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THE EFFECT OF ADDING WATER ELECTROLYSIS PRODUCTS ON STABILITY OF THE FUEL-LEAN COMBUSTION IN N-DECANE/AIR FLAMES: A NUMERICAL STUDY

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Lean combustion takes the advantage of low NO emission levels, but it faces flame instability. Clean combustion with both low NO emissions and stable flames can be achieved by adding electrolysis products of water to n-decane combustion in the air. The addition of water electrolysis products extends the extinction limit by enhancing the $OH+H_2=H+H_2O$ *reaction and* $H+O_2=O+OH$ *reaction. In the mean time, the indices of NO emission increased by the ratio of water electrolysis products via the pathway of* $N+NO=N_2+O$ *reaction and* $N+OH=NO+H$ *reaction. Clean combustion with super-stability flame can be achieved by adding a proper amount of water electrolysis products (equivalence ratio* $\Phi=0.5$ *and addition ratio of water electrolysis products* $R_{WEP}=0.3$*) to decrease the extinction residence time at the fuel-lean condition with a suitable NO emission index. Our numerical study shown the clean combustion of n-decane fuel and our research will be of great significance to diminution of carbon oxides in atmosphere globally.*

Keywords: NO emission; flame stability; water electrolysis products; clean combustion; n-decane/air flames

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1. Introduction

NO_x emission caused by the combustion of fossil fuel is drastically harmful to human health and the natural environment [1]. It is inevitable to study the clean combustion technologies with enhanced environmental protection awareness [2-4]. Fuel-lean combustion, recognized as a practical, clean combustion technology in the engine of diesel truck/motor vehicle/aircraft, has been widely used to decrease the NO_x emission by reducing the temperature of flame [5]. However, combustion at fuel-lean conditions faces the problem of flame instability, such as excessive noise, flashback, and lean blowoff [6]. Therefore, it is necessary to stabilize the poor combustion achieving clean combustion. To enhance the effectiveness of fuel-lean burst, there are two possible ways: one is the additive of H_2 to stabilize the flame, the other is the additive of O_2 to improve the burning intensity.

The additive of H_2 was reported to promote the stability in hydrocarbon/air flame [7-9]. Wang et al. found the combustion rate of synthetic gas was enhanced with the increased ratio of H_2 and CO [7]. Dong et al. claimed that the laminar H_2/CO/CH_4/air flame velocity increased with the growth of the H_2 fraction [8]. Frenillot et al. proved the stability and emissions of kerosene/air flame stabilized combustion at leaner conditions by adding H_2 gas [9]. O_2 concentration was also an essential combustion characteristic on the combustion of fossil fuel [10-12]. Yi et al. found that the burning intensity enhanced with the O_2 fraction in coal flame [10]. Bowen et al. investigated the laminar flame speed of ammonia in the high burning rate in the condition of oxygen-rich condition [11]. Wu et al. stressed that the large fraction of O_2 caused high heating speed and low fuel consumption in natural gas flame [12]. Besides the H_2/O_2 addition, other technologies for the clean combustion were reviewed by Duan, et al. very recently [4].

Some technical issues prevented the industrial application of H_2 and O_2 mixture addition to fossil fuel on the lean combustion, as the high production cost and secure store of H_2 [2] and high NO emission under the oxygen-rich burning. Adding the water electrolysis production seemed to solve these technical issues, as H_2/O_2 production by the water electrolysis was reproducible and controllable [13]. The combustion can be stabilized by adding water electrolysis products in gaseous hydrocarbon/air flame [14]. In this paper, we extended this application to long-chain hydrocarbon fuels. We investigated the coupling effects of adding water electrolysis products on flame extinction and NO emission in a numerical way. The n-decane was considered here as a representative liquid hydrocarbon fuel, as n-decane was the essential ingredient of jet fuel and the primary production in the oil industry.

2. Methods

2.1 Numerical model

The perfectly stirred reactor (PSR) model is applied in this work. The PSR model can be characterized by inlet temperature, residence time, reactor volume, pressure, flow rate, mass fraction, and heat loss. The equations for mass balance and energy balance of PSR model are listed as below:

$$\dot{m}(Y_k - Y_k^*) - \dot{\omega}_k W_k V = 0, \text{ k=1, …, K} \tag{1}$$

$$\dot{m}\sum_{k=1}^{K}(Y_k h_k - Y_k^* h_k^*) + \dot{Q} = 0 \tag{2}$$

Here ṁ represents the mass flow rate, Y represents mass concentration, $\dot{Q}$ represents the generating rate in mole, V represents the PSR volume, h is the specific enthalpy, and denotes the thermogenesis. Wk is the molecular weight and $\dot{\omega}_k$is the molar rate of production. Superscript of * and subscript of k represent inlet stream and the kth species. The residence time can be calculated as equation (3):

$$\tau = \frac{\rho V}{\dot{m}} \tag{3}$$

2.2 Chemical kinetic model

The chemical kinetic model developed by Naik et al. [15,16] is used in the calculations of this study. The sub-mechanism of H_2 and O_2 uses the combustion mechanism by O'Conaire et al. [17]. The process of NO_x is obtained from the mechanism of GRI-Mech 3.0 [18].

2.3 Addition of water electrolysis products

Considering that two moles of H_2O produced two moles of H_2 and one mole of O_2 through $2H_2O \rightarrow 2H_2 + O_2$, the addition of water electrolysis products can be replaced by adding the mixtures of 0.667 H_2 and 0.333 O_2 by volume. Considering the mass of adding water electrolysis products was limited to a small quantity. The addition ratio of water electrolysis products R_{WEP} is the ratio of addition H_2 and O_2 to n-decane and O_2 in air as shown in Eq. (4):

$$R_{WEP} = \frac{C_{H_2} + C_{O_2}^1}{C_{BF} + C_{O_2}^2} \tag{4}$$

where C_{BF} is the mole percents of n-decane, $C_{O_2}^2$ is the mole percents of O_2 in air, C_{H_2} and $C_{O_2}^1$ are the mole percents of added H_2 and O_2 in the mixtures.

Here the equivalence ratio (Φ) and the addition ratio of water electrolysis products (R_{WEP}) are set in the range of 0.6-1.4 and 0-0.5, respectively. The extinction residence time (t_{ext}) and NO emission index are calculated under different conditions. Moreover, the dominant reactions for extinction, and NO production with the addition of water electrolysis products are recognized by the sensitivity analysis.

2.4 Sensitivity analysis model

Huang et al. [19] proposed the normalized sensitivity coefficient to evaluate the important reaction shown as below:

$$S_{k_i} = \frac{\tau(2k_i) - \tau(0.5k_i)}{1.5\tau(k_i)} \tag{5}$$

Where S_{k_i} is the normalized sensitivity coefficient on ignition delay time. The negative value of S_{k_i} shows the increment the reaction rate constant of the corresponding reaction results in a shorter ignition delay time. k_i is defined as the reaction rate constant of the ith reaction, $\tau(2k_i)$, $\tau(0.5k_i)$ and $\tau(k_i)$ are defined as the ignition delay times in the condition of the double k_i, half k_i and k_i. We used the method of Huang et al. [19] for the extinction residence time, and is calculated based on the equation:

$$SE_{k_i} = \frac{t_{ext}(2k_i) - t_{ext}(0.5k_i)}{1.5t_{ext}(k_i)} \tag{6}$$

Where SE_{k_i} is the normalized sensitivity coefficient on extinction residence time and the negative value of SE_{k_i} indicates a shorter extinction residence time change of the rate constant of the corresponding reaction. $t_{ext}(2k_i)$, $t_{ext}(0.5k_i)$ and $t_{ext}(k_i)$ are the extinction residence time calculated using the double k_i, half k_i and k_i. Hence, this reaction has an enhancing effect on the reduction of extinction residence time. The positive value indicates a longer extinction residence time with increasing the reaction rate constant, and the reaction has an effect of increasing the extinction residence time.

$$S_{k_{i,j}} = \frac{\partial(\ln X_{NO})}{\partial(\ln k_j)} \tag{7}$$

where $S_{k_{i,j}}$ is the sensitivity coefficient for NO. X_{NO} is the mole percents of NO and k_j is the rate coefficient of the reaction j. The sensitivity coefficient can be used to conducted to identify the dominant chemical reactions for the effect of NO production with the addition of water electrolysis products. [20,21].

3. Results and Discussion

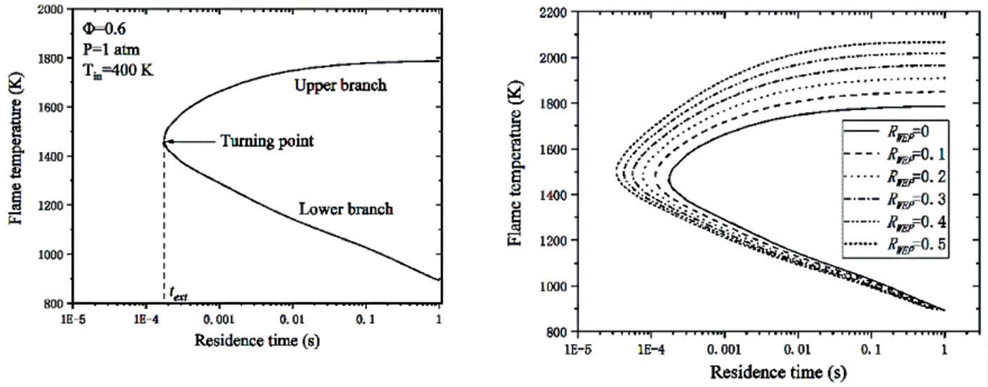
3.1 The validity of this simulation by comparison with the previous study

The mechanism calculated by the chemical kinetic model has been proved to be validated against previous series of experimental data and numerical results [15,16,22-28]. The simulated values agree well with experimental data, which is shown in detail in the work of Naik et al. [15,16]. The calculated chemical reaction mechanism with the chemical kinetic model including 597 species and 3854 reactions was demonstrated in coordinated with the primary experimental data by Hui et al. [23].

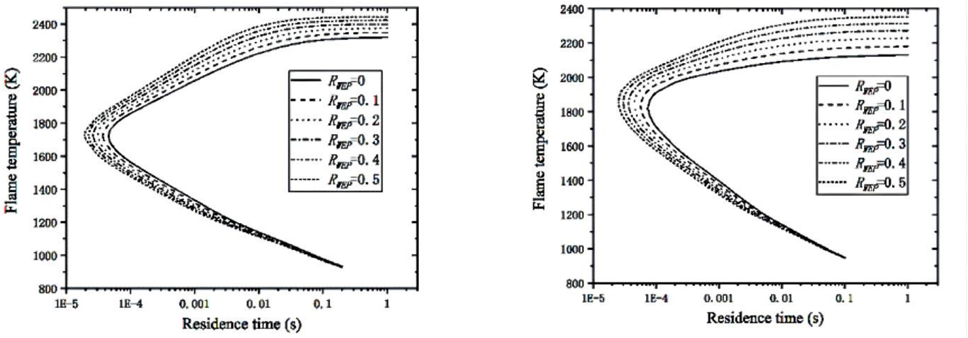
PSR approach can provide reasonable results for the NO emission modeling in the n-decane/air flame. PSR model in the work of Fichet et al. [22] was proved to be a reliable model for simulating combustion in the gas turbines. The NO_x production in the CH_4 flame was simulated in the PSR model by Hwang et al.[24] The influence of H_2 addition and water vapor addition on the n-decane combustion were also investigated by Hui et al. [23] using the PSR model respectively. We have used the chemical kinetic model to explore the combustion of fuel-rich n-decane/air flame [26].

3.2 Effects of additional water electrolysis products on extinction limit

In the PSR model, the extinction occurred when the mixtures' residence time was so short that the mixtures cannot react [16]. Fig. 1a showed the “C” shape residence time curve varying from flame temperatures.



(a) **(b) Φ=0.6**



(c) Φ=1.0 **(d) Φ=1.4**

Fig. 1. (a) PSR response curve of n-decane/air mixture at the equivalence ratio Φ of 0.6, the pressure of 1 atm, and an inlet temperature T of 400 K. (b) Flame temperature of n-decane/air mixtures with R_{WEP}=0-0.5, T=400 K, P=1atm and Φ=0.6.Similar curves for Φ=1.0 (c) and Φ=1.4 (d).

The flame temperature decreased in upper curves and increased in lower curves as reducing the time. The value of t_{ext} was select at the turning point between lower and upper curves. The addition of water electrolysis products enhanced the burning intensity and decreased the extinction residence time. Fig. 1b,c,d showed a variation of flame temperature with text at the $\Phi=0.6$, $\Phi=1.0$ and $\Phi=1.4$. The more addition ratio of water electrolysis products R_{WEP}, the higher flame temperature in upper curves. It reflected that the overall burning intensity would be enhanced as the growing addition ratio of water electrolysis products R_{WEP}. The enhanced burning rate led to a shorter extinction residence time. The reduction of extinction residence time was more practical prominent at the fuel-lean condition than that at the stoichiometric condition.

The fuel-lean mixture had the most prominent reduction in extinction residence time with water electrolysis products. Fig. 2 showed a variation of extinction residence time with the addition ratio of water electrolysis products at equivalence ratios of 0.6, 1.0 and 1.4. It can be found that for all equivalence ratio conditions, the extinction residence time decreased with the increasing R_{WEP}. The residence time of fuel-lean mixtures was significantly longer than that of fuel-rich mixtures at $R_{WEP}=0$. The residence time of fuel-lean mixtures was similar with that of fuel-rich and stoichiometric mixtures at $R_{WEP}=0.5$. Therefore, the addition of water electrolysis products can significantly extend the extinction limit of fuel-lean varieties, realizing the combustion to low NO emissions and improved stability.

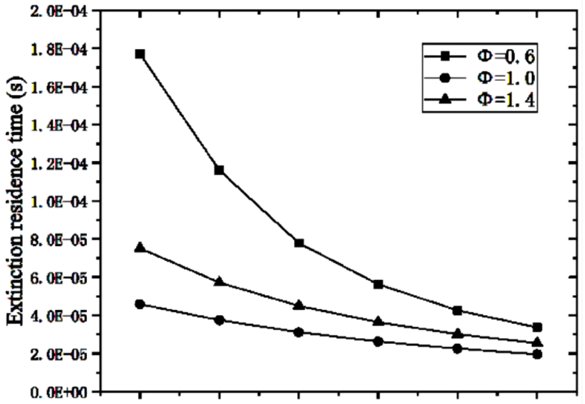


Fig. 2. The value of t_{ext} with various R_{WEP} at $\Phi=0.6$, 1.0 and 1.4, T=400 K and P=1 atm.

The addition of water electrolysis products enhanced $H+O_2=O+OH$ reaction as well as $OH+H_2=H+H_2O$ reaction. Fig. 3 showed the normalized sensitivity coefficients for the extinction residence times. The significance of the reaction $H+O_2=O+OH$ enlarged much after the water electrolysis products addition, as the result of increased concentrations of H radical and O_2. The sensitivity of the reaction $OH+H_2=H+H_2O$ also raised for the concentration increment of H_2. H_2 was consumed, and H radical was produced in this pathway. The formation of H radicals promoted the reaction of $H+O_2=O+OH$, and hence reduced the extinction residence time. O radical was also produced in the reaction $H+O_2=O+OH$, which enhanced the reaction $C_2H_4+O=CH_3+HCO$. Moreover, the addition of H_2 inhibited the reaction $HCO+H=CO+H_2$, which had a positive sensitivity coefficient. The concentrations of H radicals and O_2 were necessary for the extinction limit. The addition of water electrolysis products inhibited the extinction by increasing the concentration of H radicals and O_2.

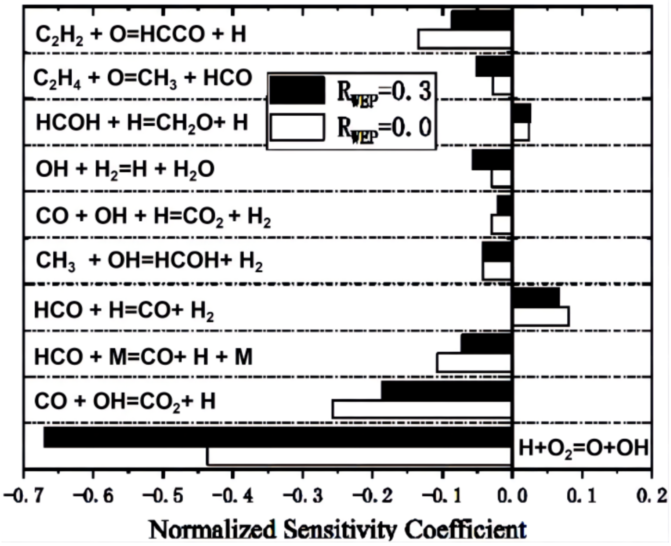


Fig. 3. The sensitivity coefficients (normalized) for extinction residence times in various chemical reactions of which R_{WEP}=0 and 0.3 at Φ=1.0, T=400 K and P=1 atm.

3.3 Influence of water electrolysis products

Fig. 4 shows a series of NO emission indices with different equivalence ratios in the adding of water electrolysis products. More extensive the NO emission index, the more NO emission. The NO emission index started to enhance to its maximum at an equivalence ratio of 1.0 and then fell down at fuel-rich conditions as increasing the equivalence ratio. A similar trend of the NO emission index against equivalence ratio can be found when adding water electrolysis products. As R_{WEP} risen from 0 to 0.5, the NO emission indices increased notably for all equivalence ratio conditions. This increment was potentially caused by the enhancement of flame temperature, as can be seen in Fig. 1.

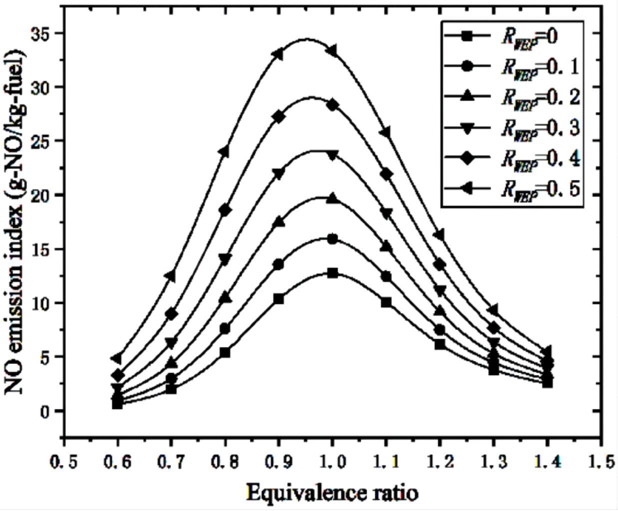
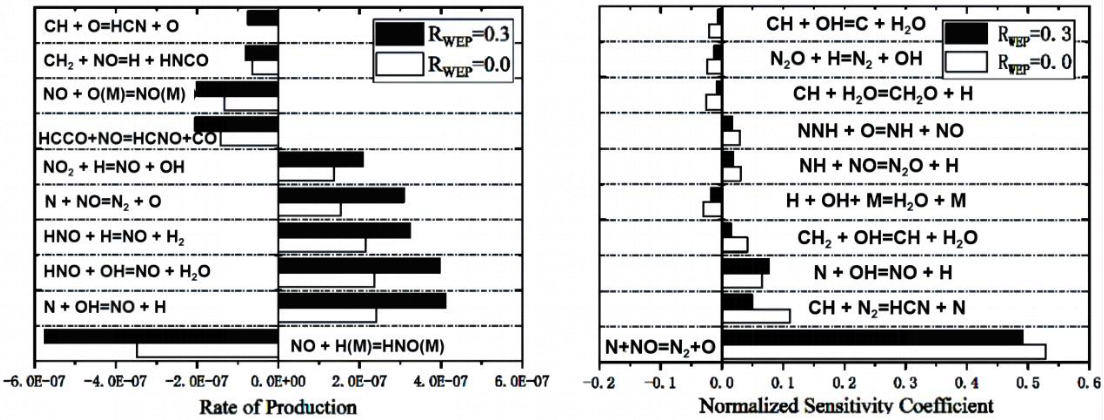


Fig. 4. NO emission index against equivalence ratio at R_{WEP}=0-0.5, t_{ext}=10 ms, T=400 K and P=1 atm.

The proper amount of water electrolysis products can decrease the extinction residence time at fuel-lean conditions, with a relatively low NO emission index. As the mixture diverged from the stoichiometric state, the increasing amount of NO emission index decreased. The NO emission index at Φ=1.0 without the water electrolysis products was more significant than that at Φ=0.6 and R_{WEP}=0.5. The index of NO emission grew less at an equivalence ratio of 0.6 as R_{WEP} increases from 0 to 0.5 compared to that from 0.6 to 1.0. This indicated that the relevance of the NO emission index on the equivalence ratio was more substantial than that on the addition ratio of water electrolysis products. Moreover, the value of t_{ext} decreased sharply at the equivalence ratio of 0.6, which can be seen in Fig. 2. Therefore, the addition of water electrolysis products in fuel-lean mixtures may have the potential of enhancing flame stability significantly without increasing too much NO production.

The addition of water electrolysis products enhanced NO production. Fig. 5 shows NO production rate and normalized sensitivity coefficients for NO production with R_{WEP}=0 and 0.3. The equations in the positive side of production rate in Fig. 5 represented the reactions of NO formation and the negative side showed the NO reduction. The order of magnitude meant the importance of chemical reaction in the formation and degradation of NO. NO was produced mainly through conversions from N radicals (N+OH=NO+H), HNO (HNO+OH=NO+H_2O and HNO+H=NO+H_2), N_2 (N_2 +O=N+NO), and NO_2 (NO_2 +H=NO+OH). However, the chemical conversions of HNO and NO_2 were balanced by conversions from NO to HNO (NO+H+M=HNO+M), and from NO to NO_2 (NO+O(+M)=NO_2 (+M)). Therefore, the reactions of N+OH=NO+H and N+NO=N_2+O were prevalent for NO output. Sensitivity analysis results also showed that these two reactions were dominant for NO production. Moreover, $CH+N_2=HCN+N$ with the production of N radicals was also dominant for NO production. $H+OH+M=H_2O+M$ was the most sensitive reaction for NO destruction because it competed with $N+OH=NO+H$, $HNO+OH=NO+H_2O$ for OH radicals and $HNO+H=NO+H_2$, $NO_2+H=NO+OH$ for H radicals. The reactions $N+OH=NO+H$, $HNO+OH=NO+H_2O$, $HNO+H=NO+H_2$, $N+NO=N_2+O$ and $NO_2+H=NO+OH$ were enhanced after adding the water electrolysis products. $N+NO=N_2+O$ was improved with the production of NO and N radicals because of the increasing concentration of O radicals. The N radicals produced by $N_2+O=N+NO$ promoted the reaction $N+OH=NO+H$, and hence increased the concentration of NO. The growing concentration of NO promoted the conversions of NO to HNO and NO_2. $HNO+OH=NO+H_2O$, $HNO+H=NO+H_2$ and $NO_2+H=NO+OH$ were then enhanced. However, the transformations of HNO and NO_2 to NO were still balanced with the conversions of NO to HNO and NO_2. We can conclude that NO production could be enhanced with the water electrolysis products addition.



(a) Rate of production for NO (b) Normalized sensitivity coefficient for NO

Fig. 5. Rate of production (a) and normalized sensitivity coefficients (b) for NO production of n-decane/air mixtures with $R_{WEP}=0$ and 0.3 at $\Phi=1.0$, $t_{ext}=10$ ms, T=400 K and P=1 atm.

3.4 Advantage of adding water electrolysis products in the combustion

The proper additive of water electrolysis products at the equivalence ratio of 0.5 and $R_{WEP}=0.3$ would have relative low NO emission. Adding water electrolysis products in n-decane/air flames can reduce the extinction residence time with the drawback of increasing the NO production. In Fig. 6, for both R_{WEP} of 0.0 and 0.3, extinction residence time decreased, and NO emission indexes increased with increasing Φ from 0.3 to 1.0. The condition at equivalence ratio of 0.6 with addition of water electrolysis products had a similar extinction residence time but much lower NO emission index to the condition at $\Phi=1.0$ without addition of water electrolysis products. A similar phenomenon can be found when comparing the condition at Φ=0.8 by adding water electrolysis products with that at Φ=0.5 without water electrolysis products. Therefore, it was possible to achieve lean combustion with improved flame stability and low NO emission levels by adding a proper amount of water electrolysis products. Addition of water electrolysis products has the potential of overcoming the unstable problem of fuel-lean combustion while maintaining low NO emissions.

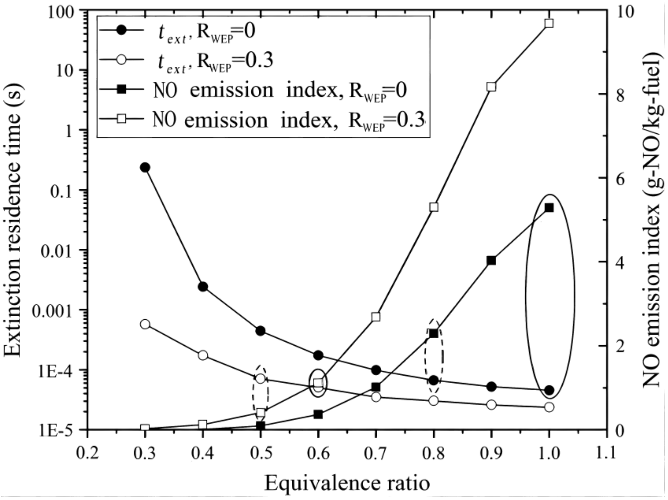


Fig. 6. Variation of t_{ext} and NO emission indices for n-decane/air mixtures with the equivalence ratio for R_{WEP}=0 and 0.3 at P=1 atm and T=400 K

6. Conclusions

The effects of adding water electrolysis products on NO emission and extinction limit of n-decane/air flames were numerically studied in the PSR model. The addition of water electrolysis products significantly decreased the extinction residence time via the reactions $H+O_2=O+OH$ and $OH+H_2=H+H_2O$ by raising the concentrations of H radicals and O_2. The addition ratio of water electrolysis products increased NO emissions via the pathways of $N+OH=NO+H$ and $N+NO=N_2+O$. Adding proper amount of water electrolysis products can decrease the extinction residence time at fuel-lean condition, without increasing too much NO emission index. Clean combustion with high stability can be realized by adding a proper amount of water electrolysis products (Φ=0.5 and R_{WEP}=0.3). Our numerical study would be of great significance to the clean combustion of hydrocarbons in industry and the efficient utilization of vehicle energy. At the same time, this research will be of great significance to the carbon oxides neutralization strategies of countries all over the world.

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