

# Ignition Characteristics of Premixed Methane/air in Micro Chamber

H L Yang, J P Huo, L Q Jiang, X H Wang and D Q Zhao

Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, China

E-mail: yanghl@ms.giec.ac.cn

**Abstract.** The ignition process of premixed methane/air in a micro-scale chamber is simulated with the combination of surface chemistry and gas-phase reactions. The effect of different parameters on the ignition characteristics are analyzed in detail and the sensitive analysis is performed on main elementary reactions. It is found that the ignition of the mixture is inhibited by surface reaction, which mainly depends on the sticking ability of the surface on  $\text{CH}_3$  radical. The ignition inhibition can be reduced by increasing the initial temperature and pressure. The increase of equivalence ratio has small impact on ignition delay time when it is larger than stoichiometric ratio. The ignition delay time would increase significantly with surface-area-to-volume ratio. The product of sticking coefficient and surface-area-to-volume ratio can be used to measure the intensity of surface reaction. The larger the product is, the stronger the inhibition of the surface reaction on ignition has.

## 1. Introduction

Due to the development of MEMS technology, the miniaturization of internal combustion engine becomes a research hotspot in recent years. The aim of maintaining stable and high efficient output is the major challenge when it is applied as a high energy power source. Micro-engines require short resident time of premixed gas in the chamber for sufficient power output, so that the short ignition delay time of fuel/air mixture is favorable [1, 2]. However, due to large surface-area-to-volume ratio of the chamber, the collision between radicals and internal wall is more frequently and the radical loss on the internal surface would not be ignored, leading to the retard of the ignition and the increase of resident time.

The study on the radical loss on the internal wall of reaction vessel was first conducted in the static-reactor experiments [3]. In this type of experiments, low temperature oxidation mechanism of hydrocarbons was studied with isothermal boundary condition in a closed quartz or silica vessel. Norrish and Froud [4] reported that the reaction rate of methane/oxygen mixture with the same operating conditions was evidently lower in the smaller vessel. The results demonstrated the existence of radical loss on the internal wall and indicated that the wall would have stronger inhibitory influence on gas phase oxidation. Bowman and Wilk [5] investigated the correlation between surface-area-to-volume ratio of the vessel and ignition delay time of methanol/air mixture. Their experimental results showed that the ignition delay time of the mixture increased with surface-area-to-volume ratio. It indicated that during the induction time, the radical loss on the wall cannot be ignored. Ignition delay time was also found sensitive to internal wall conditions in modern shock tube and jet-stirred reactor experiments [6, 7]. So it can be deduced that the homogeneous combustion assumption in micro



chamber is not appropriate as the surface reaction strongly affects the radical concentration in the radical pool. Therefore, heterogeneous surface reactions should be taken into consideration for the design of micro-combustor.

In this work, the effect of heterogeneous surface reactions on ignition delay of methane/air mixture is studied using numerical simulations. The investigation on several important parameters for the combustion process including initial temperature, pressure, equivalence ratio, sticking coefficient and surface-area-to volume ratio is conducted.

## 2. Numerical method

### 2.1. Surface reaction mechanism

The surface reaction model for methane/air developed by Raimondeau *et al* [8] was used in this work, as shown in Table 1. By using this model, numerical simulation on methane/air combustion in narrow channel was conducted by Saiki *et al.* and excellent agreement to experimental result was obtained [9].

**Table 1.** Surface kinetic mechanism of methane/air [8]

No.	Reactions <sup>a</sup>	Sticking Coefficient or Pre-Exponential (s <sup>-1</sup> )	$\Delta H$ / (kcal/mol) <sup>b</sup>
R1	$\text{CH}_3 + * \rightarrow \text{CH}_3^*$	0 ~ 1	0
R2	$\text{H} + * \rightarrow \text{H}^*$	0 ~ 1	0
R3	$\text{OH} + * \rightarrow \text{OH}^*$	0 ~ 1	0
R4	$\text{O} + * \rightarrow \text{O}^*$	0 ~ 1	0
R5	$2\text{CH}_3^* \rightarrow \text{C}_2\text{H}_6 + 2^*$	$10^{13}$	-92.3
R6	$2\text{H}^* \rightarrow \text{H}_2 + 2^*$	$10^{13}$	-105.7
R7	$2\text{O}^* \rightarrow \text{O}_2 + 2^*$	$10^{13}$	-121.1
R8	$2\text{OH}^* \rightarrow \text{H}_2\text{O} + \text{O}^* + ^*$	$10^{13}$	-17.4
R9	$\text{CH}_3^* + \text{H}^* \rightarrow \text{CH}_4 + 2^*$	$10^{13}$	-106.7
R10	$\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O} + 2^*$	$10^{13}$	-121.1

a) \* denotes reactive surface site and for example  $\text{CH}_3^*$  means an adsorbed  $\text{CH}_3$  radical.

b)  $\Delta H$  means the standard molar reaction enthalpy.

### 2.2. Numerical setup

The CHEMKIN-Pro software [10] was used to investigate the effect of surface reactions on ignition delay time of methane/air mixture. GRI-Mech 3.0 [11] was adopted as the detail gas phase kinetic mechanism of methane/air. Adiabatic boundary condition was assumed and the surface reactions were integrated into the homogeneous combustion calculation.

The influence of five main parameters on ignition delay time, including initial temperature  $T_0$ , initial pressure  $P_0$ , equivalence ratio  $\Phi$ , sticking coefficient  $\gamma$  and surface-area-to volume ratio  $SV$ , were analyzed. Series of numerical simulation were carried out and  $T_0$  ranged from 900 K to 1500 K,  $P_0$  from 1 atm to 30 atm,  $\Phi$  from 0.2 to 1.4,  $\gamma$  from 0 to 1.0 and  $SV$  from 0.1 cm<sup>-1</sup> to 100 cm<sup>-1</sup>.

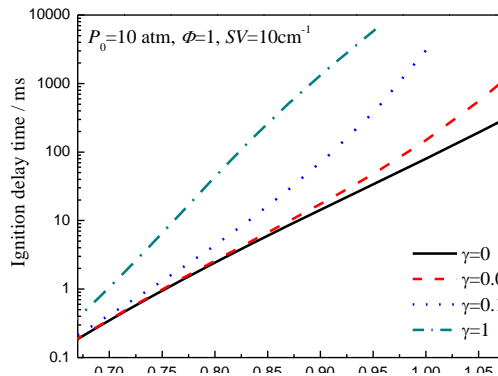
## 3. Results and discussions

### 3.1. Effect of initial temperature and sticking coefficient

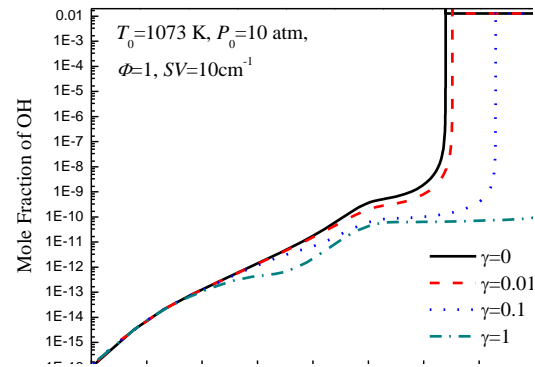
Figure 1 shows the comparison of ignition delay time for various  $\gamma$  versus  $T_0$ . Larger ignition delay time is found for larger  $\gamma$ , demonstrating that the surface reactions have strong inhibitory effect on the induction time. However, the discrepancy of ignition delay time caused by  $\gamma$  becomes smaller as initial temperature increases. It indicates that the effect of surface reaction is weak at high temperature.

The ignition delay time associates with the chain branching reaction rate, which is affected by OH concentration. In figure 2, the growth rate of OH is slowest when  $\gamma=1$ , resulting in the longest

induction time. Therefore, the wall with stronger absorption ability destroyed more radicals in the radical pool, and this is the reason why surface reaction can retard the ignition.



**Figure 1.** Comparison of ignition delay times for different  $\gamma$  versus  $T_0$



**Figure 2.** Comparison of OH mole fraction for different  $\gamma$  versus time

A sensitivity analysis was performed to study the reaction sensitivity to ignition delay time for methane oxidation as a function of sticking coefficient [12]. Figure 3 illustrates nine largest normal sensitivities among gas-phase reactions and four absorption reactions R1~R4. Both in the case of  $T_0=900$  K and  $T_0=1400$  K, the sensitivities for H, O and OH absorption can be neglected compared with the other reaction. Due to the rapid reaction rate of  $\text{H}+\text{O}_2 \rightarrow \text{OH}+\text{O}$ ,  $\text{OH}+\text{H}_2 \rightarrow \text{H}_2\text{O}+\text{H}$  and  $\text{O}+\text{H}_2 \rightarrow \text{OH}+\text{H}$ , most of the radical of H, O and OH are consumed in the gas phase and their gas-phase concentrations are relatively so low that the absorption reaction rates of R2~R4 are very small.  $\text{CH}_3$  radical, as a relatively stable molecule, is more likely to diffuse to the wall and get absorbed. Therefore, the surface effect is mainly controlled by the absorption intensity of the wall, represented by the sticking coefficient of R1.

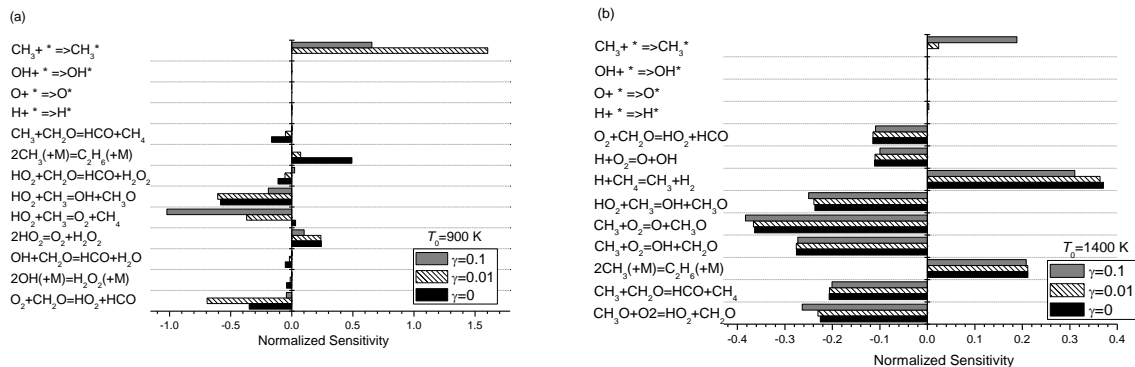
Noted that the sensitivity of R1 is higher than all the other reactions for  $T_0=900$  K, shown in figure 3(a), therefore the inhibitory effect on ignition is determined by surface reaction R1. However, for  $T_0=1400$  K, the gas-phase reaction  $\text{H}+\text{CH}_4 \rightarrow \text{CH}_3+\text{H}_2$  takes the place of R1 as the largest inhibitory factor, indicating that gas-phase reactions play a dominant role during the induction period at high temperature. According to Langmuir theory [13], the absorption reaction rate can be expressed as:

$$k_{\text{wall}} = \frac{\gamma}{\Gamma} \frac{P}{\sqrt{2\pi RTM}} \quad (1)$$

where  $\Gamma$ ,  $R$ ,  $M$ ,  $P$ ,  $T$  are the surface site density ( $\text{mol}/\text{cm}^2$ ), the universal gas constant ( $\text{J}/(\text{mol}\cdot\text{K})$ ), the molecular weight, partial pressure of the radical and the gas-phase temperature. Thus, when  $P_0$  and  $\gamma$  are constant, the absorption reaction rate would have slight decrease if increasing the initial temperature. However, chain branching reaction rate in the gas phase would have rapid increase even the temperature has a small increase. Therefore, a number of radical produced can compensate the radical loss on the wall, weakening the surface effect on the ignition.

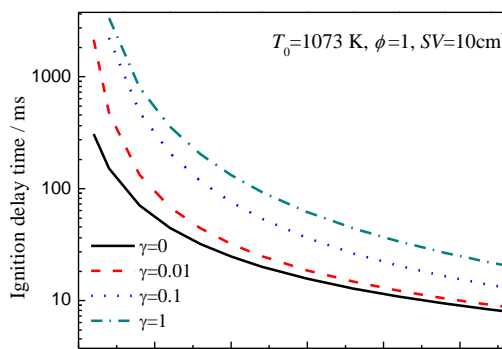
### 3.2. Effect of initial pressure and equivalence ratio

According to the equation 1, the increase of initial pressure is able to enhance the surface reaction rate. However, the ignition delay time gets shorter when increasing  $P_0$ , but also increases with  $\gamma$ , shown in figure 4. In addition, the discrepancy of various  $\gamma$  becomes smaller as the initial pressure increase. As the density of the methane/air mixture increases with  $P_0$ , the collision frequency among the radicals increase therefore less radicals crash into the wall due to gas diffusion. It can be concluded that enhancing  $P_0$  can effectively reduce the inhibitory effects of wall reaction.

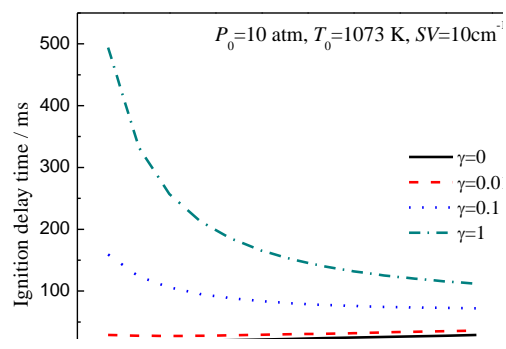


**Figure 3.** Normalized sensitivity of ignition delay time with respect to reaction rate ( $P_0=10$  atm,  $\Phi=1$ ,  $SV=10$  cm<sup>-1</sup>)

The effect of equivalence ratio  $\Phi$  on ignition with various  $\gamma$  is illustrated in figure 5. When  $\gamma < 0.1$ , there is little change for the ignition delay time. When  $\gamma$  is up to 1.0, great increase can be seen as  $\Phi$  decreases to 0.2. However, for fuel-rich condition ( $\Phi > 1$ ), the ignition delay time changes slightly and maintains stable with a certain sticking coefficient. Therefore, high-pressure and fuel-rich condition can help weaken the surface effect.



**Figure 4.** Comparison of ignition delay times for different  $\gamma$  versus  $P_0$

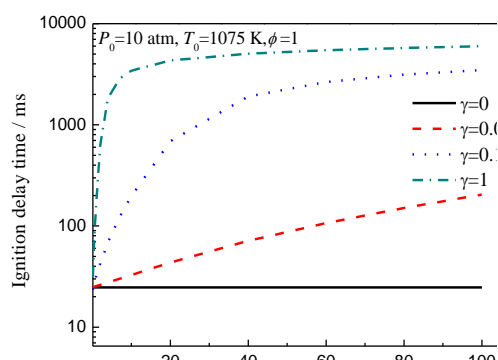


**Figure 5.** Comparison of ignition delay times for different  $\gamma$  versus  $\Phi$

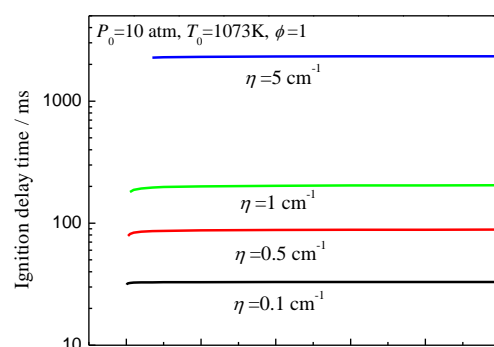
### 3.3. Effect of surface-area-to-volume ratio

The investigation on  $SV$  with various  $\gamma$  is drawn in figure 6. The ignition delay time has a significant increase with  $SV$  for  $\gamma=1$ , however becomes stable for  $SV > 10$  cm<sup>-1</sup>. The larger of the  $SV$ , the more possibility of radicals impinge to the surface and get absorbed, resulting in the rapid growth of ignition delay time. When  $SV$  is small, the heat released from surface reaction can be neglected. As  $SV$  increases to a certain degree, intense surface reactions release a lot of heat and enhance the gas-phase temperature due to the exothermic desorption reactions. Therefore, in an adiabatic closed system, the ignition delay time is sensitive to surface-area-to-volume ratio in a certain range for a certain sticking coefficient.

Both  $SV$  and  $\gamma$  affect the ignition significantly. Thus, a new parameter  $\eta = \gamma \cdot SV$  is developed in this work, called sticking intensity. Figure 7 shows that the ignition delay time almost has no change for a specific  $\eta$ . It indicates that  $\eta$  can be used to measure the inhibitory effect of surface reaction. The larger of the  $\eta$  is, the stronger the inhibition of the surface reaction on ignition has.



**Figure 6.** Comparison of ignition delay times for different  $\gamma$  versus  $SV$



**Figure 7.** The ignition delay time versus  $SV$  with specific  $\eta$

#### 4. Conclusions

The results show the inhibitory effect caused by surface reaction mainly depends on the sticking coefficient of the absorption for  $\text{CH}_3$  radical. Increasing the initial temperature and initial pressure can effectively weaken the surface effect. However, the increase of equivalence ratio has small impact on ignition delay time when it is larger than stoichiometric ratio. In an adiabatic system, the ignition delay time would increase significantly with surface-area-to-volume ratio in a certain range for a certain sticking coefficient. But it becomes stable when surface-area-to-volume ratio is sufficient large due to strong heat release from surface reactions. The product of sticking coefficient and surface-area-to-volume ratio can be used to measure the intensity of surface reaction. The larger the product is, the stronger the inhibition of the surface reaction on ignition has.

#### Acknowledgement

The current work was supported by National Basic Research Program of China (No. 2014CB239600) and National Science Foundation of China (No. 51336010).

#### References

- [1] Sher I, Levinzon-Sher D and Sher E 2009 *Appl. Therm. Eng.* **29** 401
- [2] Sher E and Sher I 2011 *Chem. Eng. Sci.* **66** 261
- [3] Lewis B and Von Elbe G 1987 *Combustion, flames and explosions of gases* (Orlando: Academic Press) pp 25-76
- [4] Norrish R G W and Frood S G 1936 *Proc. R. Soc. Lond. A* **157** 507
- [5] Bowman M J and Wilk R D 1996 *SAE paper*
- [6] Wang B L, Olivier H and Gronig H 2003 *Combust. Flame* **133** 93
- [7] Dagaut P, Lecomte F, Mieritz J and Glarborg P 2003 *Int. J. Chem. Kinet.* **35** 565
- [8] Raimondeau S, Norton D and Vlachos D G 2002 *Proc. Combust. Inst.* **29** 906
- [9] Saiki Y and Suzuki Y 2012 *Proc. Combust. Inst.* **34** 3401
- [10] *CHEMKIN-Pro* 2010 ( San Diego: Reaction Design, Inc.)
- [11] Smith G P, Golden D M, Frenklach M, Moriarty N W, Eiteneer B, Goldenberg M, Bowman C T, Hanson R K, Song S, Gardiner W C, Lissianski V V and Qin Z W. GRI-Mech 3.0, [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/)
- [12] Zhang Y J, Huang Z H, Wei L J, Zhang J X and Law, C. K. 2012 *Combust. Flame* **159** 926
- [13] Masel R I 1996 *Principles of Adsorption and Reaction on the Solid Surfaces* (New York: Wiley) pp 384-389