

Distinguishing between active radicals' chemical effect and thermal effect for combustion promotion by means of experiments using plasma jets

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Abstract

Distinguishing between the thermal effect and active radicals' chemical effect in combustion reaction was implemented using an experimental apparatus with an argon plasma jet (Ar P.J.) and oxygen plasma jet (O₂ P.J.) coupled with corresponding numerical simulation. It was conducted based on the idea that Ar P.J. has much higher temperature without active species whereas O₂ P.J. includes abundant O radicals. The experimental results show that O₂ P.J. is much more eligible for combustion promotion in both DME/air and CH₄/air mixtures, which coincides with the numerical results showing that the ignition delay time is reduced more remarkably by adding O radicals than by increasing the temperature of the fuel/air mixtures. Although the level of effect differs according to the kind of mixtures used, it is generally more advantageous for ignition/combustion promotion to be conveyed as active radicals than as heat to fuel/air mixtures with the same supply of energy.

Keywords : radicals, plasma jets, combustion promotion, chemical effect, thermal effect

1. Introduction

Chemically active radicals, such as active atoms, molecules or ions, which are very unstable with very short lives, are understood from numerous research works^{1)–5)} to play important roles in combustion reaction. However it is still desirable to clarify the effectiveness of radicals on ignition/combustion promotion as widely and universally as possible for promoting ignition in supersonic combustion^{1)–3), 6)}, developing new combustion systems^{7), 8)} or utilizing alternative fuels^{9), 10)}, since most previous studies were conducted to obtain results within each given specific situation. This study is aimed at establishing evaluation schemes which are intended to clarify the distinction of active radicals' chemical effect from the thermal effect for combustion promotion with an experiment using plasma jets.

We hence have newly developed a combustion

experiment method and apparatus with a plasma torch to obtain information on the radicals' effect for wider use¹¹⁾. Carrying out combustion experiments with dimethyl ether (DME)/air mixtures and methane (CH₄)/air mixtures using an oxygen plasma jet (O₂ P.J.) and a nitrogen plasma jet (N₂ P.J.) to investigate the radicals' effect on combustion reaction promotion in various conditions¹²⁾, we are able to report our findings on how the amount of O and N radicals included in O₂ P.J. and N₂ P.J. increased as P.J. electric power input P_{in} was raised, and accordingly how combustion reaction was promoted by their effectiveness. This time we conducted experiments additionally with an argon plasma jet (Ar P.J.) as a base index in order to distinguish between a chemical effect and a thermal one in the combustion phenomenon; Ar P.J. is supposed not to yield radicals even at high temperatures by high P_{in} , so the result can be used to

evaluate the temperature effect exclusively and to recognize purely the effect of O radicals by comparing the experimental and numerically estimated results with Ar P.J. and those with O₂ P.J. DME, which has a wide combustion limit and forms very little soot when being burned, was used as the fuel throughout the experiments.

2. Experimental apparatus and test procedure

A schematic diagram of the experimental set-up is shown in Figure 1. The combustor consists of a combustion reaction chamber, a producing and feeding system of premixed gas and a plasma torch. The reaction chamber, made of stainless steel, is 7 mm in bore and 170 mm long. When visual observation of the combustion state is conducted, the material of the combustion chamber is replaced with quartz glass. The plasma torch is placed at the center of the combustor head facing downstream. The cathode rod, made of copper with hafnium embedded at its tip for wear prevention, is 1.5 mm in diameter. The anode cylinder, made of copper, has a 1 mm jetting caliber. After the P.J. feedstock, argon (Ar) or oxygen (O₂), is exposed to arc discharges between the electrodes induced by a DC power supply, it is ejected as a plasma jet from the jetting caliber and spread into the combustion chamber as shown in Figure 2. Premixed gas, dimethyl ether (DME)/air in this study, at a flow rate and mixture ratio set with a flow meter (8300, Kojima Instrument Inc.) is supplied into the cylindrical combustion chamber coaxially and then ignited and combusted chemically and thermally by being exposed to plasma jets. While ejecting plasma jets into

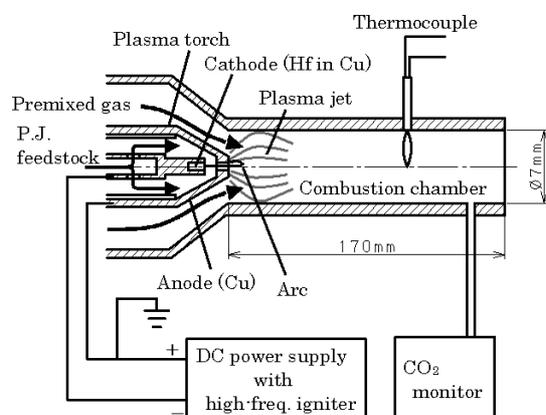


Figure 1 Schematic diagram of the experimental set-up.



Figure 2 Photo of O₂ plasma jet at $P_{in} = 100$ W with $Q_f = 1$ NL min⁻¹.

premixed gas, discharge current/voltage and carbon dioxide (CO₂) concentration in the exhaust gas at 160 mm downstream from the P.J. exit are measured with a CO₂ monitor (CGT-101 A, Shimadzu Corporation) and temperature in the combustion chamber is measured at 85 mm downstream from the P.J. exit with a R-type thermocouple. Completeness of combustion is determined from the CO₂ concentration and temperature, as well as by visual observation in the chamber at each P.J. input power, P_{in} . Measurement at the same airflow and P.J. condition but without fuel is also conducted to ensure that the increase of initial premixed gas temperature heated by the plasma jets is negligibly small. All these experiments are performed under atmospheric pressure and at room temperature.

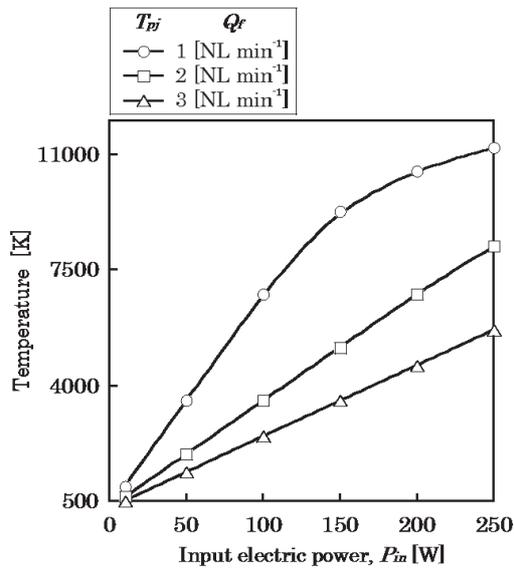
3. Results and discussion

3.1 Temperature and radicals amount in plasma jets

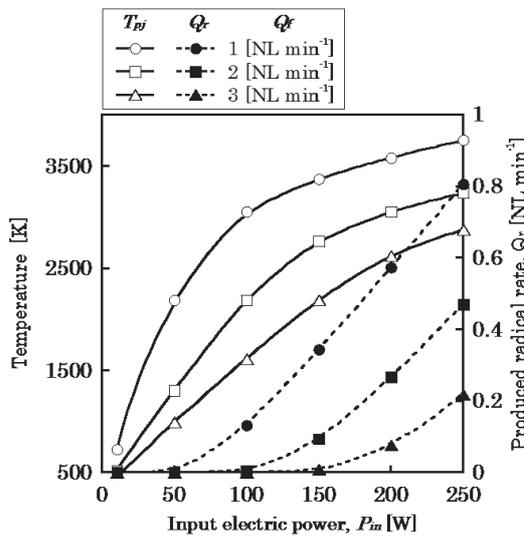
To estimate the respective temperatures in O₂ P.J. and Ar P.J., T_{pj} , and the amount of radicals produced in O₂ P.J., numerical calculation was carried out by a chemical equilibrium program (CEA)¹³. In the calculation, electric power input to the plasma jet, P_{in} was considered as the increase of the reactants' heat of formation. Figure 3(a) shows the temperature in Ar P.J. and Figure 3(b) shows the temperature and production rate of O radicals Q_r in O₂ P.J. in the range of P_{in} used in this study. The figures represent average values in plasma jets whereas the real temperature and radical densities in plasma jets have spatial distribution as reported elsewhere¹. Such estimation, however, is quite beneficial for grasping characteristics of the plasma jets. Temperature in Ar P.J. increases with increasing P_{in} as shown in Figure 3(a), but temperature increase in O₂ P.J. fails as large amounts of O radicals are being produced with increasing P_{in} because much of P_{in} is consumed on dissociation, $O_2 + 499\text{kJ/mol} \rightarrow 2O^{14}$, as shown in Figure 3(b). Hence Ar P.J., which produces no radicals as shown in the spectroscopic measurement¹¹, yields much higher temperatures than O₂ P.J. The effect of the flow rate of plasma jet feedstock, Q_f , as observed in the figures shows how much higher the T_{pj} becomes and how much higher the Q_r in O₂ P.J. becomes with lowering Q_f at the same as P_{in} . These results with our spectroscopic measurements in reference¹¹ are related to the main concern of this study, that ignition/combustion with O₂ P.J. is prompted due to both thermal effect and produced radicals' chemical effect, whereas that with Ar P.J. is only due to thermal effect.

3.2 Ignition and combustion test using plasma jets

Figure 4 shows the behaviors of CO₂ concentration and temperature increase with various P_{in} in DME/air combustion experiment using Ar P.J. at an equivalence ratio $\phi = 0.6$ and a premixed gas flow speed $V_m = 9$ m s⁻¹ or 20.8 NL min⁻¹ by flow rate. The flow rate of feedstock was set at $Q_f = 1, 2$ and 3 NL min⁻¹. A previous experimental result using O₂ P.J. under the same condition¹² is shown in Figure 5 to compare the effects of both plasma jets when used. The horizontal dash-dot lines



(a) Argon plasma jet.

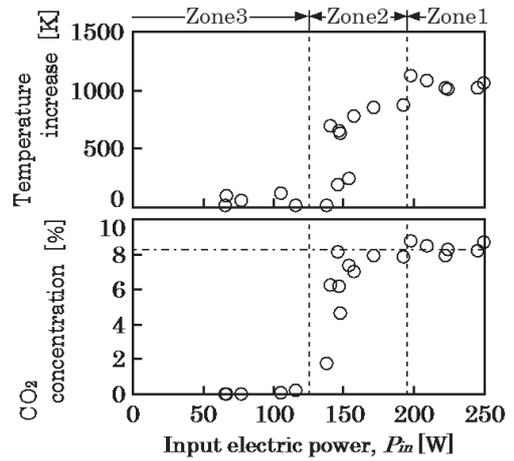


(b) Oxygen plasma jet.

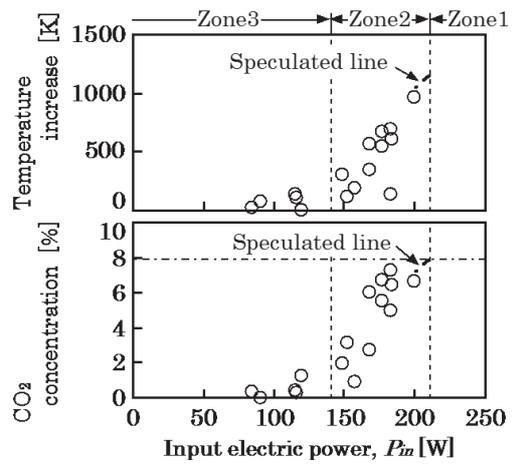
Figure 3 Temperature T_{pj} in Ar P.J. and O_2 P.J. and produced radical rate Q_f in O_2 P.J. calculated at equilibrium with various input electric P_{in} .

in the figures indicate the theoretical CO_2 concentration in the exhaust gas, excluding water, calculated by CEA¹³. As can be seen in Figures 4–5, there are three distinct zones by CO_2 concentration and temperature increase: Zone 1, where CO_2 concentration almost accords with the theoretical calculation value and hardly increases further even if P_{in} is increased, and hence combustion of the DME/air mixture can be judged to be completed; Zone 2, where CO_2 concentration and temperature sharply increase as P_{in} increases, and hence combustion of the mixture is partially completed, and becomes more completed as P_{in} increases; Zone 3, where no CO_2 concentration is detected and temperature increases very little, and hence combustion reaction of the mixture does not occur. The two vertical dashed lines which separate Zones 2 and 3 and Zones 1 and 2 in the figures correspond to a minimum power required for ignition, $P_{i,min}$ and that for combustion, $P_{c,min}$, respectively.

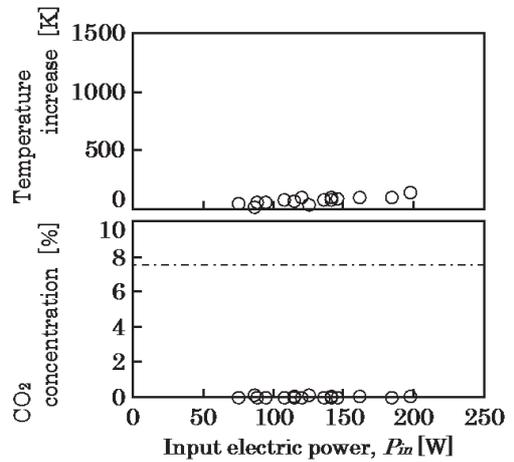
These experimental results are summarized in Table 1. They show that O_2 P.J. is more effective than Ar P.J. for



(a) $Q_f = 1 \text{ NL min}^{-1}$.



(b) $Q_f = 2 \text{ NL min}^{-1}$.



(c) $Q_f = 3 \text{ NL min}^{-1}$.

Figure 4 CO_2 concentration and temperature increase with various P_{in} in DME/air combustion experiment at $\phi = 0.6$ and $V_m = 9 \text{ m s}^{-1}$ using Ar P.J. with different Q_f .

promotion of a combustion reaction. For example at $Q_f = 3 \text{ NL min}^{-1}$, O_2 P.J. can complete combustion of DME/air mixture at $P_{in} = 155 \text{ W}$ or $P_{c,min} = 155 \text{ W}$, whereas Ar P.J. cannot at all, in spite of the fact that T_{pj} is 2244 K for the former and 3637 K for the latter. At $Q_f = 2 \text{ NL min}^{-1}$, $P_{c,min}$ is 140 W with O_2 P.J. yielding $T_{pj} = 2683 \text{ K}$, but $P_{c,min}$ is 210 W with Ar P.J. yielding $T_{pj} = 7062 \text{ K}$. Such superiority of O_2 P.J. for combustion promotion is owing to the O radicals included and increase of O_2 concentration there,

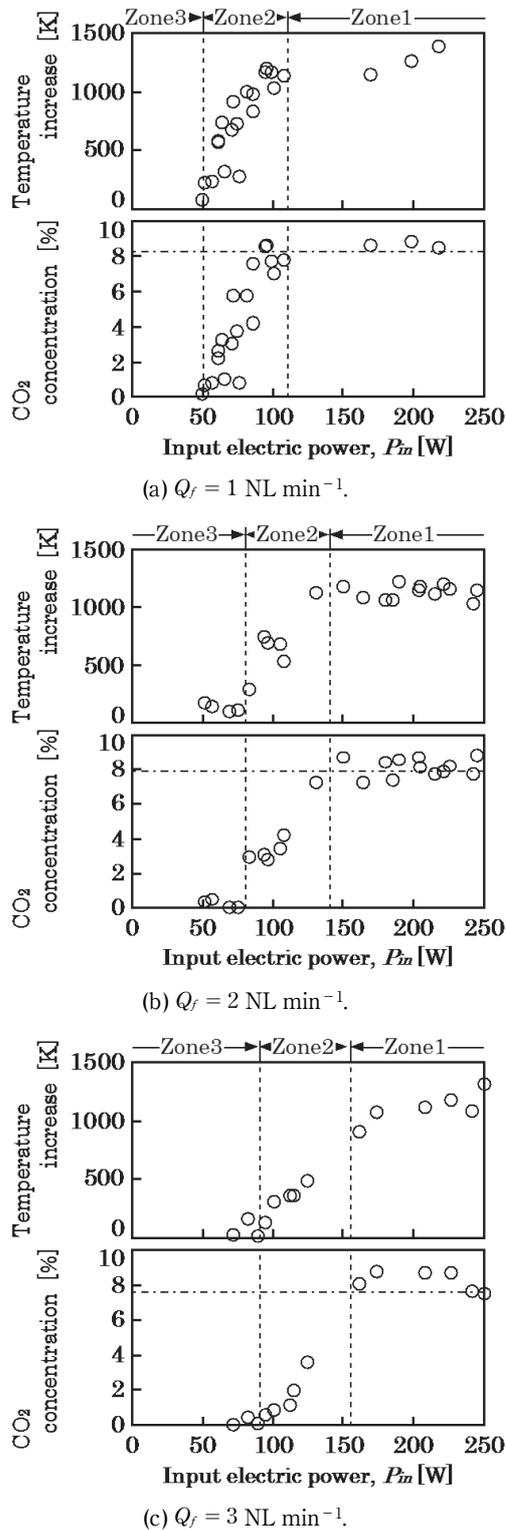


Figure 5 CO_2 concentration and temperature increase with various P_{in} in DME/air combustion experiment at $\phi = 0.6$ and $V_m = 9 \text{ m s}^{-1}$ using O_2 P.J. with different Q_f ¹²⁾.

specifically $O_r = 0.01 \text{ NL min}^{-1}$, $Q_{O_2} = 2.99 \text{ NL min}^{-1}$ at $P_{in} = 155 \text{ W}$ with $Q_f = 3 \text{ NL min}^{-1}$ and $O_r = 0.07 \text{ NL min}^{-1}$, $Q_{O_2} = 1.97 \text{ NL min}^{-1}$ at $P_{in} = 140 \text{ W}$ with $Q_f = 2 \text{ NL min}^{-1}$, where Q_{O_2} is the flow rate of O_2 in O_2 P.J. Although increase of O_2 concentration is well known to be effective for combustion promotion²⁾, it will be shown later by the numerical calculation on ignition delay that the effectiveness is much smaller than that by addition of O radicals under the condition examined here. Hence these

results above indicate that how much more advantageous the radicals' chemical effect is compared to the thermal effect by the initial temperature increase.

3.3 Numerical calculations on reaction promotion

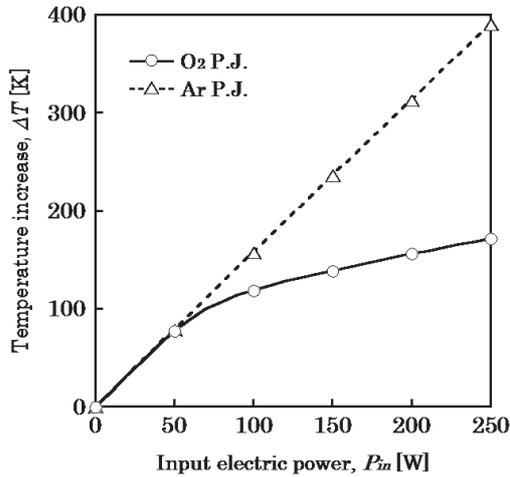
Numerical calculations on ignition delay time, t_{ig} , were conducted to compare the effectiveness of radicals and that of heat in reaction promotion since t_{ig} is an important and fundamental index of reactivity of premixed gases depending on the kind of fuel, equivalence ratio, temperature and pressure utilized here. A short ignition delay time means it is "easy-to-ignite." Calculations on t_{ig} here are conducted assuming that dissociated radicals and non-dissociated feedstock in plasma jets are uniformly merged with premixed gas and that P_{in} is used to increase the initial temperature of premixed gases. Although temperature and radicals density have steep gradients in plasma jets^{1),15)}, the calculations conducted assuming their uniformity are valid and useful to compare them for combustion promotion because they are raised and produced quasi-proportionally with P_{in} . The ignition delay adopted here is a time required causing a rise of 400 K from the initial temperature, T_0 . The DME/air oxidation reaction used for the calculation here is based on the mechanism in ref.¹⁶⁾ combining Kaiser's mechanism¹⁷⁾ with some modification to the Miller-Bowman mechanism, which treats the nitrogen-oxide mechanism of C_1 -, C_2 -hydrocarbon fuels¹⁸⁾, and the elementary reaction formulas related to argon reactions^{19),20)}.

Figure 6 shows a calculated temperature increase, ΔT , of DME/air premixed gas at $\phi = 0.6$, $V_m = 9 \text{ m s}^{-1}$, and $T_0 = 1300 \text{ K}$ when P_{in} of each plasma jet is changed under constant $Q_f = 1 \text{ NL min}^{-1}$. While ΔT for both plasma jets increases as P_{in} increases, ΔT increase fails in the case of O_2 P.J. because production of O radicals starts from $P_{in} = 40 \text{ W}$ and hence reaction energies are consumed for dissociation as shown by a symbol ● in Figure 3(b). This is because the difference in ΔT between O_2 P.J. and Ar P.J. becomes wider.

Figure 7(a) shows calculated t_{ig} trends for DME/air mixture flow with each plasma jet in the same conditions as above. The initial temperature in this calculation is set at $T_0 = (1300 + \Delta T) \text{ K}$. In the case with Ar P.J. (dashed line), t_{ig} becomes shorter as P_{in} becomes higher and thus ΔT increases. The manner of this t_{ig} shortening corresponds to the degree of effectiveness in temperature increase on reaction promotion. Up to $P_{in} = 40 \text{ W}$, O radicals are not produced in the O_2 P.J., but O_2 concentration in the main premixed gas flow is increased instead. In the case with Ar P.J., the main premixed gas flow is diluted with argon. Although increase of O_2 concentration helps promote reaction, Figure 7 shows that t_{ig} hardly differs between O_2 P.J. and Ar P.J., or that reaction promotion by increase of O_2 concentration is very slight. This is supported by the experimental results shown in Figure 4(a) and 5(a) that ignition was not possible with either O_2 P.J. or Ar P.J. at less than $P_{in} = 40 \text{ W}$. As P_{in} is heightened, t_{ig} becomes more markedly shorter with O_2 P.J. than with Ar P.J. This

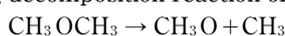
Table 1 Marginal electric power necessary for ignition, $P_{c,\min}$ and combustion, $P_{c,\min}$ with corresponding T_{pj} and Q_f estimated at $P_{c,\min}$.

Feedstock	Q_f [NL min ⁻¹]	Minimum input power [W]		T_{pj} at $P_{c,\min}$ [K]	Q_f at $P_{c,\min}$ [NL min ⁻¹]
		$P_{i,\min}$	$P_{c,\min}$		
Ar	1	125	195	10379	–
	2	140	(210)	7062	–
	3	No ignition		(3637 at 155 W)	–
O ₂	1	50	110	3132	0.17
	2	80	140	2683	0.07
	3	90	155	2244	0.01

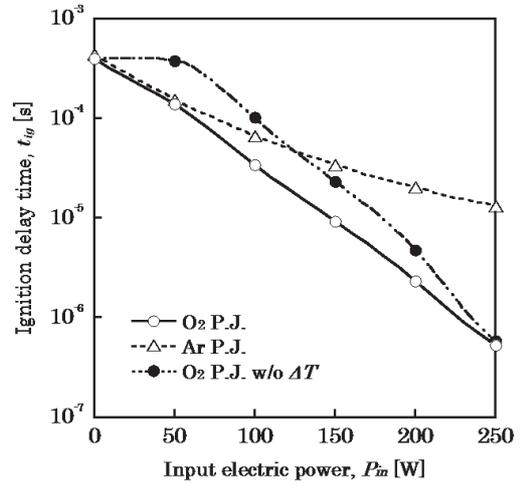
**Figure 6** Calculated temperature increase, ΔT , of DME/air premixed gas at $\phi = 0.6$, $V_m = 9 \text{ m s}^{-1}$ and $T_0 = 1300 \text{ K}$ in various P_{in} under constant $Q_f = 1 \text{ NL min}^{-1}$.

difference comes from an event in the case with O₂ P.J., the chemical effect to promote reaction by the O radicals produced is added to the thermal effect that only Ar P.J. can yield: an effect purely by high temperature is observed in the Ar P.J. experiment and a radical effect is exhibited as the difference between the effect by O₂ P.J. and that by Ar P.J. as shown in Figure 3(b). It is thus understood that effect by radicals is more distinct for reaction promotion from that by heat. Figure 7(b) shows a calculated t_{ig} using GRI-Mech3.0 reaction mechanism²⁰⁾ for CH₄/air mixture with the same condition as in Figure 7(a) for DME/air. The double dash-dot lines in Figures 7(a)–(b) indicate the calculated t_{ig} trends with O radicals and undissociated feedstock O₂ included in plasma jets without ΔT (fixed $T_0 = 1300 \text{ K}$). The difference between t_{ig} with ΔT and t_{ig} without ΔT becomes less noticeable as P_{in} becomes higher, yielding more O radicals. The amount of added radicals thus contributes to and governs the shortening of the ignition delay time, namely, the speedup of reaction. The difference in t_{ig} between with O₂ P.J. and with Ar P.J. starts appearing at $P_{in} = 60 \text{ W}$ for CH₄/air and at $P_{in} = 130 \text{ W}$ for DME/air, and it tends to be wider more remarkably for CH₄/air than for DME/air at higher P_{in} . This is what we presumed in a previous study¹⁰⁾ and try to explain in this study, that the effectiveness of each radical on ignition/combustion promotion would differ by the kind of fuel used.

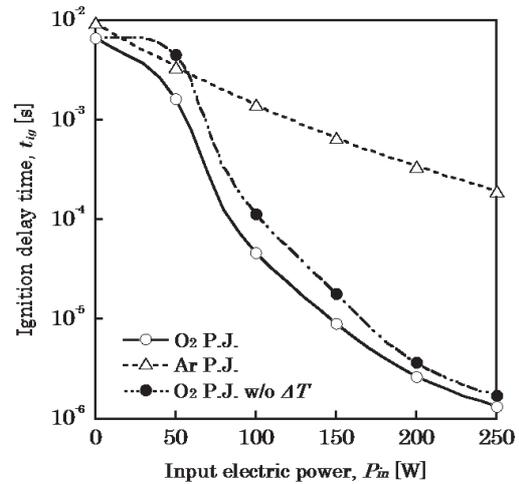
The following decomposition reaction of DME



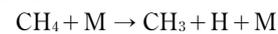
initiates the reaction, which would advance before O



(a) DME/air mixture.

(b) CH₄/air mixture.**Figure 7** Calculated t_{ig} with (a) DME/air mixture and (b) CH₄/air at $\phi = 0.6$, $V_m = 9 \text{ m s}^{-1}$, $T_0 = (1300 + \Delta T) \text{ K}$ in various P_{in} of each plasma jet at $Q_f = 1 \text{ NL min}^{-1}$.

radicals are produced and added. On the other hand, the decomposition of CH₄



advances after O or N radicals, represented as M here, are produced and added. The radical amount hence influences more effectively with CH₄ in contrast to DME.

Input electric power to plasma jets P_{in} is generally consumed both for the temperature increase of premixed gases and for dissociation of feedstock. Supposing that input electric power would be consumed only for heating premixed gases or only for dissociating feedstock, calculation to evaluate t_{ig} was carried out in each condition.

Figure 8, which is prepared in relation to Figure 9, shows two extreme cases of numerical results: one is ΔT calculated assuming that P_{in} is consumed only for the temperature rise of DME/air and CH₄/air at $\phi = 0.6$, $V_m = 9 \text{ m s}^{-1}$, $T_0 = 1300 \text{ K}$, and the other is O radical percentages in the total flow calculated assuming that P_{in} is consumed only for dissociation of O₂ to O at $Q_f = 1 \text{ NL min}^{-1}$. When P_{in} is consumed only for the temperature rise, ΔT does not fail unlike the result in Figure 6 because energy is not used for dissociation. On the contrary, when all P_{in} is consumed only to dissociate feedstock, O₂ is

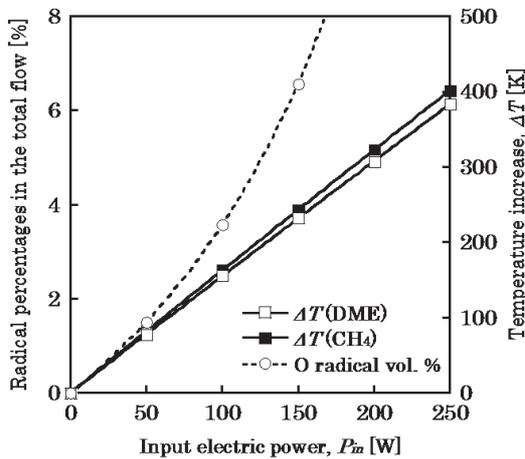


Figure 8 Temperature increase ΔT calculated assuming that P_{in} is consumed only for temperature rise of DME/air and CH_4/air at $\phi = 0.6$, $V_m = 9 \text{ m s}^{-1}$, and $T_0 = 1300 \text{ K}$, and O radical percentages in the total flow calculated assuming that P_{in} is consumed only for dissociation of O_2 to O at $Q_f = 1 \text{ NL min}^{-1}$.

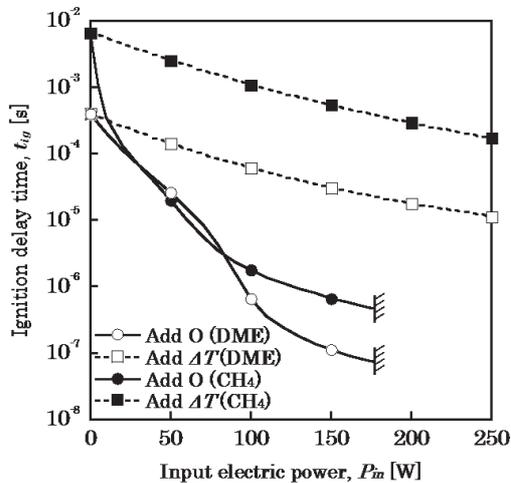


Figure 9 Ignition delay time t_{ig} calculated for DME/air and CH_4/air based on Figure 8 on various input electric power with $Q_f = 1 \text{ NL min}^{-1}$.

completely converted into O radicals approximately over 170 W. Figure 8 would hence direct both extreme cases, specifically, the mole fraction of dissociated O radicals and equivalent temperature increase of the premixed gas under the same P_{in} . At $P_{in} = 100 \text{ W}$ with DME/air, for example, $\Delta T = 155 \text{ K}$ corresponds to 3.57 volume % of O radicals added in the total flow.

Figure 9 shows t_{ig} calculated for DME/air and CH_4/air based on Figure 8. It reveals that t_{ig} would be drastically shortened if P_{in} is consumed only to dissociate feedstock to produce O radicals. In particular, in the case with CH_4 , t_{ig} is sharply shortened by adding small amounts of O radicals. As a result of these calculations, using energy for O radicals production is much more effective to reaction promotion than using it for temperature increases of premixed gases.

All these calculated and experimental results indicate how superior the effect by radicals is for combustion reaction promotion to that by temperature rises, and that the difference of superiority varies by the combination of the kinds of fuel used and radicals added.

4. Conclusions

Through ignition and combustion tests using an experimental apparatus with an argon plasma jet and oxygen plasma jet coupled with corresponding numerical simulation, this work has demonstrated that it is more advantageous to add active radicals than to add heat to fuel/air mixtures for ignition/combustion promotion. The following are specific conclusions to show the distinction between the chemical effect and the thermal one:

- 1) In spite of the fact that O_2 P.J. has a much lower temperature than Ar P.J., the former is greatly eligible for a combustion reaction. This is owing to the effect of O radicals abundantly being included in O_2 P.J.
- 2) Numerical simulation showed how ignition delay times are shortened as temperature is increased and radicals are added, but adding radicals is much more effective in both DME/air and CH_4/air mixtures.
- 3) Reaction promotion by radicals is more noticeable for the combustion of CH_4/air mixture than for that of DME/air mixture. This is due to the difference in the reaction mechanism of each mixture.

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