FLAME CHROMATOGRAPHY IN A MICRO CHANNEL WITH A TEMPERATURE GRADIENT

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Abstract: For the development of microcombustor for tiny heat sources, characteristics of gas-phase combustion in a meso-scale channel with a prescribed wall-temperature profile have been examined. Results showed that the existence of the separated multiple weak flames at various temperature levels in addition to oscillatory flames and normal propagating flames for the first time. It is then recognized that the present multiple weak flame phenomena can be applied for examining multi-stage oxidation of hydrocarbon fuels in a wide temperature range. Based on the preliminary experiments with several fuels including primary reference fuel of gasoline, research octane number (RON) of the test fuels can be clearly described by the aspects of stabilized multiple weak flames. Effects of ethanol mixing on practical hydrocarbon fuels can also be described by the multiple weak flames. The methodology can be termed “flame chromatography” and it is expected to be applied for the fuel indexing of future alternative fuels and the development of control strategy in practical combustion devices. Further system miniaturization is expected with the help of micro fabrication technology.

Keywords: Microcombustion, Weak flames, Micro flow reactor

INTRODUCTION

For developing clean and efficient spark-ignited and compression-ignition engines, profound understandings and delicate control on their combustion processes are required. Since hydrocarbon fuels and most of the alternative fuels exhibit multi-stage ignition phenomena which are specific to each fuel, understanding and high fidelity prediction of their chemical reaction process are essential for designing efficient combustion devices. Numerous studies on chemical reaction mechanisms for various fuels have been conducted [e.g., 1] and for the validations, reliable experimental data had been provided based on experiments with shock-tube [2], stirred reactor [3], flow reactor [4], rapid compression machine [5] and so forth. In general, however, these experimental methods require intricate setup with special techniques and skills for obtaining reliable data. Therefore, simple and easy method for obtaining reliable ignition and chemical reaction data has been expected to be realized. During the development of microcombustor for heat sources, series of coincidences led to the development of the methodology that can be termed flame chromatography, which enables to visualize multi-stage oxidation process from low to auto-ignition temperatures of test fuels. The method, a micro flow reactor with a prescribed temperature profile is introduced in this manuscript.

MICRO COMBUSTORS FOR HEAT SOURCES

Swiss roll microcombustors for heat sources (Fig. 1) which have nearly doubled thermal efficiency compared with ordinary electric heaters and temperature controllability within one degree in the temperature range from 673 to 1173 K, have been developed [6]. The combustor has a heat recirculating double spiral channel as shown in fig. 1, and stable combustion in the space smaller than the ordinary quenching distance for given fuel was achieved. For the development, fundamental studies on combustion in a meso-scale channel with a prescribed temperature profile were conducted for examining flame response in a narrow space surrounded by hot walls [7]. While it is originally motivated by the development of the Swissroll combustion heaters, it was then realized that the method can be applied for examining ignition and combustion characteristics including multistage oxidation process from low to auto-ignition temperatures for various fuels.

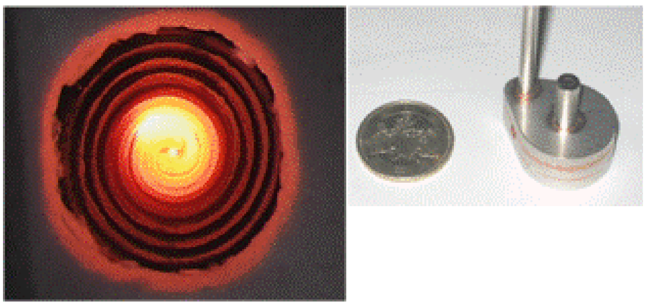

Fig. 1: Swiss roll microcombustors for heat sources, left, micro combustor with outer diameter of 64 mm in operation and right, coin-size micro combustor with o. d. of 26 mm. Swiss roll configuration has a spiral channel with an inlet and an outlet which enables effective heat recirculation from the burned gas with the incoming fresh mixture. Stable combustion is possible in a space that is smaller than the classical quenching diameter due to the strong heat recirculation (high temperature wall).

MICRO FLOW REACTOR WITH A PRESCRIBED TEMPERATURE PROFILE

Figure 2 shows a micro flow reactor with a prescribed temperature profile [7]. It consists of a meso-scale channel and an external heat source. A straight quartz tube with an inner diameter of 2 mm was used. The inner diameter of the tube was chosen so that it is smaller than the classical quenching diameter. Axial temperature profile was formed along the channel wall and ignition and combustion characteristics of given mixture can be observed as several modes of combustion which will be described below. By this method, reactive fluid behavior in laminar, small-scale channel with temperature gradient can be observed. Prescribed temperature profile can be regarded as stationary during combustion, particularly at lower inlet mixture flow velocity condition.

In general, three kinds of flames were observed at various inlet mixture flow velocities. Examples of flame images for methane/air mixture [7, 8] are shown in fig. 3. The images are a) normal, b) non-stationary oscillating and c) weak flames. Normal and weak flames are stationary laminar flames, while non-stationary flame exhibits oscillatory combustion which will be denoted below. Stabilized weak flame has propagation velocity at a couple of mm/s to cm/s. Overall flame response as a function of the inlet mixture flow velocity for stoichiometric methane/air mixture is shown in Fig. 4 [7, 8]. In the high velocity condition, normal flames were observed. The stabilized locations of normal flames shift to the upstream with the decrease of inlet mixture flow velocity.

In the intermediate velocity condition, luminous reaction zones appeared to be broadened were observed. An ignition kernel starts emitting luminescence from the point of ignition in the downstream high-temperature region and it propagates to upstream. Then it is quenched due to the large heat loss by the low temperature wall in the upstream. After some time delay, re-ignition occurs at the original ignition point. This cycle is repeated regularly. Thus, this oscillating flame phenomenon is termed as flames with repetitive extinction and ignition (FREI) [7]. Ignition and extinction points shift to the upstream side with the decrease of flow velocity. Extinction points shift to downstream and merged into ignition points near the lower velocity boundary with the low velocity condition.

In the low velocity condition, stationary flames with extremely low luminosities were observed. Long exposure was required to record those weak flame images. As shown in Fig. 4, the stabilized locations of weak flames were very close to or on the extrapolated line of the ignition positions of FREI. Therefore, weak flame temperatures are considered to be equal or close to the ignition temperature for that condition. This hypothesis was later confirmed by an independent detailed theoretical analysis [9]. Ignition points in the FREI region are connected with locations of weak flames.

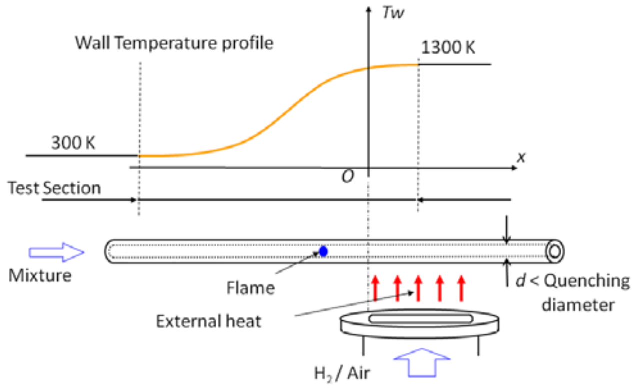

Fig. 2: Scheme of an apparatus consists of a meso-scale quartz channel and external heat source [7, 8]. Gas phase temperature profile is significantly governed by the prescribed temperature profile. Thus oxidation process in the channel is determined by the given temperature profile rather than the heat generation by itself particularly at low flow velocity.

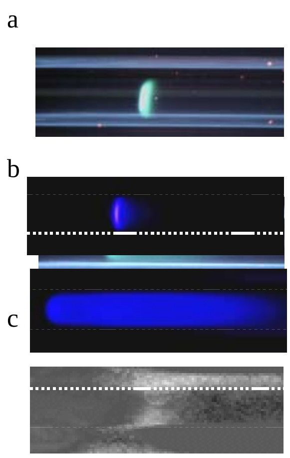

Fig. 3: Images of a) normal flame, b) Flames with repetitive extinction and ignition (FREI) and c) weak flames [7, 8].

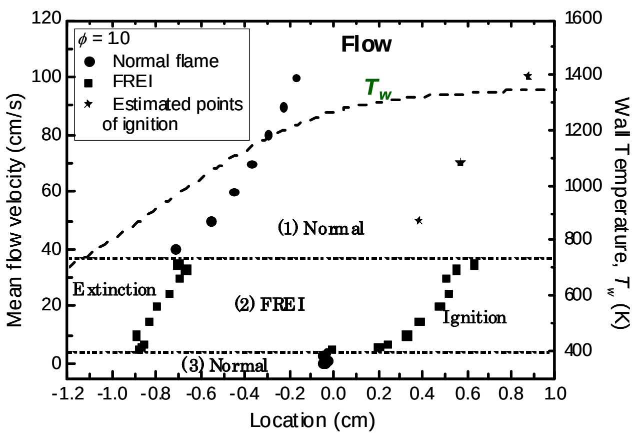

Fig. 4: Measured flame position and extinction and ignition points of FREI at various mean flow velocities for equivalence ratio, ϕ = 1.0. Estimated ignition locations in upper normal flame regime are also indicated [7, 8].

LOWER LIMIT OF WEAK FLAMES AND ITS CORRELATION WITH THE IGNITION TEMPRATURE

In the low velocity condition, no flame can be observed if the flow velocity is less than 0.2 cm/s, although weak flame at an inlet mixture flow velocity at 0.2 cm/s was observed [8]. This implies that the existence of lower limit of weak flames.

Figure 5 shows the temperature difference between the flame and the inner surface of the tube wall at the flame position measured by a thermocouple [8]. The temperature differences get smaller with the decrease of inlet mixture flow velocity and are almost zero at flow velocity is 0.2 cm/s, where the wall temperature is around 1225 K for all the equivalence ratios. This shows that the temperature differences between the flame and the wall approach to zero at the limit. It is noted that thermal quenching by intrusive thermocouple measurements is hard to occur due to the existence of the external heater in the present system since the thermocouple is inserted from the downstream side where the temperature of the leading wire of the thermocouple is maintained at high temperature and has a small temperature gradient in it. Based on two characteristics of weak flame at the limit, that is, 1) nearly zero temperature increase and 2) flame location close to the ignition point, flame temperature at the lower limit of weak flame can be considered as the lowest possible ignition temperature of the given mixture at given condition.

This also interprets that weak flame phenomena represent the ignition property of the given fuel and weak flame branch corresponds to the ignition branch in the Fendell curve.

For further understandings, reactive flow in the heated channel was modeled as a plug flow and heat transfer between wall and mixture was considered. Nusselt number was selected to be constant (Nu = 4) based on the facts that it is 4.36 for a constant heat flux and 3.66 for constant wall temperature for a steady, fully developed and laminar flow of a constant density fluid. Detailed chemical reaction of methane/air mixture was computed with GRI-Mech 3.0. Wall temperature profile was given as a steady temperature profile to the computation. This assumption is reasonable particularly at the low velocity condition, which is the main interest of the present study.

Figure 6 shows computational flame position as a function of the inlet mixture flow velocity. Flame response shows total four branches in the figure and the stable high velocity branch (1) and stable low velocity branch (3) are supposed to be normal and weak flames in Fig. 4. The intermediated velocity branch (2) is unstable and thus, FREI in the above discussion should be observed in this velocity condition. Another notable feature of the figure is the existence of extremely low velocity branch (4) which is supposed to be unstable. This implies the existence of lower limit of weak flame branch (3), which was observed experimentally. Lower limit of weak flames was considered to be induced by species dissipation of chemical intermediates due to mass diffusion based on the detailed examination of chemical species distributions [8].

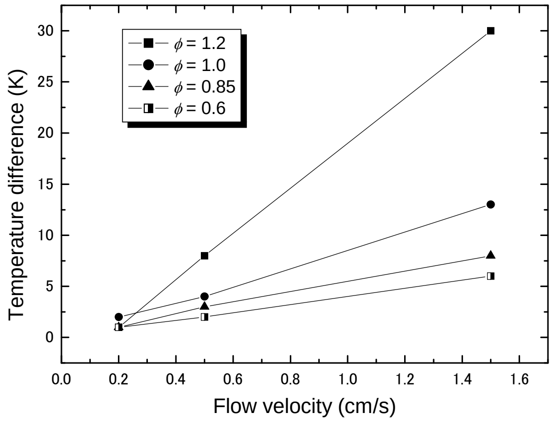

Fig. 5: Measured temperature difference between flame and the inner surface of the tube wall at the flame position (ϕ = 0.6, 0.85, 1.0 and 1.2) [8]. Temperature difference reduced to almost zero at lower flow velocity.

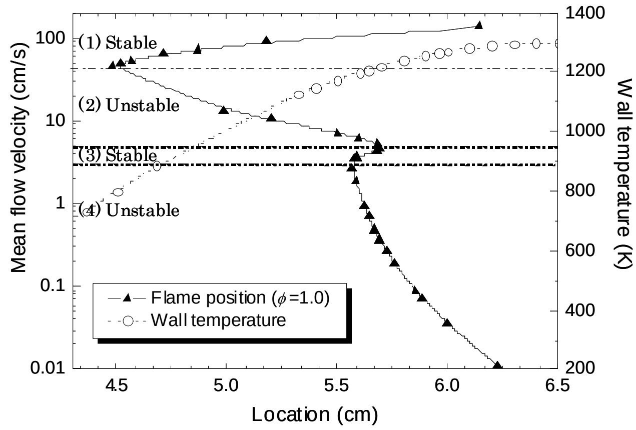

Fig. 6: Computational flame position as a function of inlet mixture flow velocity (ϕ = 1.0) [8]. Note that vertical axis for mean flow velocity is in log scale.

MULTIPLE WEAK FLAMES AND MULTISTAGE OXIDATIONS

Since weak flame behavior is expected to represent ignition properties of the tested fuels, higher hydrocarbon fuels which normally exhibit multiple oxidation characteristics were examined. As a representative of hydrocarbon fuels, n-heptane was chosen here. By injecting a liquid fuel into air flow by a syringe, gaseous mixture of n-heptane and air was applied for the present micro flow reactor. Results show that flame responses with typical three types of flames, as was observed in the case of methane, at the various inlet mixture flow velocities were observed. Multiple stationary weak flames observed at the flow velocity of 3.0 cm/s is indicated in Fig. 7 [10]. Long exposure up to a couple of minutes is required to capture such image.

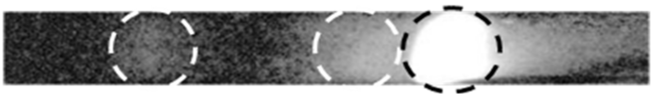

Fig. 7: Multiple weak flames observed at inlet mixture flow velocity of 3.0 cm/s for n-heptane/air mixture (ϕ = 1.0) [10]. Flow direction is from left to right.

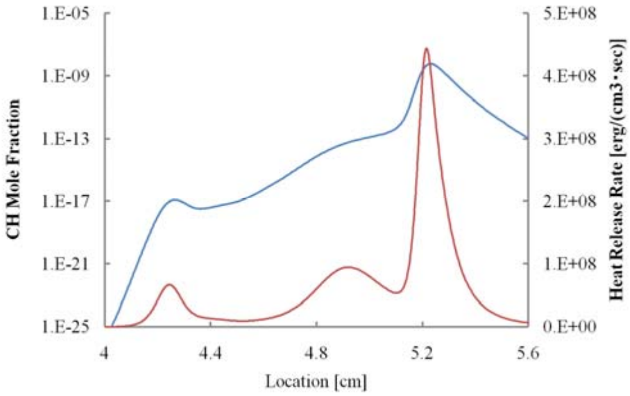

Fig. 8: Computational CH and heat release rate profiles for multiple weak flames observed at inlet mixture flow velocity of 3.0 cm/s for n-heptane/air mixture (ϕ = 1.0) [10].

CH filtered still camera was used for the flame observation. The figure shows that the existence of the three luminous zones at the wall temperatures around 750, 925 and 1190K. For examining origin of these luminous zones, the plug flow model computation with reduced chemistry of n-heptane [11] was conducted. Computational CH and heat release rate profiles are shown in Fig. 8 [10]. Three peaks were seen in the heat release rate profiles and the increases in the CH fraction were also found. Therefore, these three heat release rate peaks are supposed to be experimental three luminous zones. For further examinations, species concentration measurements and computational species concentration profiles, respectively shown in figs. 9 and 10, are compared. Experimental species concentration profiles were obtained by probe sampling and GC analysis. Measured and computational concentration profiles are qualitatively in good agreement showing the typical C1 reaction path along the temperature increase in the micro flow reactor. That is, with the progress of decomposition of the fuel, CH2O production which is a typical sign of the progress of low-temperature reaction was started around 600K. And then the CO and CH4 peaks were seen around 1000K and finally main reaction proceeded around 1200K.

Based on these experimental and computational observations, the experimental first, second and third luminous zones can be interpreted as cool, blue and hot flames which were observed under the special conditions such as reduced pressure chamber experiments. Accordingly, multiple reaction zones which correspond to the multi-stage oxidation can be observed as plural stationary weak flames by the present micro flow reactor. That is, multi-stage oxidation, which is usually observed in compression ignition phenomena, is converted into stationary, multiple steady weak flames in this reactor.

It is indicated that the reaction temperatures of these weak flames (wall temperatures at the each reaction zone) can be regarded as the multi-stage ignition temperatures of the fuel.

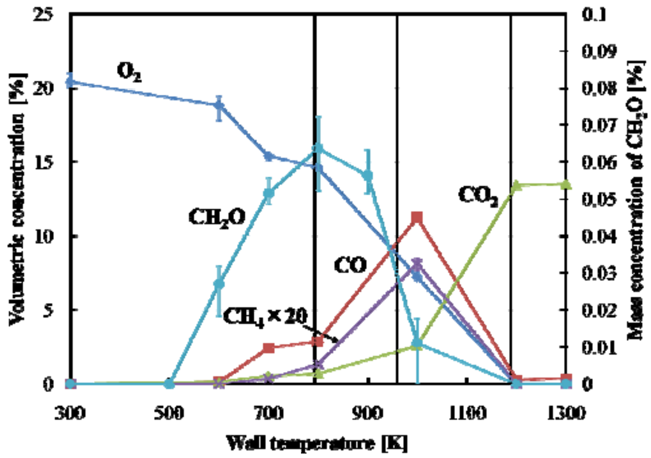

Fig. 9: Measured species concentration profiles of O2, CH2O, CH4, CO and CO2 in multiple weak flames at inlet mixture flow velocity of 3.0 cm/s for n-heptane/air mixture (ϕ = 1.0). Three vertical lines are locations of three weak flames [10].

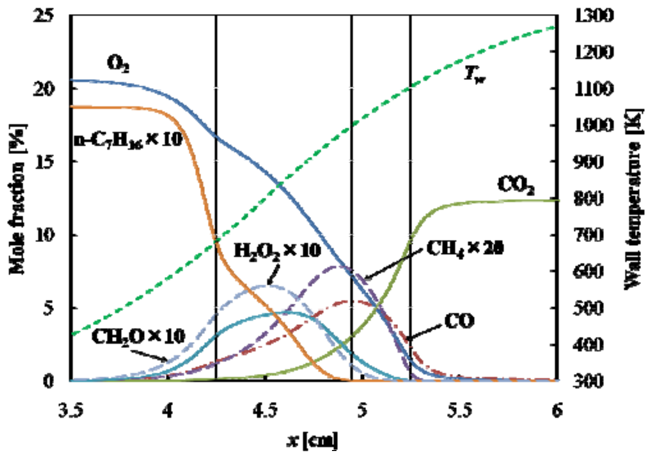

Fig. 10 Computational species concentration profiles of various chemical species in multiple weak flames at inlet mixture flow velocity of 3.0 cm/s for n-heptane/air mixture (ϕ = 1.0). Three vertical lines are locations of three heat release rate peaks [10].

Fundamental experiment was initiated by the methane case which does not exhibit multiple weak flames. On the other hand, multiple weak flames were obtained for DME [12], n-heptane [10], iso-octane [13] and several other hydrocarbon fuels. These phenomena are expected to be utilized for studying combustion and ignition characteristics of various practical fuels. At this stage, it is inferred that the present micro flow reactor is expected to be utilized for characterization of ignition properties of various fuels such as bio and synthetic fuels which generally exhibit different ignition characteristics.

FLAME CHROMATOGRAPHY: OCTANE NUMBER EVALUATION BASED ON WEAK FLAME APPEARRANCE

Based on the above results, it is expected that the present micro flow reactor possess the capability for fuel characterization. Since development of modern SI and compression-ignition engines with higher efficiency and lower emission requires understanding on fuel ignition properties, blended fuel of n-heptane and iso-octane is applied for examining fuel indexing capability of the present micro flow reactor. The blended fuel of n-heptane and iso-octane is known as the simplest primary reference fuel (PRF), which represents the ignition characteristics of gasoline. As extensively known, the mixing ratio of n-heptane and iso-octane corresponds to research octane number (RON), which is an index of anti-knocking capability. Experiments and computation were conducted in the same manner with the approach for the case of n-heptane using PRF.

Weak flame responses of fuels with RON of 0, 20, 50 and 100 were examined at the inlet flow velocity of 1.2 cm/s [13]. PRF0 denotes the 100% of n-heptane. Figure 11 shows that weak flame images for the cases of these fuels. For PRF0 (n-heptane 100%), two luminous zones in the downstream high temperature region and an additional weak luminous zone in the low temperature region which corresponds to a cool flame were observed. This three-stage oxidation process of n-heptane is identical to the previous observation in the above [10]. Luminosity of the cool flame was weakened for PRF20. However, cool flame could not be observed for PRF50 and PRF100. These observations show that luminosity of cool flame decreases with the increase of RON. Note also that main flame location shifted to the higher temperature with the increase of RON. Such tendency qualitatively agrees with anti-knocking ability of PRF.

Computation with the detailed reaction mechanism of PRF by Curran et al. [14] was also conducted. Figure 12 shows the computational heat release rate profiles for fuels of PRF 0, 20, 50 and 100 at the inlet flow velocity of 1.2 cm/s. Prescribed temperature profile is also shown in the figure.

For PRF 0, three peaks of the heat release rate profile were seen at x = 4.25, 4.98 and 5.33 cm. Based on the gas sampling analysis, these three reactions correspond to the three luminous zones observed in the case of PRF0/air in Fig. 11. Note that the peak value of the heat release rates at the cool flames decrease with the increase of RON, and no heat release can be seen at the cool flame location for PRF100. Main flame locations shifted to downstream with the increase of RON. Overall tendencies of experimental and computational weak flame response are qualitatively in good agreement.

Investigations on reaction characteristics in each separated temperature region for fuels with different research octane number showed that the capability of the present micro flow reactor for obtaining ignition characteristics of practical fuels. Further understandings on the ignition properties of alternative fuels as well as fuel indexing based on the weak flame aspects which systematize ignition characteristics of practical fuels are expected in the future.

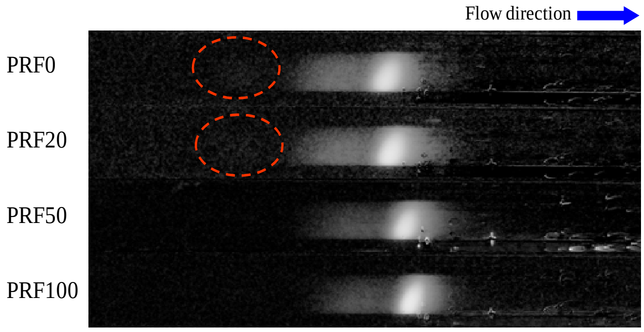

Fig. 11: Experimental weak flame images observed at the inlet mixture flow velocity of 12 mm/s for PRF/air mixture of RON 0, 20, 50 and 100 (ϕ = 1.0) [13].

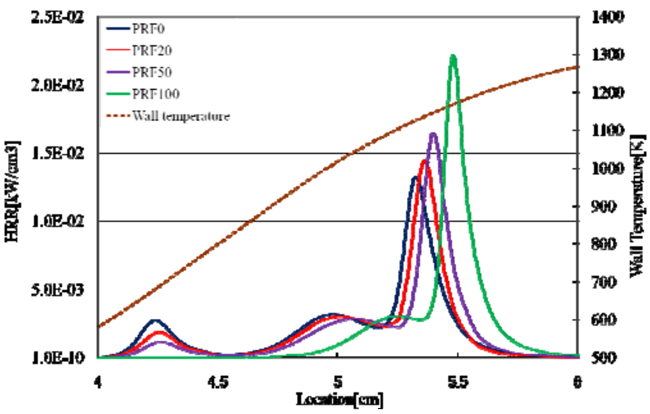

Fig. 12: Computational heat release rate profiles in weak flames at the inlet flow velocity of 12 mm/s for PRF/air mixture of RON 0, 20, 50 and 100 (ϕ = 1.0) [13].

CONCLUSIONS

During the development of microcombustor for heat sources, combustion in a meso-scale channel with temperature gradient was investigated by a straight quartz channel with an external heat source. Three types of general flame responses, normal, oscillating and weak flames were observed. It is then realized that the weak flame branch has a lower limit and it is able to represent ignition characteristics of test fuels.

Higher hydrocarbons are applied for the identical method, and multiple stationary weak flames which correspond to multi-stage oxidation are successfully observed. For examining the fuel indexing capability of the present method, blended fuels of n-heptane and iso-octane, primary reference fuel of gasoline, were applied. Results showed that stationary three weak flames which correspond to cool, blue and hot flames were observed for PRF0. However, only a weak luminosity was observed for the cool flame of PRF20 and no cool flame could be observed for PRF50 and 100. Computational results support the experimental results showing that cool flame intensities decrease with the increase of RON. On the other hand, main flame location shifted to higher temperature region with the increase of RON. This is also supported by the computations. These weak flame behaviors qualitatively represent the anti-knocking capability of PRF. It is expected that the present micro flow reactor can be utilized for future fuel indexing.

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