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The effect of chemical structure of dimethyl ether (DME) on NOx formation in nonpremixed counterflow flames †

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Abstract

To clarify the effect of chemical structure of Dimethyl ether(DME) on NOx formation in nonpremixed counterflow flame, DME flame was investigated numerically to compare the flame structures and NOx emissions with C_2H_6 and Mixed-fuel. Numerically, the governing equations were solved using the Oppdif code coupled with CHEMKIN package, and DME flames were calculated by Kaiser's mechanism, while the C_2H_6 flames and Mixed-fuel flames were calculated by the C_3 mechanism. These mechanisms were combined with the modified Miller-Bowman mechanism for the analysis of NOx. Numerical results of nonpremixed counterflow flames show that the EI_{NO} of DME nonpremixed flame is low as much as 50 % of the C_2H_6 nonpremixed flame. The cause of EI_{NO} reduction is attributed mainly to the characteristics of partial premixed flame due to the existence of oxygen atom in DME and partly to the O-C bond in DME, instead of C-C bond in hydrocarbon fuels.

Keywords: Dimethyl ether (DME); Nitrogen oxide (NOx); Nonpremixed flame

1. Introduction

Dimethyl ether(DME; CH_3-O-CH_3) has been regarded as one of the attractive alternative fuels to replace petroleum in respect of availability, economics, acceptability, environment and emissions. [1] In particular, DME is considered as the efficient alternative fuel for diesel engine. [2] This is not only because of its high cetane number for self-ignition and its almost instantaneous vaporization when injected into the cylinder, but also because of smoke-free combustion characteristics. [3, 4] Although some fundamental studies were reported in about burning velocities, spray and ignition characteristics, compression ignition delay of Dimethyl ether [5-7], most studies on NOx emissions of DME were concentrated on the engine application. Because successful utilization of DME in respect of clean combustion, many researches have been mainly focused on NOx emissions in a diesel engine. Comparative values of NOx emissions from DME and those from diesel fuel seem to vary depending on the engine operating conditions and the fuel supply system. Some papers reported that NOx emissions with DME fuelling was found to be higher or similar level than with diesel fuel in a compression ignition engine which was tested at the same operating conditions recommended for diesel fuelling. [8] On the other hand, some papers reported that, when operating conditions of engine was optimized for each fuel, NOx emissions from DME were lower than from diesel fuels. [9] These researches provided the very valuable information about the effects of operating conditions on NOx emissions in a practical engine system.

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However, it is difficult to understand definitely the intrinsic NOx formation characteristics of DME compared to those of hydrocarbon fuels, because the change of fuel type in engine can modify significantly the combustion environments affecting NOx formation such as combustion mode, flame temperature, and residence time. Therefore, the studies in about NOx emissions of DME are necessary. Some papers reported fundamental studies of NOx emissions of DME. Christopher [10] reported comparison of CO and NO emissions from propane, n-butane, and DME. This conclusion was NO production from DME was generally less than or similar to propane and n-butane over the same stoichiometric range. Chun [11] studied characteristics of combustion and NOx formation for nonpremixed DME flame. This research compared the CH_4 fuel as main component of natural gas and DME as an alternative fuel of utility combustor. However, these studies only focused CO or NO emissions and it is not confirmed about change of NOx characteristics by NOx creation factors which are independent. To better understand the intrinsic NOx formation characteristics of DME, fundamental studies employing simple flames are required prior to studies with complex engine systems.

Motivated by such consideration, this study presents experimental and numerical results concerning the NOx emission characteristics and clarifies the effect of chemical structure in NOx creation factors of DME nonpremixed counterflow flame.

Before the present research, it was presented that brief experimental study was conducted to identify the flame shapes and NOx emissions in co-axial jet flames. [12] Laminar co-axial jet flame was adopted to identify the flame shape and NOx emission of DME with comparing those of C_3H_8 and C_2H_6. The inner diameter of fuel and air nozzles was 8 mm and 50 mm, respectively. Fuel flow-rate was adjusted from 6.56 to 13.12 mg/s, and the ambient air flow was fixed by 30 slpm. To intercept an external flow and measure NOx concentration at the downstream region, a pyrex chimney having 1 m length was used. Details of combustor and measurement used can be found elsewhere. [13] Experimental results show that the flame length of DME becomes shorter compared with hydrocarbon fuels for the same flow rate. In addition, DME nonpremixed flame has two different characteristics from hydrocarbon fuels. One is that some portion of DME burn as like partial premixed flame. The other is the difference of O-C bond in DME instead of C-C bond in hydrocarbon fuels. However, in respect of chemical reaction, the role of the partial premixed flame and O-C atom in DME on NOx emission characteristics has not been found until now. Thus, to clarify the detailed difference of NOx emission characteristics between DME and hydrocarbon fuels, numerical simulations of counter nonpremixed flames with same flame thickness were carried out using detailed reaction mechanisms. First, to investigate the effect of burn as like partial premixed flame, the maximum flame temperature of C_2H_6 and C_2H_6-1/2O_2 mixed fuel(called to Mixed fuel; which has the equivalent C, H and O elements compared to DME) make the same value and compared. In this case, the initial temperature of C_2H_6 reactant is adjusted to 600 K and Mixed fuel reactant is 298 K, respectively. Second, to clarify the effect of O-C bond in DME, the maximum flame temperature of Mixed fuel and DME make the same value and compared. DME reactant is adjusted to 475 K and Mixed fuel reactant is 298 K too.

NOx emissions could be optimized in practical systems, where it is anticipated that the current fundamental results would enhance the understanding of the intrinsic NOx emission characteristics for DME nonpremixed flames. NOx emission include NO_2 and N_2O not only NO. However, it will be able to ignore N_2O, because N_2O was little created in hydrocarbon fuels and almost changed NO again and cause of NO_2 was almost produced NO reactions, NO_2 does not influence NO emissions too. [14] So in this study, mainly focus in NO production and reduction.

2. Numerical methods

To investigate numerically, the NOx emission characteristics of DME/air nonpremixed flames, the system of an axisymmetric, counterflow configuration was adopted as shown in Fig. 1. Using the boundary layer approximation in the axial direction, the conservation equations were solved using the Oppdif code [15] coupled with Chemkin-II [16] and Transport package. [17] Radiative heat loss was considered by using optically thin model. [18] Nozzle separation distance was 2 cm and the global strain rate was fixed by 100 s^{-1} to sustain stable flames for all fuels.

The DME and C_2H_6 oxidations were calculated by Kaiser's mechanism [19] and modified C_3 mechanism [20] respectively. And various NOx mechanism options were evaluated to determine which is to be

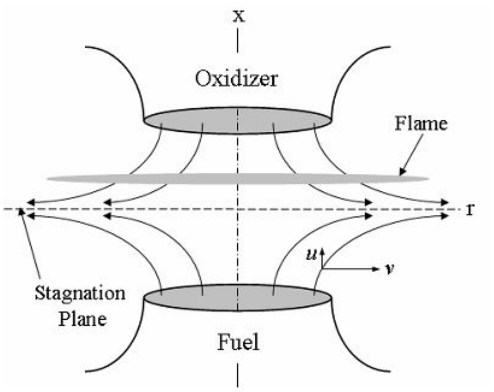


Fig. 1. Schematics of counter flow non premixed flame.

combined with the DME and the modified C_3 mechanism. These numerical results compared to experimental data obtained by Ravikrishna [21] and Lim [22] et al. so it was found that the modified Miller and Bowman mechanism ([23], called to MMB) was matched with experimental data better than others NOx mechanisms. Therefore, it was combined the MMB NOx mechanism with the oxidation mechanisms developed by modified C_3 mechanism for C_2H_6 and Kaiser's mechanism for DME. Then, these mechanisms were compared and verified with regard to the temperatures, major and minor species, and velocity profiles both with and without the NOx mechanism for C_2H_6 and DME nonpremixed flames established at a global strain rate = 100 s^{-1} in the previous research [12]. Therefore, the review of the reaction mechanisms in this study was omitted in this paper.

3. Results and discussion

Fig. 2 shows the comparisons with regard to the temperature, major species and velocity profile with MMB NOx mechanism for C_2H_6 and DME nonpremixed flames(T_R=298 K). It can be seen from the two figures that combination of MMB NOx mechanism into the C_3 and Kaiser mechanisms does not affect the simulation results on flow field, temperature and major chemical species. Even though the simulation results are not presented here, the combination of NOx mechanism also does not cause any difference in radical concentrations, such as CH and OH, which is closely related in NOx formation. These results indicate that NOx mechanism combined into two fuel oxidation mechanisms cause no effect on the flame structure except for NOx formation processes. In addition, it can be noted that two fuel flames are very similar in terms of flame structure except the following differences; that is, CO concentration in DME flame is much higher than that of C_2H_6, the maximum temperature of DME is high as much as 25 K, and the locations of stagnation plane and flame surface for DME move about 1 mm toward air side due to the momentum increase of DME in fuel side.

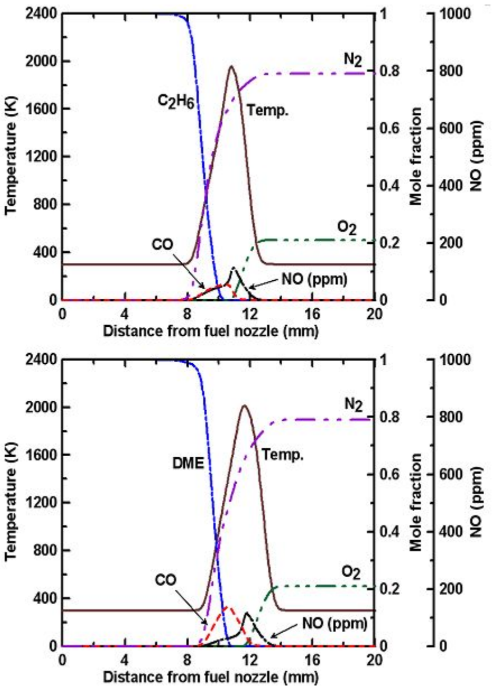


Fig. 2. Flame structures of C_2H_6 and DME (T_R=298 K).

Fig. 3 shows the NO profiles (lower part) and fuel production rate(upper part) of C_2H_6 and DME flames under the same condition of Fig. 3 The NO profiles of C_2H_6 and DME are similar and two fuels have nearly same maximum NO concentration near flame surface. However, the DME flame has lower NO concentration in the left side of the flame surface than the C_2H_6 flame does. From the comparison of fuel production rates, it is noted that DME consumption rate is much higher than that of C_2H_6 and DME oxidation process is starting at the upstream of stagnation plane. To compare quantitatively the NOx emission among fuels, the EI_{NO} of all flames calculated in this study are shown in Table 2. The EI_{NO} of C_2H_6 and DME flames is 0.5263 and 0.2463 g/kg of fuel, respectively. That is, the EI_{NO} of DME is low as much as 50% of the C_2H_6 fuel. The reduction of EI_{NO} in DME flame, in spite of similar profiles of NO concentration, can be understood by comparing the fuel consumption

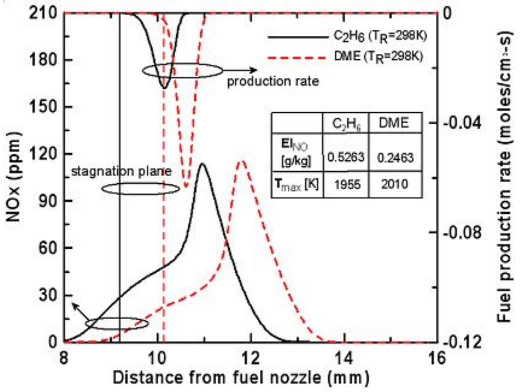


Fig. 3. Comparison of NOx profiles and fuel production rates for C_2H_6 and DME (T_R=298 K).

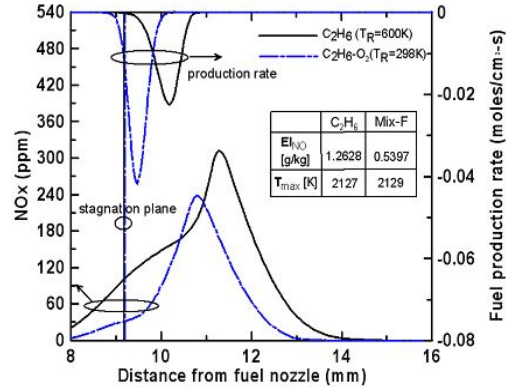


Fig. 4. Flame structures of C_2H_6 (T_R=600 K) and Mixed fuel (T_R=298 K).

rates. The cause of difference between two fuels will be discussed later.

As the DME has one oxygen atom in fuel itself, DME nonpremixed flames have two distinct characteristics from general hydrocarbon nonpremixed flames.

One is DME flame burns as like partial premixed flame with about 7 equivalence ratio in terms of C, H and O mole fractions. The characteristics can be simulated with the mixed fuel of C_2H_6+1/2O_2. The other is the difference of O-C bond in DME instead of C-C bond in hydrocarbon fuels. To clarify the two distinct characteristics on the NOx formation in DME, three kinds of flames are compared under the same maximum flame temperature.

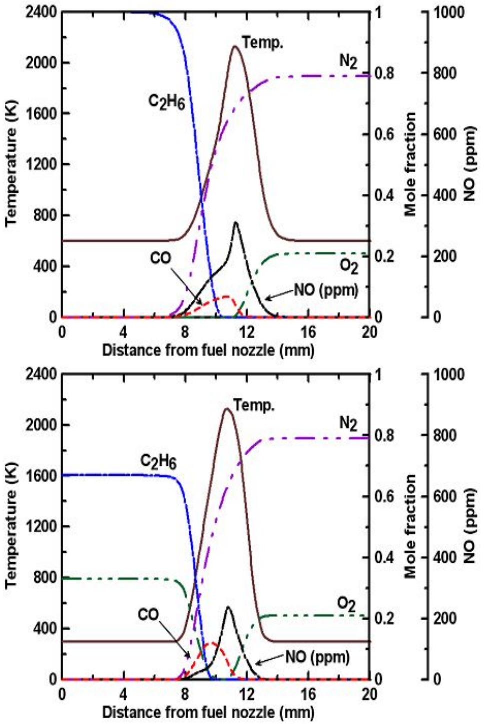
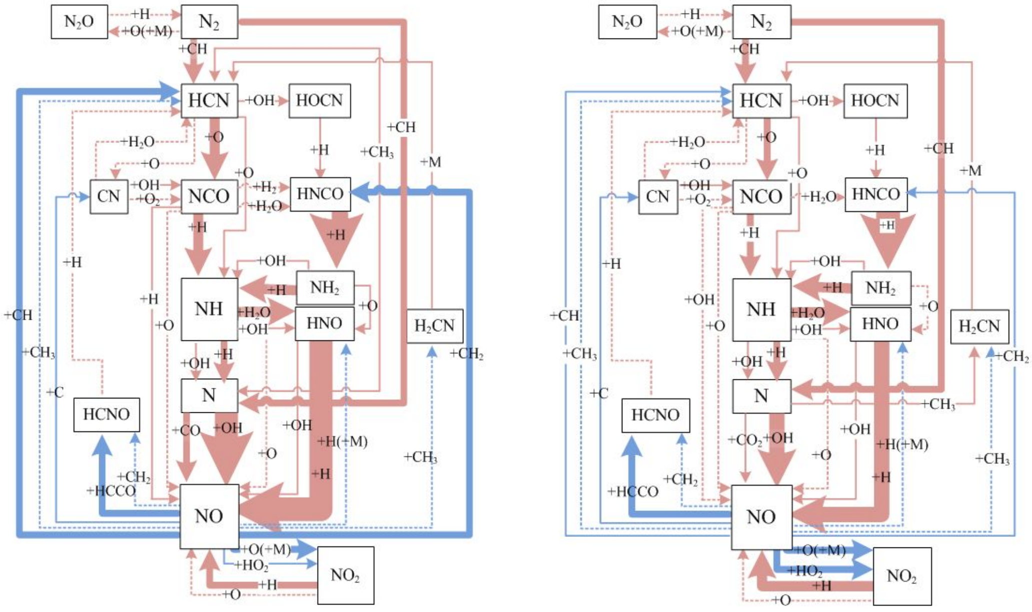


Fig. 5. Comparison of NOx profiles and fuel production rates for C_2H_6 (T_R=600 K) and Mixed fuel (T_R=298 K).

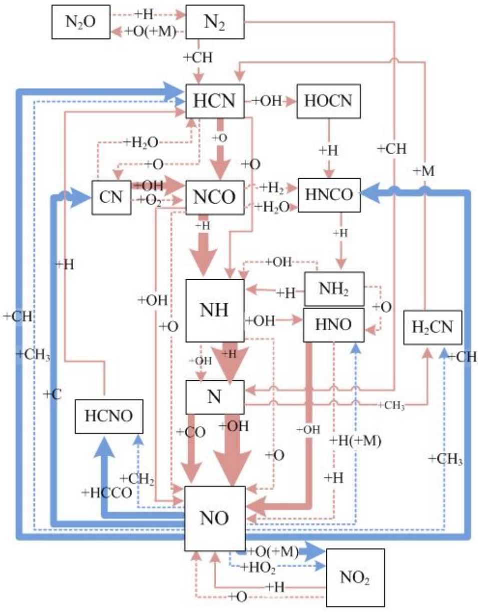
To investigate the effect of burn as like partial premixed flame, the maximum flame temperature of C_2H_6 and Mixed fuel made the same value and compared. Fig. 4 shows the flame structures and Fig. 5 shows the NO profiles and fuel production rates of C_2H_6 and the Mixed fuel flames respectively. In the figure, the NO profiles of the mixed fuel has lower NO concentrations at all flame region, especially in the left side of the flame surface compared to the C_2H_6 flame. In addition, mixed fuel is consumed at the more upstream region and its rate is much higher than that of C_2H_6 flame. From these results, the EI_{NO} of mixed fuel is reduced as much as 43 % of the C_2H_6 fuel. This result indicates the reduction of EI_{NO} in DME flame attributed to the characteristics of partial premixed flame due to the existence of O atom in DME.

Fig. 6(a) and (b) show the reaction path diagram for the formation of NOx in C_2H_6(T_R=600 K) and Mixed fuel(T_R=298 K) nonpremixed flames. This diagram expressed major species production rate that included each reaction by integral calculus in every calculated field. [24] The thickness of the arrow, divided into six levels, gives a visual indication of the relative importance of particular reaction paths with respect to their reaction rates integrated over the entire computational domain. The NOx formation route for the C_2H_6, Mixed fuel, and DME flames shown in Fig. 6 can be



(a) C_2H_6 (T_R=600K)

(b) C_2H_6-O_2 (T_R=298K)



(c) DME (T_R=475K)

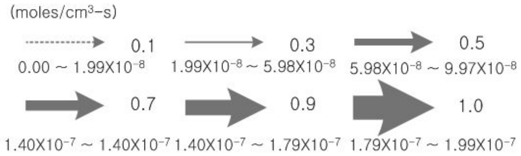


Fig. 6. Reaction path diagram of NO in C_2H_6 (T_R=600 K), Mixed fuel (T_R=298 K) and DME (T_R=475 K) nonpremixed flame.

explained by the major production and destruction routes. The major production path of $N_2 \rightarrow HCN \rightarrow COH \rightarrow N \rightarrow NO$ shows that NO is produced through complex interactions between thermal NO and prompt NO mechanisms.

The destruction of NO mainly occurs through reburning chemistries of NO with intermediates generated from pyrolysis and oxidation of fuel such as C, CH, CH_2, and HCCO. In case of C_2H_6 flame, NOx emissions are reduced through reburning NO reactions. However it is more produced due to thermal NO reaction and prompt NO reaction such as N + OH = NO + H, HNO + H = NO + H_2. As results, C_2H_6 flame produces more NO species rather than any conditions. On the other hand, Mixed-fuel flame is more decreased NO species rather than C_2H_6 flame, because of reduced thermal and prompt NO production reactions.

To clarify the effect of O-C bond in DME, instead of C-C bond in hydrocarbon fuels on NOx formation, Fig. 7 shows the NO profiles and fuel production rates of the Mixed fuel(C_2H_6-O_2) and DME flames. To make a same maximum flame temperature, the initial temperature of DME reactant is adjusted to 475 K. In the figure, the NO profiles of DME fuel has lower NO concentrations at all flame region, but DME fuel is consumed a little more than Mixed fuel is. Therefore, NO concentrations and EI_{NO} of DME were lower than that of Mixed fuel. Detail NO reactions show in Fig. 6(c). Fig. 6(c) indicates the reaction path diagram for the formation of NOx in DME(T_R=475 K) nonpremixed flames. When comparing the reaction paths of NOx for Mixed fuel and DME(T_R=475 K), we found that the overall routes of NOx formation are very similar too. On the other hand, in case of DME nonpremixed flame, thermal NO reaction and prompt NO reaction are decreased, and the NO destruction also increases consistently with various reburning NO chemistries. In particular, the roles of the NO + C = CN + O and NO + CH = HCN + O reactions in NOx destruction of the DME flame become more prominent than in the case of the Mixed fuel flame.

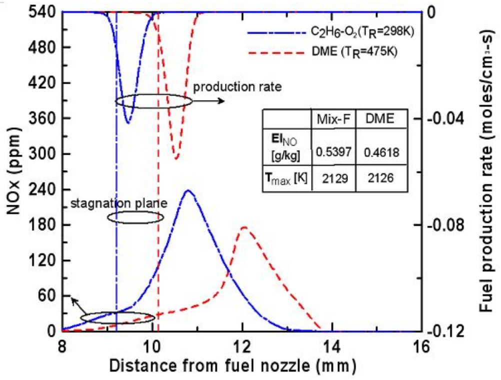


Fig. 7. Comparison of NOx profiles and fuel production rates for Mixed fuel (T_R=298 K) and DME (T_R=475 K).

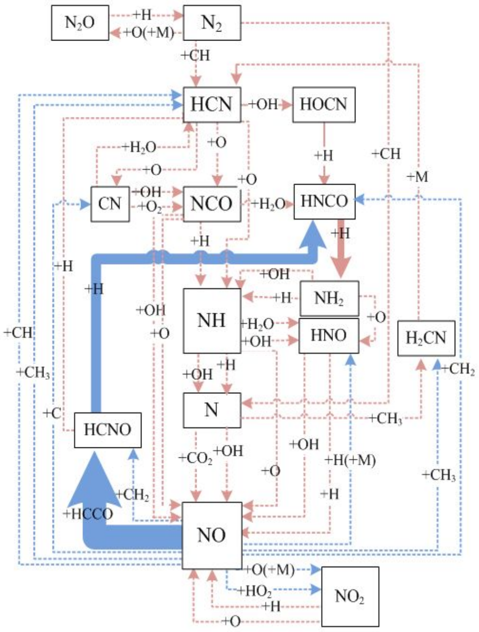


Fig. 8. Reaction path diagram of NOx formation at x = -1.0 mm from the location of T_{max} in the Mixed fuel (T_R=298 K) nonpremixed flame.

Fig. 8 shows the reaction path diagram of NOx at a relative distance of x = -1 mm from the location of the maximum temperature of the Mixed fuel flame. It allows for the examination about NOx reduction in the fuel-rich region of the Mixed fuel flame. NOx is not generally produced in this region and is mainly diffused from the flame surface. Before the present work, [12] Reaction path of NOx at a relative distance of x = -1 mm from the location of the maximum of the DME flame was studied already. As shown in Fig. 8, NO production by thermal and prompt NO mechanisms is very small, while NO destruction actively occurs through reburning reaction paths, such Fig. 6(c) indicates the reaction path diagram for the formation of NOx in DME as NO + HCCO = HCNO + CO. For the C_2H_6 flame, the reaction path diagram is not presented in the current study because the local NO reaction rate at the relative distance of x = -1 mm is

Table 1. Maximum flame temperature (T_{MAX}) and NO emission index (EI_{NO}) of calculated flames.

	C_2H_6 (T_R=298 K)	CH_3OCH_3 (T_R=298 K)	C_2H_6 (T_R=600 K)	C_2H_6-O_2 (T_R=298 K)	CH_3OCH_3 (T_R=475 K)
T_{MAX} [K]	1955	2010	2127	2129	2126
EI_{NO} [g/kg]	0.5263	0.2463	1.2628	0.5397	0.4618
EI_{NO} [g/10Mcal]	0.45646	0.3570	1.0952	0.4681	0.6693

too small in comparison to the case of Mixed fuel flame. This result that, although the overall NOx reaction paths of DME and Mixed fuel flame is similar to that exhibited by the C_2H_6 flame, DME and Mixed-fuel flames have a distinct NO reduction mechanism through reburning NO chemistry in the fuel-rich region because of fast pyrolysis and oxidation reactions.

As seen in Table 1, EI_{NO} of DME is reduced as much as 85 % of Mixed-fuel. This result indicates the O-C bond in DME also contributes to the reduction of EI_{NO} in DME, but its contribution rate is small compared to the effect of partial burning of DME with premixed flame mode.

4. Conclusions

To clarify the effect of chemical structure of Dimethyle ether(DME), DME flame was investigated numerically to compare the flame structures and NOx emissions with C_2H_6 and Mixed-fuel in counterflow nonpremixed flame. In the numerical results of counterflow nonpremixed flames, NOx emission of DME is similar to any hydrocarbon fuels although DME has double fuel consumption rate. In other word, NOx emission of DME produced half percentage compared to different hydrocarbon fuels under the same mass flow rate conditions.

EI_{NO} of DME is reduced about 57 % to compare with it of C_2H_6. The reasons are that thermal NO and prompt NO reactions are reduced due to partial burning characteristics in DME and reburning NO reactions are more activated due to O-C bond in DME.

Consequently, the cause of EI_{NO} reduction is attributed mainly to the characteristics of partial premixed flame due to the existence of O atom in DME and partly to the O-C bond in DME, instead of C-C bond in hydrocarbon fuels.

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