**Study on combustion and ignition characteristics of
ethylene, propylene, 1-butene and 1-pentene
in a micro flow reactor with a controlled temperature profile**

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Abstract

Weak flames of four alkenes (ethylene, propylene, 1-butene and 1-pentene) were observed using a micro flow reactor with a controlled temperature profile to investigate their combustion and ignition characteristics. Weak-flame based investigation which enables to elucidate general ignition property of each fuel was conducted. One-dimensional computations with detailed reaction mechanisms were conducted to compare and analyze experimental results. Single luminous zone of hot flame was observed for all four alkenes. The order of weak flame position was ethylene, 1-pentene, 1-butene and propylene from the lower temperature side and thus the reactivity of those fuels are higher in the same order. Computational results captured the order of the experimental weak flame position. Alkene results were compared with alkane results in terms of carbon number and the order of weak flame position agreed between the alkene and alkane results. Weak flame structures of alkenes were analyzed using the computations. A similar overall flame structure was obtained for the four alkenes from the mole fraction profiles of major species. Rate of consumption was investigated to clarify fuel consumption of alkenes. Reactions with O, H and OH radicals proceed in the fuel consumption of alkenes. H-atom addition reaction of alkene where the reaction occurs at the double bond of the alkene is a unique reaction compared with the alkane and consumes a significant amount of the fuel. H-atom abstraction reaction with OH, which is important in alkane, is also important in the alkene consumption. Reaction path analysis was conducted to examine the high reactivity of ethylene. OH production through HO_2 in the initial stage of oxidation is important against the weak flame position. Ethylene has a high rate of HO_2 production compared with the other alkenes through $\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$, $\text{C}_2\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{HO}_2$ and $\text{C}_2\text{H}_3 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_2 + \text{HO}_2$, which results in a high reactivity.

Keywords

Micro flow reactor, Micro-combustion, Weak flame, Alkene

Nomenclature

A	cross-sectional area	[cm ²]
A_i	frequency factor of elementary reaction	[reaction-dependent]
c	specific heat	[J/(g· K)]
d	inner diameter of reactor	[mm]
h	specific enthalpy	[J/g]
j	mass flux	[g/(cm ³ · s)]
K	total number of species	[-]
$\dot{M}$	mass flow rate	[g/s]
Nu	Nusselt number	[-]
p	pressure	[atm]
T	temperature	[K]
V_k	diffusion velocity	[cm/s]
u	mean flow velocity	[cm/s]
W	molecular weight	[g/mol]
x	spatial coordinate	[mm]
X	mole fraction	[-]
Y	mass fraction	[-]
$[A]$	mole density of species A	[mol/cm ³]
λ	thermal conductivity	[W/(cm· K)]
ρ	density	[g/cm ³]
$\dot{\omega}$	molar production rate	[mol/(cm ³ · s)]
t	camera exposure time	[s]

Subscripts

ad	adiabatic
i	elementary reaction index
k	species index
p	constant pressure
w	wall
0	origin

1. Introduction

Combustion characteristics of alkenes are receiving interest not only because they are essential components in practical fuels but they are also a key intermediate in alkane oxidation [1,2]. Alkanes are main components of practical fuels and understanding their reaction process in detail is critical to improve various combustion devices. Many reaction mechanisms were developed for alkanes but further improvement is required. As a key intermediate in alkane oxidation, understanding alkene reaction process could definitely lead to the improvement of understanding alkane. Despite the importance of understanding alkenes, there are limited numbers of researches on them compared with the extensively-studied alkanes. Therefore, alkene combustion is not as clearly understood as alkanes. Ethylene is mostly studied among all alkenes since it is also known as an important intermediate for soot formation. Modeling of ethylene combustion were done in studies such as in Chaoqi et al. [3] and Carrier et al.[4]. Ignition characteristics were studied experimentally with shock tube and rapid compression machines by Sexena et al. [5] and Kumar et al. [6]. Larger alkenes like pentene have been broadly studied since it is seen in gasoline oxidation. Kukkadapu et al. [7] added pentene to a gasoline surrogate in order to study its effect on ignition delay. Prabhu et al. [8] studied pentene oxidation and its interaction with nitric oxide. Experimental and modeling studies of pentene were done by Minetti et al. [9], Ribaucour [10] and Touchard et al.[11,12]. Studies on lower alkenes, such as propylene [13–15] and butene [16], or studies focusing on alkene isomers [17–19] were also seen in the study of alkenes. However, not many researches apply multiple alkenes with different carbon size and compare each other. Most of the comparisons for alkenes were done with their conjugate alkanes or their own isomers.

In this study, four alkenes of ethylene, propylene, 1-butene and 1-pentene were chosen as test fuels. These alkenes have different carbon number (C₂–C₅) with a similar molecular structure which is a straight chained alkene with a double bond locating at the end of the carbon chain. Therefore, carbon number dependence could be examined along with their individual combustion characteristics. In addition, the effect of double bond existence could be observed by the comparison against their conjugate alkanes of ethane, propane,

n-butane and *n*-pentane.

To investigate combustion characteristics of the fuels, a micro flow reactor with a controlled temperature profile (denoted as micro flow reactor from here on) [20,21] was applied. The micro flow reactor is a recently introduced setup which could investigate combustion and ignition characteristics of given fuels in a well defined simple system. In particular, weak flame phenomenon is specific to this reactor and the weak-flame based investigation enables to elucidate general ignition property of given fuels [22-24]. A quartz tube with an inner diameter smaller than the quenching diameter of the introduced gas mixture is used as a reactor. A part of the reactor channel is heated using an external heat source to form a stable temperature gradient along the flow direction at the inner wall. The premixed fuel/oxidizer is introduced into the reactor and the various flames are observed. In the micro flow reactor, the pressure is constant the flow condition is laminar and the gas-phase temperature strongly depends on the wall temperature profile. In the past studies using the micro flow reactor [22–26], three types of flame were observed depending on inlet flow velocities: stable flat flames were observed at high flow velocities; unstable flames called *flames with repetitive extinction and ignition* (FREI) were observed at intermediate flow velocities; and stable flames with weak luminescence (weak flame) were observed at very low flow velocities. Special attentions has been given to the weak flame which is a unique phenomenon observed only in the micro flow reactor. Minaev et al. [27] showed that the weak flame branch in the micro flow reactor is on the ignition branch of the Fendell curve based on theoretical analysis. Oshibe et al. [26] applied dimethyl ether (DME) and Yamamoto et al. [22] applied *n*-heptane to the micro flow reactor and observed multiple weak flames both experimentally and numerically. In these studies, gas sampling and analysis indicated that the three-stage oxidation (three weak flames) corresponds to the typical cool, blue and hot flames known in the ignition phenomenon in other systems where cool flame is characterized by formation of CH_2O [20], blue flame is characterized by CH_2O consumption and CO and CH_4 formation [29], and hot flame is characterized by CO and CH_4 consumption and CO_2 formation [29]. In the weak flame region, gas-phase temperature profile nearly equals to the wall temperature profile and the rapid increase in the gas-phase is suppressed by the wall temperature. Therefore, the oxidation process is separated into different temperature ranges which are observed as multiple weak

flames. The ignition process known to be a transient and spontaneous phenomenon is reproduced as a stationary phenomenon represented by steady weak flames in the micro flow reactor. Past studies by Hori et al. [23] and Suzuki et al. [24] focused on weak flame positions to examine reactivity of fuels. In these studies, gasoline primary referenced fuels (PRF) and diesel surrogate fuels were applied to the micro flow reactor. As the octane/cetane number increased/decreased the weak flame positions located at the higher temperature side which indicates lower reactivity. Another study by Hori et al. [30] investigated the effect of toluene addition to *n*-heptane and observed the inhibition of oxidation with toluene addition. The capabilities of the micro flow reactor to investigate general combustion and ignition characteristics of fuels have been demonstrated from these past studies.

The objective of this study is to investigate combustion and ignition characteristics of four alkenes (ethylene, propylene, 1-butene and 1-pentene) based on their weak flames using the micro flow reactor. Weak flames of these fuels were observed and analyzed using one-dimensional computation with detailed reaction mechanism. Weak flame position was used to compare reactivity of these fuels. Comparison was also conducted against their conjugate alkanes. Reaction path analysis was conducted to further investigate the oxidation process of the alkenes.

2. Experimental method

Figure 1a shows the schematic diagram of the experimental setup. A quartz tube with an inner diameter $d = 2$ mm, an outer diameter of 4 mm and a length of 200 mm was used as a reactor. Even though the inner diameter of the quartz tube is very small, wall chemical effect is confirmed to be negligible in the present experimental conditions [23,31,32]. A part of the quartz tube was heated from the bottom using a hydrogen/air premixed flat-flame burner to form a stationary wall temperature gradient of 300–1300 K in the flow direction as it is shown in the figure.

A gaseous pre-mixture with an equivalence ratio $\phi = 1.0$ was introduced to the reactor with an inlet mean flow velocity $u = 2$ cm/s. Two kinds of mixture supplying methods were applied for gaseous and liquid fuels. For ethylene, propylene and 1-butene, which are gaseous at the standard condition, fuel/air pre-mixtures were used. The fuel and air were supplied separately using mass flow controllers (KOFLOC) to control equivalence ratio and inlet mean flow velocity independently. For 1-pentene, which is liquid at the standard condition, preparation of the gaseous mixture was done as follows. First, a stainless tank is evacuated using a vacuum pump and the liquid fuel was supplied using a syringe to obtain a specific pressure in the tank. And then nitrogen gas was added to the tank to form a gaseous fuel/N₂ mixture. The gaseous fuel/N₂ mixture was placed for a sufficient amount of time to assure the mixing. The gaseous fuel/N₂ mixture and pure oxygen were both controlled using mass flow controllers (Brooks). The gaseous fuel/ N₂ mixture is mixed with pure oxygen to form the gaseous fuel/O₂/N₂ mixture which was introduced to the reactor. The gaseous fuel/O₂/N₂ mixture was controlled to form the same mixing ratio as it is in fuel/air mixture. Gaseous mixture entered the reactor tube and it was heated by the reactor wall and the flame was stabilized at a certain temperature range. The stabilized stable flame was observed using a digital still camera (Nikon D800) with an optical band-pass filter (Optical Coatings Japan: DIF-BP, center wavelength 431.2 nm, FWHM 6.4 nm, transmission 60%) in order to only observe the chemiluminescence from the flame. Since the luminescence of the weak flame is very weak, the images were taken in a dark room with a long exposure time ($t = 180$ s). In addition, the obtained flame images were processed by subtracting the background image. The flame position was determined by outputting the brightness profile from the flame image and the peak point of the brightness

profile was taken.

After obtaining the flame images, the gaseous mixture was switched to air while keeping the same flow velocity as the gaseous mixture to measure the wall temperature profile. The Peclet number for the micro flow reactor system is quite small; therefore, the axial air temperature profile (without reaction) almost equals the wall temperature profile in the flow direction. The input chemical energy in the mixture is very small (ex. 0.05 W for ethylene) compared to the external heat source; therefore, the wall temperature without reaction nearly equals the wall temperature with reaction. The wall temperature profile was measured using a K-type sheathed thermocouple with a diameter of 50 μm which was inserted from the reactor exit. Measured experimental wall temperature profile is shown in Fig. 1b.

3. Computational method

One-dimensional steady-state computations were conducted using a PREMIX-based code [33] which was modified to replicate the micro flow reactor setup. A heat convection term between the gas phase and the wall was added to the energy equation [20] (the last term on the left side in Eq.1).

$$\dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left(\lambda A \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^K \rho Y_k V_k c_{pk} \frac{dT}{dx} + \frac{A}{c_p} \sum_{k=1}^K \omega_k h_k W_k - \frac{A}{c_p} \frac{4\lambda Nu}{d^2} (T_w - T) = 0 \quad (\text{Eq. 1})$$

The same wall-temperature profile of 300–1300 K as the experiment was given in T_w of the heat convection term. The Nusselt number was a constant value of $N_u = 4$ which was determined by taking the intermediate number between constant wall temperature condition ($N_u = 3.66$) and constant heat flux condition ($N_u = 4.36$) assuming fully developed flow inside the tube. The multicomponent model was employed for mass diffusion. The computational region was 10 cm long. Adaptive grid was applied and the grid size at the reaction zone was 40 μm . A detailed reaction mechanism of Natural Gas III (293 species, 1536 reactions) [34–39] developed by Curran's group from Combustion Chemistry Centre in National University of Ireland Galway (NUIG) was employed. Since transport data were not available for this mechanism, transport data of *iso*-octane mechanism [40] by the Lawrence Livermore National Laboratory (LLNL) were adopted. This set of reaction mechanisms was applied in this study for two reasons: the computational results captured the experimental tendency of the weak flame position which is discussed later; and computational results showed good agreement in the past study by Kamada et al. [41] for ethane, propane and *n*-butane which proved the reliability of the mechanism in the present micro flow reactor configuration. Computational flame position was defined as the peak of the heat release rate (HRR) profile. The same conditions in the experiment were used in the computation, i.e., $\phi = 1$, $u = 2 \text{ cm/s}$, $p = 1 \text{ atm}$ and $d = 2 \text{ mm}$.

Reaction path analysis was conducted to analyze the flame structure. Subroutine inside the CKLIB in CHEMKIN-II was used and the rate of progress for each elementary reaction was calculated. From this, the production/consumption rate of a specific species by a specific elementary reaction was calculated and the elementary reaction with high contribution in the production/consumption was chosen to analyze the reaction

path.

4. Results and Discussion

4.1 Experimental and computational weak flames of alkenes

Figure 2a shows weak flame images of ethylene, propylene, 1-butene and 1-pentene at $u = 2$ cm/s, $p = 1$ atm and $d = 2$ mm. The weak flame images on the right of fig. 2a are image processed by increasing the color level and changing it to grey scale to focus on the blue flame. Figure 2b shows experimental weak flame position where the error bars indicate half brightness width. The flow direction is from left to right. Single strong luminous zone from the hot flame was observed for all alkenes. Focusing on the weak flame positions for the four alkenes, the wall temperature values at the hot flame positions were 1120 K for ethylene, 1193 K for propylene, 1152 K for 1-butene and 1146 K for 1-pentene (Fig. 2b). Therefore, the order of weak flame position becomes ethylene, 1-pentene, 1-butene and propylene from the lower temperature side which means that ethylene has the highest reactivity and propylene has the lowest reactivity among the four alkenes.

Figure 3 shows the computational heat release rate (HRR) profiles in the same condition as the experiments for ethylene, propylene, 1-butene and 1-pentene. A sharp HRR peak which corresponds to the hot flame observed in the experiment was obtained for all four alkenes. Smaller HRR peaks right before the sharp HRR peak were obtained in the ethylene and 1-pentene HRR profiles. In the micro flow reactor studies using DME or *n*-heptane, such smaller HRR peak obtained before the hot flame HRR peak is known to correspond to the blue flame. Blue flame was also observed in the experiments for DME or *n*-heptane. In the present experiment, apparent blue flame luminescence was not observed in any of the alkenes addressed here. The reason why the computational results indicate apparent blue flame HRR peak where it is not observed in the experiments is because blue flame luminosity is very weak compared to the hot flame and the blue flame reaction itself is weaker for lower hydro carbons. Very closely looking at Fig. 2, luminous zone is spread towards the lower temperature region (region upstream of the high intensity emission). This region is most strongly seen for 1-pentene; and from previous micro flow reactor studies, blue flame is observed in this region. Therefore, the blue flame HRR seen in the computation corresponds to this region. Focusing on the weak flame position, wall temperatures at hot flame HRR peak points are 1142 K for ethylene, 1191 K for propylene, 1185 K for 1-butene and 1156 K for 1-pentene (Fig. 3). Therefore, the order

of weak flame position in the computation becomes ethylene, 1-pentene, 1-butene and propylene from the lower temperature side. The computations captured the order of weak flame positions in the experiments, while wall temperature values at the weak flame positions did not agree quantitatively between the experiments and computations except for propylene. The quantitative flame positions were different because the reaction mechanism still needs to be improved. In the previous study by Hori et. al. [25], good agreement was observed for hot flame positions using PRF. This is because the mechanism for PRF is well developed since it is one of the most studied fuels. Further study needs to be conducted to give a better agreement for alkenes and validation of reaction mechanisms using micro flow reactor could be effective.

4.2 Comparison between alkane and alkene

To compare with the alkene results in Section 4.1, micro flow reactor results for lower alkanes of ethane, propane, *n*-butane and *n*-pentane were hereafter shown. These alkanes have a similar molecular structure with the tested alkenes. The comparison was done in terms of carbon number of the hydrocarbon from C2 to C5. The results for ethane, propane and *n*-butane were taken from our past study by Kamada et al. [41] while the *n*-pentane result was newly obtained in this study.

Figure 4 shows the weak flame images of ethane, propane, *n*-butane and *n*-pentane at $u = 2$ cm/s, $p = 1$ atm and $d = 2$ mm. A strong luminosity from the hot flame was observed for all alkanes. . Focusing on the weak flame position, the wall temperature values at the hot flame are 1146 K for ethane, 1176 K for propane, 1169 K for *n*-butane and 1152 K for *n*-pentane. The order of weak flame position becomes ethane, *n*-pentane, *n*-butane and propane from the lower temperature side. Figure 5 shows the computational HRR profiles for ethane, propane, *n*-butane and *n*-pentane. The wall temperature values at the hot flame HRR peak points are 1156 K for ethane, 1172 K for propane, 1167 K for *n*-butane and 1165 K for *n*-pentane. The order of weak flame position becomes ethane, *n*-pentane, *n*-butane and propane from the lower temperature side which agrees with the experiments.

By comparing the alkene and alkane results from the perspective of the fuel carbon number, the order of weak flame position agreed where the order is C2, C5, C4, and C3 from the lower temperature side. C2

hydrocarbon possesses a high reactivity, in objective to the order of carbon number, in both alkane and alkene cases.

4.3 Flame structure of alkene

Weak flame structure for each alkene was investigated using the calculated mole fraction profiles of the species. Figure 6 shows the mole fraction profiles of reactant, product and major intermediate species for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene. The overall tendency of the oxidation process was similar for all of the alkenes; however, the temperature region where the oxidation process take place differ slightly among fuels. First of all for ethylene in Fig. 6a, with the decreases of ethylene and oxygen, CH_2O , H_2O_2 and CO begins to increase. The mole fraction peak for H_2O_2 locates at $x = 4.88$ cm where the local wall temperature is 972 K. CH_2O mole fraction peak ($x = 4.95$ cm, $T_w = 1000$ K) locates at a higher temperature than H_2O_2 mole fraction peak. CO mole fraction peak ($x = 5.17$ cm, $T_w = 1079$ K) locates at a higher temperature than CH_2O . This is due to the difference in temperature region where CH_2O oxidation to CO proceeds at lower temperatures than and CO oxidation to CO_2 . The CO oxidation to CO_2 , which is the last step of the oxidation, occurs at the sharp HRR of hot flame while H_2O_2 and CH_2O consumptions occur at the small HRR before the hot flame. For propylene in Fig. 6b, the temperature region of the whole oxidation locates at a higher temperature compared to ethylene. The peaks of the mole fractions of CH_2O and CO are at $x = 5.17$ cm ($T_w = 1079$ K) and $x = 5.47$ cm ($T_w = 1167$ K) respectively. For 1-butene in Fig. 6c, the oxidation process was very close to the case of propylene in Fig. 6b. The temperature range of the oxidation was close to that of propylene where there are small differences in the mole fraction peak positions of CH_2O at $x = 5.16$ cm ($T_w = 1076$ K) and CO at $x = 5.39$ cm ($T_w = 1146$ K). For 1-pentene in Fig. 6d, the oxidation region locates at a temperature region close to ethylene where mole fraction peaks for CH_2O , H_2O_2 and CO locate at $x = 4.91$ cm ($T_w = 984$ K), $x = 4.82$ cm ($T_w = 947$ K) and $x = 5.21$ cm ($T_w = 1092$ K). Another difference seen among the four alkenes is the concentration of H_2O_2 . In ethylene and 1-pentene, larger amounts of H_2O_2 mole fractions are observed compared to 1-butene and propylene. This is probably because in ethylene and 1-pentene, significant heat releases in the lower temperature region occur which

correspond to the blue flames. Therefore, more reaction precedes in the lower temperature region which results in higher concentrations of H_2O_2 .

4.4 Fuel consumption of alkenes

The initial step of oxidation, which is the fuel consumption, was examined to investigate the characteristics of alkene oxidation. Figure 7 shows calculated net rate of fuel consumption and rates of fuel consumption from elementary reactions with high contribution to the fuel consumption. Ethylene, propylene and 1-butene cases (Fig. 7a,b,c) show two peaks in the fuel consumption where 1-pentene case (Fig. 7d) shows only one peak. By comparing the fuels with two consumption peaks, H-atom abstraction reactions of the fuel by OH radical (R251, R471 and R735) show a significant contribution at lower temperature. H-atom addition reactions to the fuel (R163 and R721) also show high contribution at lower temperature for ethylene and 1-butene case. Unlikely, in the case of propylene, R480 is much significant compare to the H-atom addition reaction of R456. Propylene shows a different tendency because the temperature range in which the fuel consumption is taking place is at a slightly higher temperature. In R456, NC_3H_7 is formed by the H-atom addition to propylene and then fragmentizes into $\text{C}_2\text{H}_4 + \text{CH}_3$, which are the products of R480. In R480, propylene fragmentizes to $\text{C}_2\text{H}_4 + \text{CH}_3$ by H-atom addition in one-step. At the temperature range of propylene consumption, $\text{C}_2\text{H}_4 + \text{CH}_3$ are directly formed through R480 instead of forming NC_3H_7 in between. As a result, H-atom addition reactions are significant at lower temperatures in ethylene, propylene and 1-butene cases. At higher temperature, radical addition and fragmentation becomes most significant for ethylene, propylene and 1-butene cases. O-atom addition and forming $\text{CH}_3 + \text{HCO}$ for ethylene (R249)[1] and H-atom addition and forming $\text{CH}_3 + \text{C}_2\text{H}_4$ for propylene (R480). For 1-butene, R721, which is an H-atom addition to form SC_4H_9 , is most significant. The SC_4H_9 then fragmentizes to $\text{CH}_3 + \text{C}_3\text{H}_6$. As a result, 1-butene undergoes a similar process with ethylene and propylene. 1-Pentene only has one fuel consumption peak and it is mostly consumed by H-atom abstraction reaction by OH radical. This characteristic of 1-pentene consumption could be caused by two reasons. One is that the fuel consumption takes place at low temperature where OH reaction seems to be active. Second reason is that in

the view point of the molecular structure, 1-pentene has a long C-C straight chain. Therefore, the fuel consumption characteristic becomes closer to the alkane characteristic.

In the oxidation of alkane, assuming the chain reaction has started and the radical pool is formed, alkane is consumed through a reaction of $RH + X \Rightarrow R + XH$ where X is mostly OH radical and the reaction being $RH + OH \Rightarrow R + H_2O$ [1]. This was also confirmed by Kamada et al. for ethane and *n*-butane in the micro flow reactor system [32]. Unlike the alkane, alkene consumption experiences different reactions. From the analysis, alkene consumption occurs with O, H and OH radicals. One distinct reaction seen in alkenes is the H-atom addition reaction by H radical. The H-atom addition occurs at the double bond of the alkene. The double bond between two carbon atoms consists of one π -bond and one σ -bond. The π -bond energy is smaller compared with the σ -bond energies ($C=C$ sp^2 and $C-H$ sp^3 hybrid orbitals). Therefore, the π -bond of the double bond is easily broken and the H radical is added to the alkene to form an alkyl radical. H-atom abstraction reaction by OH radical, which is important for alkanes, is also important for alkenes. For example, R471, which is an H-atom abstraction reaction of propylene to form $C_3H_5\cdot$ (allyl radical), is known to be important in the oxidation of propylene [42].

4.5 High reactivity of ethylene

As it is mentioned before in Section 4.1 and 4.2, ethylene has a high reactivity compared with propylene, 1-butene and 1-pentene. In this section, the reason for this high reactivity of ethylene is examined by focusing on OH radical formation because of the reasons below. Radicals such as H, O and OH are important throughout the oxidation process. OH radical especially plays a significant role in the oxidation since OH radical reacts with key species such as fuel, CH_2O and CO. At the initial step of oxidation, significant amount of fuel is consumed through H-atom abstraction reaction with OH. Major intermediate species CH_2O reacts with OH radical to form HCO through R43: $CH_2O + OH \Rightarrow HCO + H_2O$. At the final step of oxidation CO reacts with OH radical to form CO_2 through R24: $CO + OH \Rightarrow CO_2 + H$. In addition, OH radical is also

important for the formation of H radicals which is also important in alkene fuel consumption. OH radical plays an important role and the efficient production of OH radicals enhances the combustion process.

Figure 8 shows the rate of OH production from reactions with high contribution to OH production for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene. OH radicals are produced in two regions; one is at the hot flame region where the sharp HRR peak is seen and another is at the region before the hot flame, there are significant HRR peaks of blue flames for ethylene and 1-pentene. In the hot flame region, OH radicals are highly produced by R1: $\text{H} + \text{O}_2 \Rightarrow \text{O} + \text{OH}$ and R11: $\text{HO}_2 + \text{H} \Rightarrow \text{OH} + \text{OH}$. In R24, OH radical is consumed and H radical is produced. This H radical returns to R1 and R11 to form OH radical again which reacts with CO through R24 again. This reaction loop controls the hot flame. However, from the analysis, initial build up of OH radicals in front of the hot flame becomes important. This is because; OH radical reacts with the fuel and CH_2O in this region and also the initial OH build up could affect the following hot flame. From Fig. 8, OH radicals are mainly produced through H_2O_2 decomposition reaction (R16) or reaction with HO_2 (R109 and R499). The contribution of R499 is high for propylene because $\text{C}_3\text{H}_5\text{-A}$ is a reactant in R499 as well as a product of propylene consumption (R471 and R477), which gives a high concentration of $\text{C}_3\text{H}_5\text{-A}$ to promote R499. Figure 9 shows the rate of H_2O_2 production for reactions with high contribution to H_2O_2 production for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene. R14 and R15 are defined duplicated reactions in the reaction mechanism. From the figures, H_2O_2 is produced from R14+R15 which are HO_2 combination or R47 and R332 which are H-atom abstractions from aldehyde by HO_2 radical. Therefore, HO_2 radical is very important for H_2O_2 production. Since H_2O_2 production is controlled by HO_2 radical, OH production is also controlled by HO_2 radical. Figure 10 shows the HO_2 mole fraction (Fig. 10a) and net rate of HO_2 production (Fig. 10b) for the ethylene, propylene, 1-butene and 1-pentene cases. In Fig. 10a, ethylene has the highest HO_2 mole fraction followed by 1-pentene, 1-butene and propylene. In Fig. 10b, alkene with the highest net rate of HO_2 production in the lower temperature region is ethylene followed by 1-pentene, 1-butene and propylene. Both the orders of HO_2 mole fraction and net rate of HO_2 production agree with the order of the flame position. From this reason, reactivity of different fuels could be possibly examined by looking at the OH production through HO_2 radicals at the initial oxidation process.

The high reactivity of ethylene results from the efficient production of HO₂ radicals. Figure 11 shows rate of HO₂ production from reactions with high contribution to HO₂ production for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene. HO₂ radicals are mainly produced by R27 in the lower temperature region for all the cases. R27 as well as R9, R184 and R264 in the ethylene case have significantly higher contributions compared with the other alkene cases.

Main oxidation path of ethylene was investigated to clarify the efficient production of HO₂ radicals. The reaction path analysis was conducted for the present micro flow reactor condition (equivalence ratio of 1.0, $u = 2$ cm/s, $p = 1$ atm and $d = 2$ mm) integrated along the reactor. The main reaction path found in the micro flow reactor for ethylene is illustrated in Fig. 12. As it was discussed in Section 4.4, ethylene is consumed through several reactions where they could be classified as two main paths. One is the path where ethylene is directly decomposed to HCO by R249. This path is much more effective at higher temperatures. The second is the path where ethylene is oxidized to HCO through CH₂O. Ethylene is oxidized to CH₂O through several paths. In the initial ethylene consumption, R163, R250 and R251 relate to the CH₂O formation. In R163, C₂H₅ is formed by H-atom addition to ethylene and half of it returns to ethylene through $C_2H_5 + O_2 \Rightarrow C_2H_4 + HO_2$. The other half becomes C₂H₅O through $C_2H_5 + HO_2 \Rightarrow C_2H_5O + OH$ which decomposes to CH₂O and CH₃. In R251, C₂H₃ is formed and C₂H₃ is further oxidized by O₂. Main reaction path here is $C_2H_3 + O_2 \Rightarrow CH_2CHO + O$ where CH₂CHO isomerizes to CH₃CO. CH₃CO decomposes to CH₃ and CO where CH₃ becomes CH₂O through CH₃O. Note here that some of the C₂H₃ oxidizes into C₂H₂ which leads to CO formation, and this is another oxidation path. In R250, CH₂CHO is formed and the reaction path described in the above is traced. After the formation of HCO, HCO becomes CO and it is further oxidized to CO₂ to complete the ethylene oxidization.

The reason of the high reaction rate for R27, R184 and R264 is because reactants in the reactions, HCO, C₂H₅ and C₂H₃, are products from the ethylene consumption reactions (R163, R249 and R251). This means that, these species have higher concentrations which promote the HO₂ production from R27, R184 and R264. R9 also contributes to the HO₂ reaction in the lower temperature region in ethylene's case. The high reactivity of ethylene comes from the efficient production of HO₂ radicals which leads to high OH production. The

significant blue flame peak in the computational HRR profile possibly comes from the effect of these reactions actively proceeding.

4.6 Blue flame HRR of ethylene

Computational HRR of ethylene showed significant HRR peak at the blue flame region where there were no corresponding luminosity observed in the experiment. One possibility for this is from the effect of H_2O_2 decomposition reaction. The importance of H_2O_2 decomposition reaction to OH radical formation has been pointed out for a long time [43,44]. In a recent study by Kuwahara et al. [45], the authors proposed an effect of a reaction loop initiated by H_2O_2 decomposition. This reaction loop is composed of four reactions, $\text{H}_2\text{O}_2 + \text{M} \rightarrow 2\text{OH} + \text{M}$, $\text{OH} + \text{CH}_2\text{O} \rightarrow \text{HCO} + \text{H}_2\text{O}$, $\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$ and $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ [45]. In this reaction loop, overall reaction becomes $2\text{CH}_2\text{O} + \text{O}_2 \Rightarrow 2\text{H}_2\text{O} + 2\text{CO} + 473 \text{ kJ}$ where heat is generated without the consumption of H_2O_2 . The heat release rate depends on the H_2O_2 concentration and the amount of heat depends on the CH_2O concentration. This reaction loop is said to be active until the start of thermal ignition. The effect of the reaction loop discussed by Kuwahara et al. is that a significant amount of heat produced by this reaction loop increases the temperature up to where the thermal ignition occurs. This means that the thermal ignition occurs faster with the reaction loop activated due to the quick temperature raise. When Tanaka et al. applied ethane in a homogeneous charge compression ignition (HCCI) engine condition [46], they pointed out that the enhanced ignition of ethane comes from the efficient HO_2 production which leads to this reaction loop.

Considering this significant heat release from this reaction loop, HRR peak of the blue flame obtained in the ethylene probably relates to this effect. Table 1 shows the top twenty reactions which contribute to the heat release at HRR peak of the blue flame. The exothermic reactions mentioned in the H_2O_2 reaction loop [45] show significant contribution to HRR of the blue flame in the micro flow reactor. As it is discussed before, ethylene has an efficient HO_2 production which leads to this reaction loop to produce a significant heat release at the blue flame region. The possibility for the reason why the blue flame was not observed experimentally for ethylene was that the CH chemiluminescence is not significant in this reaction loop.

5. Conclusions

Four alkenes of ethylene, propylene, 1-butene and 1-pentene were applied to a micro flow reactor with a controlled temperature profile to investigate their combustion and ignition characteristics based on their weak flames. Single luminous zone of hot flame was observed in the experiment for all four alkenes. The order of weak flame position in the experiment was ethylene, 1-pentene, 1-butene and propylene from the lower temperature side. One-dimensional computations using detailed reaction mechanism captured the order of experimental weak flame positions. Alkene results were compared with conjugate alkanes of ethane, propane, *n*-butane and *n*-pentane. The comparison was conducted in the perspective of carbon number in these fuels. Carbon number dependency of the order of weak flame position agreed between alkene and alkane cases.

Further analysis was conducted for the weak flames using the computation. From the mole fraction profiles of major species, a similar flame structure was obtained for the four alkenes. Difference was seen in the H_2O_2 mole fraction. A significant amount of H_2O_2 was only seen in ethylene and 1-pentene cases. Rate of consumption was investigated to clarify fuel consumption of the four alkenes. Reactions with O, H and OH radicals proceed in the fuel consumption of alkenes. H-atom addition reaction of alkene where the reaction occurs at the double bond of the alkene is a unique reaction compared with the alkane and consumes a significant amount of the fuel. H-atom abstraction reaction with OH, which is important in alkane, is also important in the alkene consumption.

Reaction path analysis was conducted to examine the high reactivity of ethylene. Ethylene oxidation could be classified into two main paths; one is the path where ethylene is directly decomposed to HCO by R249: $\text{C}_2\text{H}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{HCO}$ and another is the path where ethylene is oxidized to HCO through CH_2O . OH production through HO_2 in the initial stage of oxidation is important against the weak flame position. Ethylene has a high rate of HO_2 production through R27: $\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$, R184: $\text{C}_2\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{HO}_2$ and R264: $\text{C}_2\text{H}_3 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_2 + \text{HO}_2$ because the reactants of HCO, C_2H_5 and C_2H_4 are the products in ethylene consumption reactions which gives high concentration of these species. Therefore, these reactions of R27, R184 and R264 becomes promoted and results in the high HO_2 production.

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List of captions for figures and Table

Figure 1. (a) Schematic diagram of the experimental setup and (b) experimental and computational wall temperature profile.

Figure 2. Weak flame images of ethylene, propylene, 1-butene and 1-pentene at $u = 2$ cm/s, $p = 1$ atm, $t = 180$ s and $d = 2$ mm. Temperature values on the right indicate the wall temperature values at the weak flame positions.

Figure 3. Computed HRR of ethylene, propylene, 1-butene and 1-pentene at $u = 2$ cm, $p = 1$ atm and $d = 2$ mm. Temperature values indicate the wall temperature values at the peaks of HRR.

Figure 4. Weak flame images of ethane, propane, *n*-butane and *n*-pentane at $u = 2$ cm/s, $p = 1$ atm, $t = 60$ s and $d = 2$ mm [32]. Temperature values on the right indicate the wall temperature values at the weak flame positions.

Figure 5. Computed HRR of ethane, propane, *n*-butane and *n*-pentane at $u = 2$ cm/s, $p = 1$ atm and $d = 2$ mm [32]. Temperature values indicate the wall temperature values at the peaks of HRR.

Figure 6. Profiles of mole fraction of major species and HRR in (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene weak flames at $p = 1$ atm.

Figure 7. Net rate of fuel consumption and rate of fuel consumption from elementary reactions for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene. Arrows indicate peak points of HRR.

Figure 8. Rate of OH production from reactions for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene at $p = 1$ atm. Arrows indicate peak points of HRR.

Figure 9. Rate of H₂O₂ production from reactions for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene at $p = 1$ atm. Arrows indicate peak points of HRR.

Figure 10. (a) Profiles of HO₂ mole fraction and (b) net rate of HO₂ production for ethylene, propylene, 1-butene and 1-pentene at $p = 1$ atm. Arrows indicate peak points of HRR.

Figure 11. Rate of HO₂ production from reactions for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene at $p = 1$ atm. Arrows indicate peak points of HRR.

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* Exothermic reaction in the H₂O₂ reaction loop [35].

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(b) experimental and computational wall temperature profile .

Shogo Kikui

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Shogo Kikui

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Shogo Kikui

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Shogo Kikui

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Shogo Kikui

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Shogo Kikui

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Shogo Kikui

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Shogo Kikui

Figure 9. Rate of H_2O_2 production from reactions for (a) ethylene, (b) propylene, (c) 1-butene and (d) 1-pentene at $p = 1$ atm. Arrows indicate peak points of HRR.

Shogo Kikui

Figure 10. (a) Profiles of HO_2 mole fraction and (b) net rate of HO_2 production for ethylene, propylene, 1-butene and 1-pentene at $p = 1$ atm. Arrows indicate peak points of HRR.

Shogo Kikui

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Shogo Kikui

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Shogo Kikui

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* Exothermic reaction in the H_2O_2 reaction loop [35].

Elementary Reaction	HRR [kW/cm ³]	Contribution to HRR [%]
* $\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$	1.26E-03	14
$\text{C}_2\text{H}_3\text{O} + \text{H}_2 \rightleftharpoons \text{CH}_3\text{CO}$	5.13E-04	6
$\text{C}_2\text{H}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{HCO}$	4.86E-04	5
$\text{HO}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	4.75E-04	5
* $\text{CH}_2\text{O} + \text{OH} \rightleftharpoons \text{HCO} + \text{H}_2\text{O}$	4.44E-04	5
$\text{C}_2\text{H}_4 + \text{H} (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_5 (+\text{M})$	3.97E-04	4
$2\text{CH}_3 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_6 (+\text{M})$	3.95E-04	4
$\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{OH}$	3.92E-04	4
$\text{H} + \text{O}_2 (+\text{M}) \rightleftharpoons \text{HO}_2 (+\text{M})$	3.92E-04	4
$\text{HO}_2 + \text{H} \rightleftharpoons 2\text{OH}$	3.65E-04	4
$\text{C}_2\text{H}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{HCO}$	2.88E-04	3
$\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_4 + \text{O}_2$	2.71E-04	3
$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$	2.37E-04	3
* $\text{H}_2\text{O}_2 + \text{O}_2 \rightleftharpoons 2\text{HO}_2$	1.79E-04	2
$\text{HCCO} + \text{O}_2 \rightleftharpoons \text{OH} + 2\text{CO}$	1.67E-04	2
$\text{CH}_2\text{O} + \text{H} \rightleftharpoons \text{HCO} + \text{H}_2$	1.59E-04	2
$\text{C}_3\text{H}_8 (+\text{M}) \rightleftharpoons \text{CH}_3 + \text{C}_2\text{H}_5 (+\text{M})$	1.30E-04	1
$\text{C}_2\text{H}_4 + \text{OH} \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	1.26E-04	1
$\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$	1.19E-04	1
$\text{C}_2\text{H}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CHO} + \text{O}$	1.11E-04	1