# Reactivity of CO/H<sub>2</sub>/CH<sub>4</sub>/air Mixtures derived from In-cylinder Fuel Reformation Examined by a Micro Flow Reactor with a Controlled Temperature Profile

Yuki Murakami<sup>1</sup>, Hisashi Nakamura<sup>1</sup>, Takuya Tezuka<sup>1</sup>, Go Asai<sup>2</sup> and Kaoru Maruta<sup>1,3</sup> <sup>1</sup>Institute of Fluid Science, Tohoku University 2-1-1 Katahira, Aoba, Sendai 980-8577, Japan <sup>2</sup> Yanmar Co., Ltd., 2481 Umegahara, Maibara, Shiga 521-8511, Japan <sup>3</sup>International Combustion and Energy Laboratory, Far Eastern Federal University Russky Island, Vladivostok, Russia

## 1 Introduction

To reduce soot and  $NO_x$  emissions by large machines in the transport sector such as trucks and ships, an engine with in-cylinder fuel reformation is under development. A conceptual scheme of an in-cylinder fuel reforming engine is presented in Fig.1a. In this engine, some cylinders are used for fuel reforming and the rests are used for power output. In a reforming cylinder, a reformate gas, which mainly includes CO and H<sub>2</sub>, is produced by partial oxidation of mixtures of a liquid fuel and air by compression. Subsequently, combustion of the mixture of reformate gas and air takes place to extract the work output in power cylinders. According to  $\phi$ -T diagram [1] in Fig.1b, the combustion condition of diesel engines covers large areas of the conditions for soot and  $NO_x$  formation in the diagram while that of the in-cylinder fuel reforming engine avoids those regions. This avoidance can be realized based on the following principles. The flame temperature is expected to be lower because of extremely fuel-rich conditions in a reforming cylinder, which mitigates soot formation. In power output cylinders, even near a stoichiometric condition, one can realize a lower flame temperature condition because of diluents included in the produced reformate gas. However, compositions of the produced reformate gases may vary significantly depending on the reforming conditions. In our earlier study [2], we computationally investigated the characteristics of fuel reforming of a large hydrocarbon in an engine cylinder using an internal combustion engine simulation mode of the homogeneous zero-dimensional reactor model in Chemkin-Pro. In the computation, equivalence ratio and initial gas temperature of fuel/air mixtures for fuel reforming were widely varied and the effects on the compositions of produced reformate gases were investigated. Figure 1c shows the mole fractions of CO, H<sub>2</sub>,

Correspondence to: murakami@edyn.ifs.tohoku.ac.jp

#### Murakami, Y.

#### Reactivity Evaluation of CO/H<sub>2</sub>/CH<sub>4</sub>/air Mixtures

CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, and Fig. 1d indicates the maximum gas temperatures obtained in the computation. CO and H<sub>2</sub> were the major products for the lower equivalence ratio conditions, whereas other species, especially small hydrocarbons such as CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> were formed in higher equivalence ratio conditions, where the maximum gas temperature becomes relatively low (1300–1700 K). Therefore, the effect of these small hydrocarbons on the reactivity of reformate gases should be investigated for the design and the development of the in-cylinder fuel reforming engine. Although several studies have assessed the reactivity of CO/H<sub>2</sub> mixtures with several diluents [3, 4], only a limited number of reports describe experimental investigations of the reactivity of CO/H<sub>2</sub> mixtures with small hydrocarbons. Consequently, to obtain comprehensive knowledge related to the reactivity of multi-component reformate gases, this study specifically addressed the effects of CH<sub>4</sub> on CO/H<sub>2</sub> mixtures.



Figure 1. (a): A conceptual scheme of in-cylinder fuel reforming engine, (b): Combustion conditions of conventional diesel engines and in-cylinder fuel reforming engine described on  $\phi$ -T diagram [1], (c): Computed mole fractions of CO, H<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> produced in fuel reforming of n-tridecane/air mixtures using an internal combustion engine simulation mode of the homogeneous zero-dimensional reactor model in Chemkin-Pro [2] and (d): Computed maximum gas temperatures during one cycle of piston compression in the simulation.

For the evaluation of ignition properties of test mixtures, a micro flow reactor with a controlled temperature profile (MFR) was used [5]. MFR comprises a quartz tube with an inner diameter smaller than a conventional quenching diameter and an external heat source. Along the inner wall of the tube, a stationary temperature profile is formed by the external heat source. Past studies using MFR revealed flame responses of three types depending on the inlet mixture velocity: normal flames at high flow velocities, flames with repetitive extinction and ignition (FREI) at intermediate flow velocities, and weak flame at low flow velocities. Minaev et al. conducted a theoretical analysis of these flame responses and showed that a weak flame corresponds to a flame response on the ignition branch of the Fendell curve [6]. Based on the fact, weak flames in MFR are said to be a phenomenon that corresponds to the ignition phenomenon. Weak flames in MFR have been used to evaluate ignition-related properties of various fuels. Kamada et al. investigated weak flame responses of natural gas components and could evaluate their reactivity [7]. Because of a prescribed temperature profile formed by an external heat source, MFR has been applied for low reactivity mixtures such as a very high ratio of CO to H<sub>2</sub>. In another study, MFR was also applied for  $CO/H_2$  mixtures to investigate effects of  $CO/H_2$  ratio on reactivity [8]. Therefore, in the present study, reactivity of stoichiometric CO/H<sub>2</sub>/CH<sub>4</sub>/air mixtures at various compositions were evaluated using weak flame responses in MFR at atmospheric pressure.

## 2 Experiment and Computational Method

In the present study, compositions of CO,  $H_2$  and CH<sub>4</sub> were selected based on the trend of reformate gas compositions at the initial gas temperature of 530 K in Fig. 1c, a practical operating temperature of this engine. The computed fractions of these components at each equivalence ratio condition were extracted and expressed as percentages in Fig. 2a. According to the variation in the normalized fractions, the  $H_2$  fraction was replaced with the CH<sub>4</sub> fraction at an almost identical proportion, although the CO mole fraction kept almost constant (around 50%) over the wide range of the equivalence ratio. Consequently, we selected eleven mixture compositions (CO/H<sub>2</sub>/CH<sub>4</sub> = 50/50/0, 50/45/5, 50/40/10, 50/35/15, 50/30/20, 50/25/25, 50/20/30, 50/15/35, 50/10/40, 50/5/45, 50/0/50) based on the following rule: the CO fraction is constant (50%) and the H<sub>2</sub> fraction is replaced with the CH<sub>4</sub> fraction every 5%. In the experiment, four conditions  $(CO/H_2/CH_4 = 50/50/0, 50/45/5, 50/25/25, 50/0/50)$  were examined. The experiment setup is depicted in Fig. 2b. To prevent formation of CO complex, which reportedly affects the combustion characteristics [9], brass materials were used for parts of the experiment setup which CO is expected to contact. A quartz tube (I.D. 1 mm, O.D. 3 mm) was used as the reactor channel. The maximum wall temperature was set to 1300 K. The measured wall temperatures and an estimated temperature profile were shown in Fig.2c. Each experiment was conducted at atmospheric pressure condition. The mixture flow velocity was set to 3 cm/s. Flames were observed using a digital still camera with a CH bandpass filter (431.4 nm transparent wavelength, 6.5 nm half bandwidth) to exclude the effect of thermal radiation from the heated reactor wall. The exposure time for each picture was fixed as 3 minutes because of the extremely low luminosity of weak flames. For comparison of experimentally measured flame locations with computational ones, a flame location for the experiment was defined as the location of the peak of the brightness profile of a flame picture.



Figure 2. (a): Normalized fractions of CO,  $H_2$  and  $CH_4$  at the initial gas temperature of 530 K and equivalence ratios of 1–10 [2], (b): Schematic of the experiment setup, (c): Measured wall temperature of the reactor and estimated wall temperature profile used in the computation.

At the low flow velocity condition (3 cm/s), the flow in a reactor can be considered as a one-dimensional steady-state reactive diffusive flow without a boundary layer. Such a reactive flow condition can be simulated with a model for one-dimensional freely propagating premixed flame with additional heat transfer term between the wall and gas in the energy equation. Thus, modified PREMIX in ANSYS Chemkin-Pro v17.2 was used for this purpose [5]. The computational domain was 10 cm long. In the computation, all the CO/H<sub>2</sub>/CH<sub>4</sub> compositions mentioned in the above were considered. The estimated wall temperature profile portrayed in Fig. 2c was used. Computational flame location was defined as the peak location of [CO]\*[O] profile based on a literature of the chemiluminescence from various syngas mixtures [10]. Computations were conducted using four detailed chemical reaction models for comparison: USC mech ver. II [11], San

#### Murakami, Y.

Diego mechanism [12], AramcoMech1.3 [13], and HP-mech [14]. Note that AramcoMech1.3 was used instead of AramcoMech2.0 and AramcoMech3.0 at this moment because no converged solution was obtained with these newer mechanisms due to high computational loads.

## **3** Results and Discussion

Experimental and computational results of weak flame locations are plotted as a function of the wall temperature in Fig. 3a. Both of the experimental and computational flame locations shift to higher temperature side (downstream) of the reactor as the  $H_2$  fraction decreases and the  $CH_4$  fraction increases. which interprets the reactivity of the  $CO/H_2/CH_4$  mixture decreases. Experimental results show that the difference of the wall temperature at flame locations for  $CO/H_2/CH_4 = 50/50/0$  and 50/0/50 was around 234 K. According to an earlier study on RON evaluation by the weak flame location, difference in the wall temperature at flame locations was approximately 40 K between RON = 0 and 100 [15]. Based on this fact, it must be emphasized that the variation in the reactivity of the mixtures investigated in this study is significantly large. Although the experimental and computational weak flame positions show qualitative agreement in each condition, computational weak flames tend to be located in the upstream side compared to the experiment. A further investigation must be conducted to assess the quantitative difference. Among four chemical reaction models used in this study, HP-mech showed a better agreement with the experimental weak flame positions than others. Consequently, further analyses of chemical reactions have been conducted based on results with HP-mech. In order to investigate a correlation with a general indicator of ignition properties, ignition delay times of the same mixtures were assessed computationally using a zerodimensional homogeneous reactor model by AURORA package of Chemkin-Pro v17.2. Ignition delay time was defined as the duration until a pressure gradient dP/dt takes the maximum value. Initial gas temperatures were varied over the range of 700–1600 K under atmospheric condition. HP-mech was used as mentioned in the above. Figure 3b presents computational ignition delay time of CO/H<sub>2</sub>/CH<sub>4</sub>/air mixtures. Ignition delay times increase consistently as H<sub>2</sub> fraction decreases and CH<sub>4</sub> fraction increases in the temperature range over 900–1300 K, where weak flames of CO/H<sub>2</sub>/CH<sub>4</sub>/air mixtures stabilized. Difference in ignition delay times between CO/H<sub>2</sub>/CH<sub>4</sub> = 50/50/0 and 50/0/50 is quite large (approx. a factor of 2000 at T = 1000K), this difference interprets large difference in the weak flame position in MFR.



Figure 3. (a): Weak flame locations of  $CO/H_2/CH_4/air$  mixtures obtained from the experiment (Black plots) and the computations (Colored plots), (b) Computed ignition delay times of stoichiometric  $CO/H_2/CH_4/air$  mixtures at atmospheric pressure and initial temperatures of 800–1600 K by HP-mech.

For the further investigation on the cause of the reduced reactivity seen in weak flame responses, the rate-of-production analysis for OH radicals was conducted. Figure 4 portrays results of the rate-of-production of OH radicals by fuel components. In the case of  $CO/H_2/CH_4 = 50/50/0$ , OH radicals are mostly consumed by

#### Reactivity Evaluation of CO/H<sub>2</sub>/CH<sub>4</sub>/air Mixtures

 $H_2$  and CO through R4:  $H_2+OH=H+H_2O$  and R30: CO+OH=H+CO<sub>2</sub>. However, once CH<sub>4</sub> is included as a fuel component (CO/H<sub>2</sub>/CH<sub>4</sub> = 50/45/5, 50/25/25, 50/0/50), CH<sub>4</sub> starts consuming OH radicals through R174: CH<sub>4</sub>+OH=CH<sub>3</sub>+H<sub>2</sub>O and competes for OH radicals with CO and H<sub>2</sub>. As can be seen in Fig. 4c and 4d, consumption of OH radicals by CH<sub>4</sub> becomes more significant than by H<sub>2</sub> and CO in the upstream of the reactor, which indicates that CH<sub>4</sub> consumes more OH radicals than H<sub>2</sub> and CO in an early stage of the reactions as the CH<sub>4</sub> fraction increases. Both CO and H<sub>2</sub> consume OH radicals and produce H radicals through R4 and R30 while CH<sub>3</sub> radicals are produced through the reaction of CH<sub>4</sub> and OH radicals. H radicals lead a chain-branching reaction with O<sub>2</sub> and play an important role in OH radical formations. Produced OH radicals, leading to suppression of the OH formation from H radicals. Therefore, CH<sub>4</sub> has a large inhibitory effect and the reactivity of CO/H<sub>2</sub>/CH<sub>4</sub> mixtures largely decreases as the CH<sub>4</sub> fraction increases. This competition for OH radicals by CO, H<sub>2</sub>, and CH<sub>4</sub> and the larger production of CH<sub>3</sub> radicals appear to be the primary factor in the large decrease in the reactivity of CO/H<sub>2</sub>/CH<sub>4</sub> mixtures, further comparisons were not included in this manuscript due to the limited space.



Figure 4. Result of rate-of-production analysis for OH radicals in the cases of  $CO/H_2/CH_4 = (a)$ : 50/50/0, (b): 50/45/5, (c): 50/25/25 and (d): 50/0/50.

## 4 Conclusions

The reactivity of stoichiometric CO/H<sub>2</sub>/CH<sub>4</sub>/air mixtures at various compositions were examined by weak flame responses in MFR. Both experimental and computational results showed that weak flame locations of  $CO/H_2/CH_4$  mixtures shifted greatly to the higher temperature side as H<sub>2</sub> fraction decreases and CH<sub>4</sub> fraction increased, which interprets the reactivity of CO/H<sub>2</sub>/CH<sub>4</sub>/air mixtures decreases considerably. Computational ignition delay times of the same mixtures at atmospheric pressure also indicated that the reactivity of those mixtures largely decreases as CH<sub>4</sub> fraction increases. According to the rate-of-production analysis for OH radicals, it was demonstrated that OH radicals are consumed mainly by fuel components, CO, H<sub>2</sub>, and CH<sub>4</sub> in all mixture compositions. For CO/H<sub>2</sub> mixtures, OH radicals are mainly consumed by H<sub>2</sub> and CO. Subsequently, H radicals are produced through R4: H<sub>2</sub>+OH=H+H<sub>2</sub>O and R30: CO+OH=H+CO<sub>2</sub>. However, once CH<sub>4</sub> is included in CO/H<sub>2</sub> mixtures, CH<sub>4</sub> starts consuming OH radicals through R174: CH<sub>4</sub>+OH=CH<sub>3</sub>+H<sub>2</sub>O and produces CH<sub>3</sub> radicals. The consumption rate of OH radicals by CH<sub>4</sub> became larger than that by  $H_2$  and CO especially at early stage of reactions as  $CH_4$  fraction increased. Therefore, primary factor of the significant reduction of reactivity of CO/H<sub>2</sub>/CH<sub>4</sub>/air mixtures seems to be the increase of OH consumption by CH<sub>4</sub> and CH<sub>3</sub> production rate due to the increase of CH<sub>4</sub> fraction. Investigating the effects of CH<sub>4</sub> on the reactivity at high pressure conditions must be interesting as a next subject, however, it may require to solve vulnerability issues of MFR.

Murakami, Y.

### References

[1] Kamimoto T, Bae M. (1988). High Combustion Temperature for the Reduction of Particulate in Diesel. SAE Paper: 880423.

[2] Murakami Y, Nakamura H, Tezuka T, Hasegawa S, Asai G, Maruta K. (2017). Properties of incylinder fuel reformation and ignition characteristics of  $CO/H_2/CH_4$  mixtures. 11th Asia-Pacific Conf. Combust: P350.

[3] Donohoe N, Heufer KA, Aul CJ, Petersen EL, Bourque G, Gordon R, Curran HJ. (2015) Influence of steam dilution on the ignition of hydrogen, syngas and natural gas blends at elevated pressures, Combust. Flame. 162: 1126.

[4] Petersen EL, Kalitan DM, Barrett AB, Reehal SC, Mertens JD, Beerer DJ, Hack RL, McDonell VG. (2007). New syngas/air ignition data at lower temperature and elevated pressure and comparison to current kinetics models. Combust. Flame. 149: 244.

[5] Maruta K, Kataoka T, Kim NI, Minaev S, Fursenko R. (2005). Characteristics of combustion in a narrow channel with a temperature gradient. Proc. Combust. Inst. 30: 2429.

[6] Minaev S, Maruta K, Fursenko R. (2007). Nonlinear dynamics of flame in a narrow channel with a temperature gradient. Combust. Theory Model. 11: 187.

[7] Kamada T, Nakamura H, Tezuka T, Hasegawa S, Maruta K. (2014). Study on combustion and ignition characteristics of natural gas components in a micro flow reactor with a controlled temperature profile. Combust. Flame. 161: 37.

[8] Nakamura H, Takahashi H, Tezuka T, Hasegawa S, Maruta K, Abe K. (2016). Effects of CO-to-H<sub>2</sub> ratio and diluents on ignition properties of syngas examined by weak flames in a micro flow reactor with a controlled temperature profile. Combust. Flame. 172: 94.

[9] Williams TC, Shaddix CR. (2007). Contamination of carbon monoxide with metal carbonyls: Implications for combustion research. Combust. Sci. Technol. 179: 1225.

[10] Kopp M, Brower M, Mathieu O, Petersen E, Güthe F. (2012). CO<sub>2</sub><sup>\*</sup> chemiluminescence study at low and elevated pressures. Appl. Phys. B Lasers Opt. 107: 529.

[11] Wang H, You X, Joshi AV, Davis SG, Laskin A, Egolfopoulos F, Law CK. USC Mech Version II. High-Temperature Combustion Reaction Model of H<sub>2</sub>/CO/C<sub>1</sub>-C<sub>4</sub>, Compounds. http://ignis.usc.edu/USC\_Mech\_II.htm. May 2007.

[12] "Chemical-Kinetic Mechanisms for Combustion Applications". San Diego Mechanism web page. Mechanical and Aerospace Engineering (Combustion Research). University of California at San Diego (http://combustion.ucsd.edu).

[13] Burke M, Ahmed SS, Curran HJ. (2013). A hierarchical and comparative kinetic modeling study of  $C_1$ - $C_2$  hydrocarbon and oxygenated fuels. Int. J. Chem. Kinet. 45: 638.

[14] Shen X, Yang X, Santner J, Sun J, Ju Y. (2015). Experimental and kinetic studies of acetylene flames at elevated pressures. Proc. Combust. Inst. 35: 721.

[15] Hori M, Yamamoto A, Nakamura H, Tezuka T, Hasegawa S, Maruta K. (2012). Study on octane number dependence of PRF/air weak flames at 1–5 atm in a micro flow reactor with a controlled temperature profile. Combust. Flame. 159: 959.