# The effect of surface reactions on gas-phase reactions of $CH_4$/Air mixture in a micro flow reactor with a controlled temperature profile

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## 1 Introduction

For the downsizing of mobile devices, the demand for micro power source are increasing. Micro combustion systems are expected to be one of the possible power sources having high energy density. Due to a large surface-to-volume ratio, the ratio of heat loss to the wall to heat generation increases in micro combustion and it is difficult to maintain a stable combustion. Therefore, it is important to clarify the effect of radical quenching at the wall surface on gas-phase reactions. However, there exist few comparisons between experimental and numerical studies on the effect of radical quenching on gas-phase reactions.

Raimondeau et al. [1] simulated micro scale methane-air mixture at high temperature micro burners with radical quenching mechanisms. They showed that the heat loss at the burner lip and radical quenching at the wall surface are key components for flame propagation in micro devices. Saiki et al. [2] investigated the spatial radical distributions provided by methane-air premixed flame formed at the inlet of a narrow planar channel with different wall materials by OH-PLIF and numerical simulation. They shows that radical quenching exist even on the quartz wall at high temperatures.

This study attempts to provide additional knowlege on the effect of radical quenching on both gas-phase reactions and flames stabillized in gas-phase by a micro flow reactor with a controlled temperature profile [3]. In the micro flow reactor, a quartz glass tube with an inner diameter smaller than the ordinary quenching diameter is heated by an external heat source so as to have a stationary temperature profile along the inner surface of the tube in the axial direction. A fuel/air mixture flows into the tube, and then a flame is formed in the tube. Due to the small inner diameter, the gas-phase temperature in the tube strongly depends on the temperature of the inside surface of the tube. Flow in the tube is laminar and pressure in the tube is constant. In previous studies, combustion characteristics

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in the micro flow reactor were investigated for methane/air [4], DME/air [5], *n*-heptane/air [6] and gasoline PRF/air [7] mixtures. These studies proved that the availability of the micro flow reactor as the method to examine the combustion characteristics of various fuels and showed possibility for validation of chemical kinetics by comparison between experiment and computation.

In this study, we applied $CH_4$ to the micro flow reactor as a fuel. The objective of this study is to examine the quantitative effect of radical quenching on the gas-phase reaction, i.e., $CH_4$/Air flames. The flame locations were measured and gas sampling analysis was conducted. The results were compared with two-dimensional computation including detailed gas-phase kinetics with/without radical quenching reaction mechanism.

# 2 Experimental / Computational methods

## 2.1 Experimental method

Figure 1 shows a schematic of the experimental setup. A quartz tube was used as a reactor channel and its inner diameter, *d*, was chosen to be 1.5 and 2.0 mm in this study. The quartz tube was heated by a $H_2$/air flat-flame burner to obtain a stationary temperature profile from 300 K to 1300 K along the inner surface of the tube in the axial direction. A stoichiometric $CH_4$/Air mixture was supplied into the tube at atmospheric pressure. Flow rates of $CH_4$ and air were controlled by mass flow controllers. An inlet mean flow velocity, *U*, was chosed to be 50 cm/s (for $d$ = 2.0 mm) and 60 cm/s (for $d$ = 1.5 mm) which are near lower limit of the stable planer flame branch [4]. Images of the flame were captured with a digital still camera. The camera was equipped with optical band-pass filters (transparent wavelength: 431.4 nm, half bandwidth: 6.4nm) for better observation of chemiluminecsence from hydrocarbon flames by filtering thermal radiation from the heated tube. The exhaust gas was analyzed by a gas chromatograph with a thermal conductivity detector. Helium was used as a carrier gas. Shincarbon ST was used as a column. Gas sampling was conducted with micro-syringe (Hamilton: 1700 series) at the exit of the tube. $CH_4$, $O_2$, CO, $CO_2$ and $N_2$ gases were measured. Absolute calibration method using standard gases was employed.

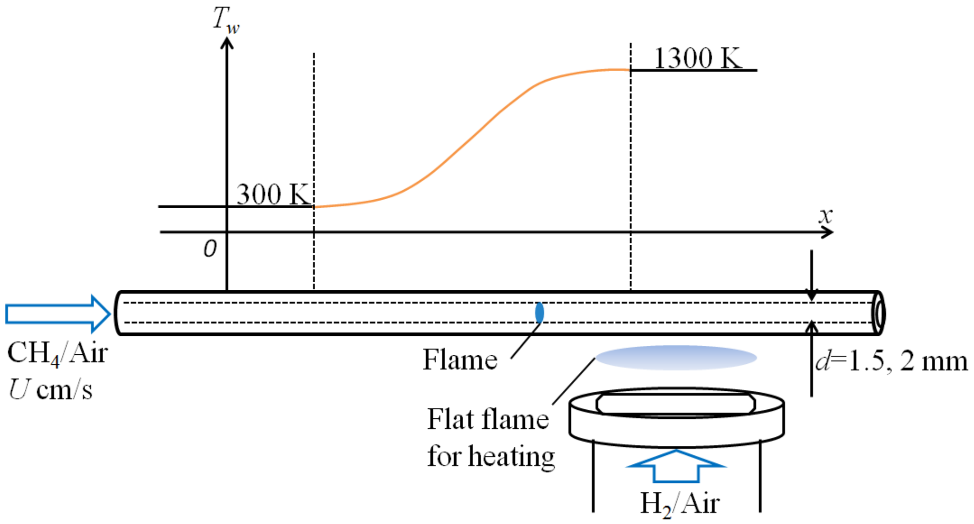

Figure 1. Experimental setup.

## 2.2 Computational method

Two-dimensional computations were conducted by FLUENT 6.3.26 considering gas-phase and surfase reactions. The pressure-based conservation equations of mass, momentum and energy were solved. Because of the symmetry of the cylindrical tube, the computational domain was a half of the tube (100 mm in the axial direction and from central axis ($r$ = 0 mm) to the wall ($r$ = 0.5$d$ mm) in the radial direction). The number of grids was chosen to be 500×10 in the axial and radial direction. The boundary condition of the wall surface was modeled as non-slip wall and a specified wall temperature profile which is the same as the experimental wall-temperature profile was given to the wall surface. GRI mech-3.0 [8] without N reactions was used as a detailed gas-phase chemical mechanism. In order to evaluate the effect of radical quenching on the gas-phase reactions, two surface conditions were considered; (a) the inert wall case: gas-phase kinetics without surface reactions and (b) the quench wall case: surface reactions of radical quenching and gas-phase kinetics. Hereafter, terms of “inert” and “quench” will be used for describing these two kinds of walls. The surface reaction mechanism for radical quenching by Raimondeau et al. [1] was employed. The flame location was defined as CH peak at $r$ = 0 mm because chemiluminescence of $CH_4$/air flame mainly comes from excited CH.

# 3 Results and discussion

Figure 2 shows the computational distributions of $CH_4$, $O_2$, $CO_2$ and $H_2O$ mole fractions on the axis ($r$ = 0 mm) at the flow velocity of 50 cm/s in the inert case for $d$ = 2 mm ($\phi$ = 1.0). Gas-phase and wall temperature plofiles on the wall surface ($r$ = 1 mm) are also shown in Fig 2. $CH_4$ and $O_2$ were rapidly consumed, and then $CO_2$ and $H_2O$ were produced in a reaction zone.

Figures 3 and 4 show the computational distributions of CH mass fractions at $d$ = 2.0 and 1.5 mm for (a) inert and (b) quench cases. The dashed red lines indicate the experimentally observed flame locations. In both Figs. 3 and 4, there is no significant difference in the flame locations between the inert and quench cases. The computational flame locations agree well with the experimental results. These results indicate that there is no significant effect of radical quenching on the flame locations.

Figure 5 shows the mole fraction profile of CO on the axis ($r$ = 0 mm) and the wall ($r$ = 1 mm) for $d$ = 2.0 mm in the inert and quench cases. On the axis ($r$ = 0 mm), the CO profile in the inert case agrees well with that in the quench case at the reaction zone. Behind the reaction zone, however, CO mole fraction in the inert case is smaller than that in the quench case. This tendency can be also seen on the wall ($r$ = 1 mm). The difference in CO mole fractions between the inert and quench cases can be seen at the exit of the quartz tube. The flame location was not affected by radical quenching but CO mole fraction behind the reaction zone was significantly affected. At the exit of the tube, in the both cases, CO mole fraction at $r$ = 1 mm agree with that at $r$ = 0 mm. This indicates that there is no dependence of the sampling position along the radial direction on mesurement of CO mole fraction. By measuring CO mole fraction of burned gas and comparing measured and computational results, the validity of the mechanism of radical quenching can be investigated.

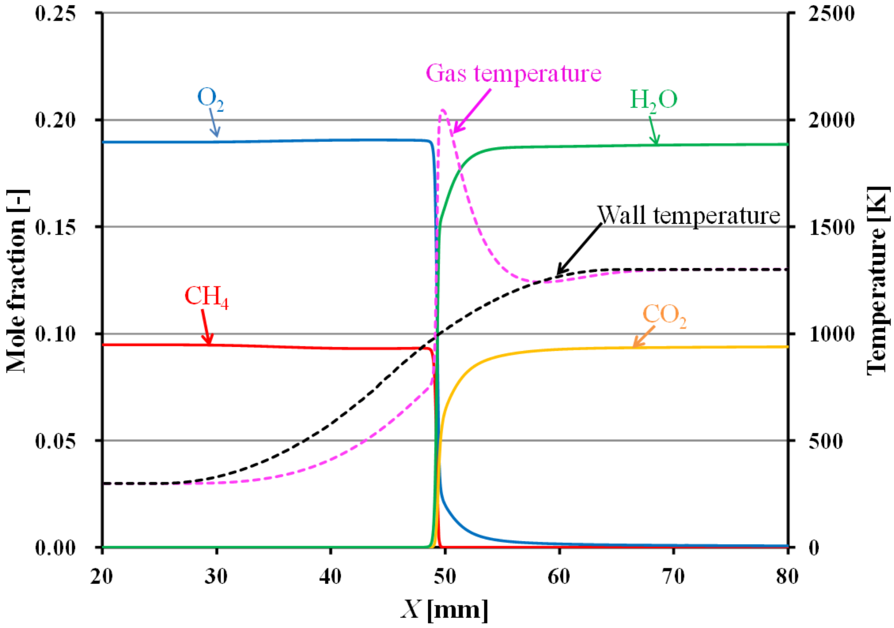

Figure 2. Distributions of mole fractions ($CH_4$, $O_2$, $CO_2$ and $H_2O$), gas phase temperature and wall temperature in the inert case ($d$ = 2.0 mm; $U$ = 50 cm/s; $\phi$ = 1.0).

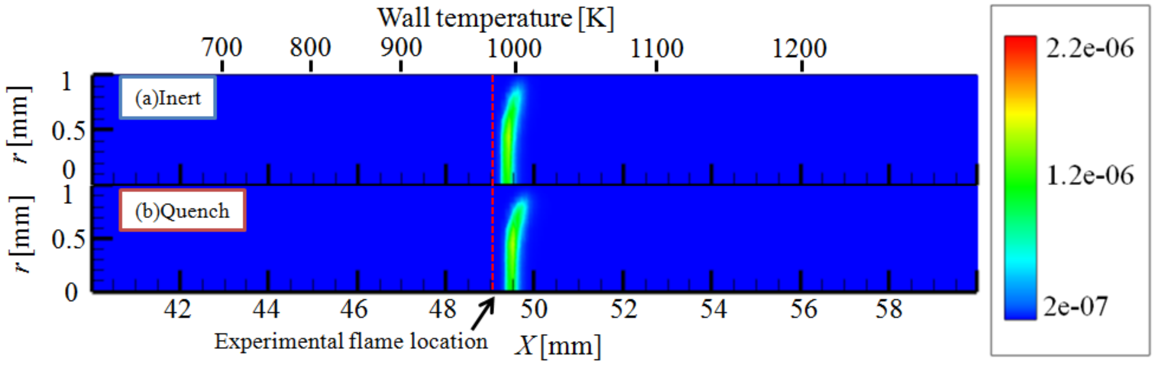

Figure 3. Distributions of CH mass fractions (*d* = 2.0 mm; *U* = 50 cm/s; ϕ = 1.0).

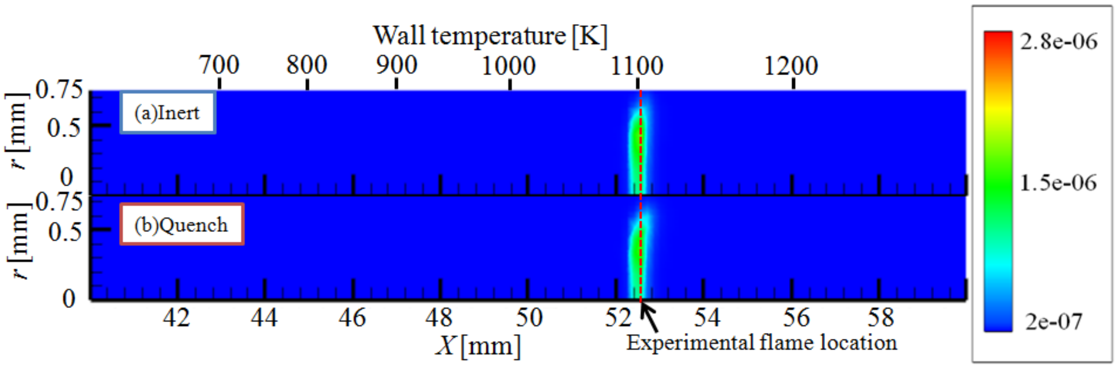

Figure 4. Distributions of CH mass fractions (*d* = 1.5 mm; *U* = 60 cm/s; ϕ = 1.0).

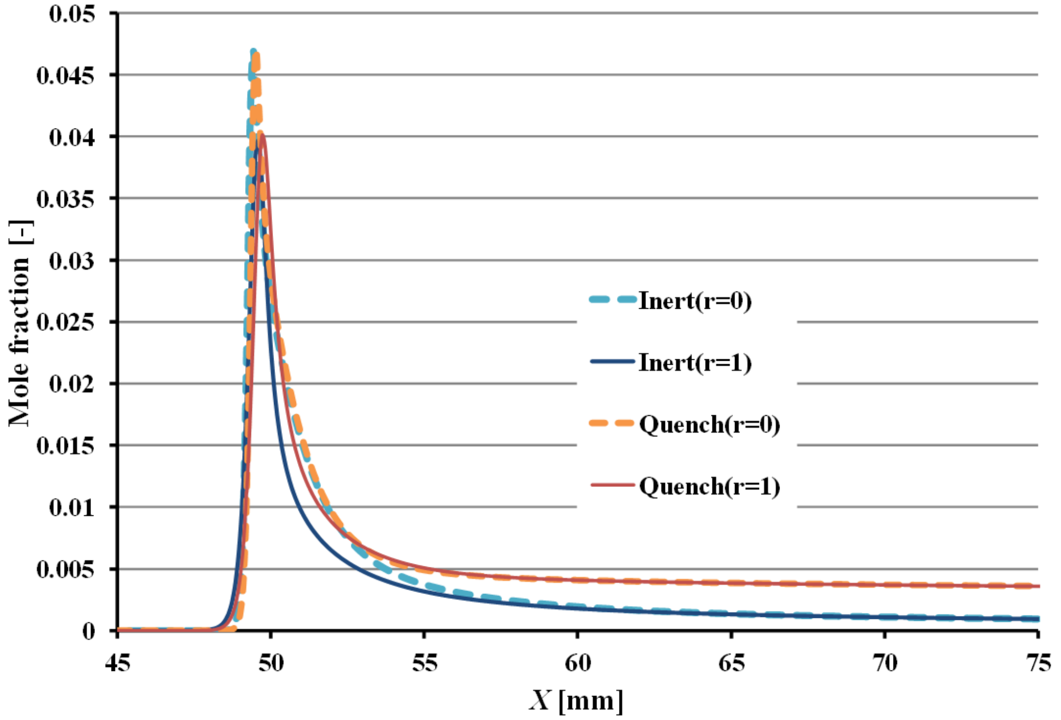

Figure 5. Profiles of CO mole fraction (*d* = 2.0 mm; *U* = 50 cm/s ; ϕ = 1.0).

Figure 6 shows the measured and computational CO mole fractions in burned gas for equivalence ratios, $\phi$, from 0.8 to 1.2 at (a) $d$ = 2.0 mm and (b) $d$ = 1.5 mm. At $d$ = 2.0 mm, CO mole fractions in the inert case and that of experiments are quite low level at $\phi < 1$ and increase with the increase of $\phi$ when $\phi > 1$. At the all equivalence ratios, CO mole fractions for inert case agree well with those for experiments and are much smaller than those for quench case. This tendency can be also seen at $d$ = 1.5 mm. Note also that for inert case, CO mole fractions at $d$ = 2.0 mm agree well with those at $d$ = 1.5 mm at the all equivalence ratios. For quench case, however, CO mole fractions at $d$ = 1.5 mm are larger than those at $d$ = 2.0 mm, due to higher surface-to-volume ratio. These results indicated that the present surface reaction mechanism overestimated the effect of radical quenching on gas-phase reactions.

It is intersting to note the comparable results by Saiki et al. [2] where their computations agreed with experiments when sticking coefficients S in radical quenching mechanism were lowered down from S = 1 to S = 0.01 for quartz and S = 0 for $Al_2O_3$ at wall temperature of 1273 K.

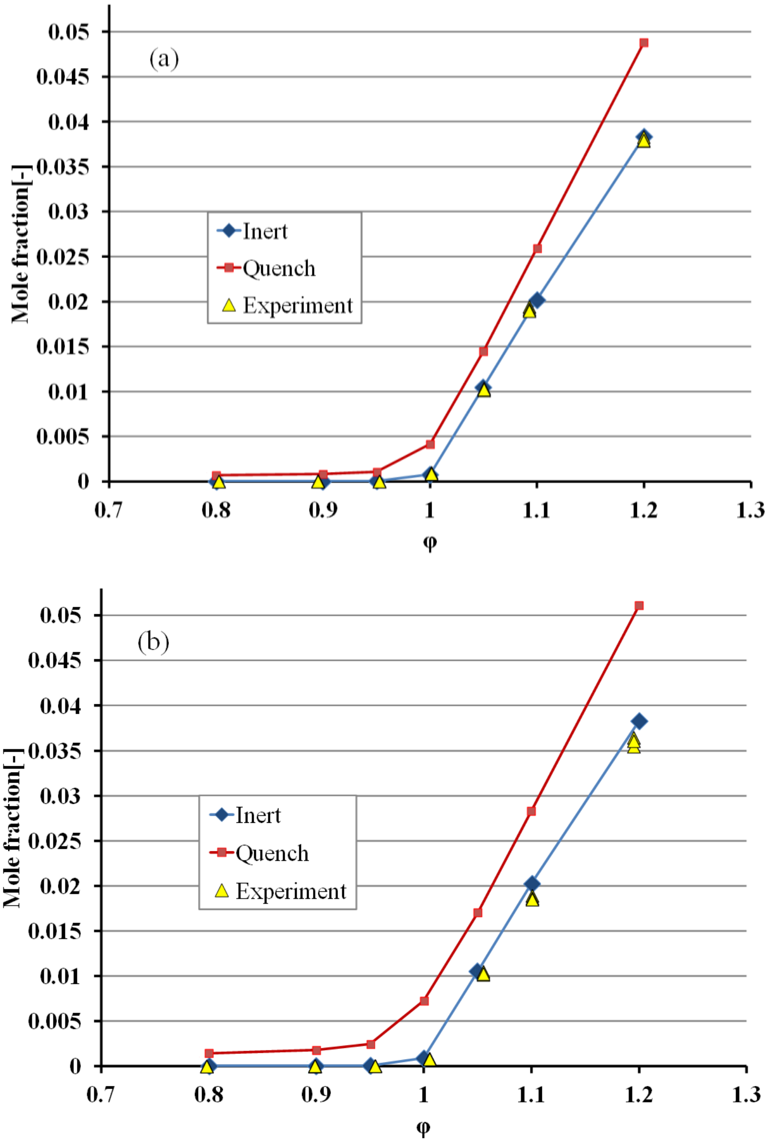

Figure 6. Equivalence ratio dependence of CO mole fraction of burned gas (a) $d$ = 2.0 mm, (b) $d$ = 1.5 mm.

## 4 Conclusions

The effect of radical quenching on gas-phase reactions of a $CH_4$/Air flame was investigated using a micro flow reactor with a controlled temperature profile. There was no significant difference in the flame locations between the inert and quench wall cases. The measured flame location agreed with the computational flame locations. The effect of radical quenching on the flame locations were neglegible. However, significant difference in CO mole fractions in burned gas between the inert and quench wall cases were observed. The measured CO mole fraction agreed well with the computed CO mole fraction in the inert case, i.e., when no radical quenching effect was considered. This indicates that the present radical quenching mechanism overestimates its effect and the effects of surface reactions on gas-phase reactions can be neglected at the conditions addressed in this study.

## References

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