_2H_4 (2.5×10^{-3}s, 1000K, 10 atm) and C_2H_2 (6.1×10^{-4}s, 1000K, 10 atm) additions have less ignition delays than reported α-methylnaphthalene additions [25] (4.0×10^{-3}s, 1000K, 10atm) of n-decane/air mixtures. C_2H_6 (6.0×10^{-6}s, 1500K; 9.5×10^{-6}s, 1400K, Φ_F =1.1, R=1.0) and C_2H_4 (5.5×10^{-6}s, 1500K; 8.3×10^{-6}s, 1400K, Φ_F=1.1, R=1.0) have more ignition delays than H_2 (7.5×10^{-6}, 1400K) [17] at 20 atm, whereas C_2H_2 (3.0×10^{-6}s, 1500K; 4.5×10^{-6}s, 1400K, Φ_F=1.1, R=1.0) is more sufficient addition than H_2 on ignition of fuel-rich n-decane/air mixtures. Gribi et al. [20] found that H_2O_2 addition was highly efficient on combustion ignition delay times. Our studies show that C_2H_2 has the similar ignition delays, but C_2H_2 seems to be more economical and safer. The C_2H_2 addition is still active under low pressure conditions with about 3×10^{-5} s at 1 atm and less than 1.0×10^{-5}s at 5 atm, 1500K. Therefore, our numerical studies on ignition delay recommend the C_2H_2 as a potential addition of fuel-rich n-decane/air flame, especially at low-pressure high altitude regions.

4. Conclusion

In this study, the effects of adding ethane, ethylene and acetylene on ignition of fuel-rich n-decane/air mixtures are studied numerically and compared by the closed homogeneous reactor model with a detailed chemical kinetic mechanism. Ignition delays with addition of ethane, ethylene and acetylene under varied temperature, equivalence ratio and pressure are calculated and compared. Some conclusions are listed as follows:

(1) C_2H_6 addition inhibits ignition when T_0<1150 K and promotes ignition when T_0>1150 K. C_2H_4 addition affects little the ignition at T_0=1000 K, and promotes ignition when T_0>1000 K. The addition of C_2H_2 decreases the ignition delays effectively at all temperatures studied. The order of promoting ignition from intense to weak is C_2H_2, C_2H_4 and C_2H_6.

(2) For T_0<1150 K, the addition of C_2H_6 inhibits the ignition by decelerating the accumulation of H_2O_2, and the addition of C_2H_2 promotes the ignition by accelerates the accumulation of H_2O_2. For T_0>1150 K, each addition of C_2H_6, C_2H_4 and C_2H_2 accelerates the accumulation of H atom, which promotes ignition through enhancing $H+O_2=O+OH$. In addition, the added C_2H_4 promotes $C_2H_4+OH= C_2H_3+H_2O$ and $C_2H_3+O_2=CH_2CHO+O$, and the added C_2H_2 promotes $C_2H_2+O_2= HCCO+OH$.

(3) The equivalence ratio and pressure do not affect the order of C_2H_6, C_2H_4 and C_2H_2 in promoting ignition of n-decane/air mixtures.

Finally, the results would have a directed guidance to the ignition of real jet at high altitude regions. The hydrocarbon C_2H_2 has the potential to be designed as the initiator for motor vehicles and civil aviation. The combustion simulations on small hydrocarbon/mixture also have great significance in the safe production of oil industry.

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