Evaluation of Chemical Reaction Models and Numerical Simulations of Detonations in C_2H_4/O_2 Mixtures

Takayuki Araki[1], Youhi Morii[2], Nobuyuki Tsuboi[1], A.Koichi Hayashi[3]

[1]Department of Mechanical and Control Engineering, Kyushu Institute of Technology Kitakyushu, Fukuoka, Japan

[2]JAXA's Engineering Digital Innovation Centre, JAXA, Sagamihara, Kanagawa, Japan

[3]Department of Mechanical Engineering, Aoyama Gakuin University Sagamihara, Kanagawa, Japan

1 Introduction

Recently, computer simulation technology has improved dramatically, and numerical studies about combustion have been conducted in all over the world. The numerical studies on detonations have also been done since 1960s, but most of them have been conducted by using a one or two-step chemical reaction model in terms of the calculating cost and/or the stiffness. In the numerical simulation of detonation, the more detailed reaction models are needed to investigate the mechanisms in detail. When one discusses the initiation or propagation limit of detonations, it is essential to estimate the chemical reactions exactly. Owing to many experimental data, detailed chemical reaction models have been developed, and recent computer technology enables to make a simulation with a detailed reaction model. Existing detailed models for hydrocarbon combustion, however, contain many species and elementary reactions, and they require much CPU time and memory to simulate detonation. Therefore, the reliable reduced reaction model, which has less species and reactions, is reasonable in simulation of detonations.

In the past studies, experimental studies about ethylene (C_2H_4) ignition have been conducted to find the reaction rate coefficient, or to investigate effect of double-bond between carbon atoms. The ethylene oxidation reaction plays an important role in chemistries of practical fuels and the mechanisms are becoming revealed. The ethylene is known as one of the detonable gases and it has wide explosion limit, and it is discussed the usage as a propellant for the Pulse Detonation Engines (PDE), thus the mechanism of the ethylene detonation has to be revealed in terms of safety engineering. Numerical studies on the ethylene detonations, however, have not been conducted today.

Correspondence to: e-mail:takaboy400@gmail.com

Before doing calculation, evaluation of the detailed reaction model is necessary. The reaction model which shows good accuracy in high pressure conditions is reasonable for simulating detonations. Assuming a detonation in stoichiometric ethylene/oxygen mixture under the condition of 300 K and 0.1 atm, the temperature increase to approximately 2000 K and pressure rises to 6 atm behind the shock wave. In case of detonation, a rapid chemical reaction occurs in a high-temperature and high-pressure condition behind a strong leading shock wave. Recently, shock tube studies under high pressure were conducted [8] [9]. Although there are a few experimental reports conducted in such as high temperature and pressure conditions, they are essential to investigate the applications of the reaction models to detonation analysis.
This study aims to reveal the detonation wave structures in ethylene/oxygen mixtures under condition of 0.1 atm and 300 K. This paper reports what is the reasonable reaction model for the ethylene detonation by comparing to the experimental reports. This paper also shows the results of two-dimensional detonation analysis using the selected reaction model. The discussion on the initiation or the propagation limit of detonation is not referred in this report, but this numerical study considering detailed chemical reactions will be able to be the first step for the investigations of initiation and propagating limits of detonations.

2 Detailed and reduced models

The models evaluated in this paper are shown in Table 1. Each model was developed for hydrocarbon combustion [1]-[6]. USC-mech II was developed for C1-C4 hydrocarbons by Wang *et al.* in University of Southern California. It contains many species and elementary reactions, and complex species such as aromatic hydrocarbon are considered. GRI-mech3.0 is known as a model for n-alkane, and regards nitrogen as a reactant, hence it perhaps be valid for combustion in air. In the present study, it was investigated for its application to the ethylene combustion. The remaining four models (UC San Diego model, VW model34, VW model23, and Li model) were developed in the same institute, University of California, San Diego. UC San Diego model does not take accounts so much complex species, and taking account of usage for simulating detonations. The reduced models (VWmodel34, VWmodel23, and Li model) seem to show good agreement to the detailed model, UC San Diego. Because they contain less species, they are applicable for detonation analyses if they show good accuracy in detonation conditions. Yungstar *et al.* [7] reported the one-dimensional simulation of ethylene detonation using the Li model.

Table 1 Chemical reaction models for hydrocarbon combustion.

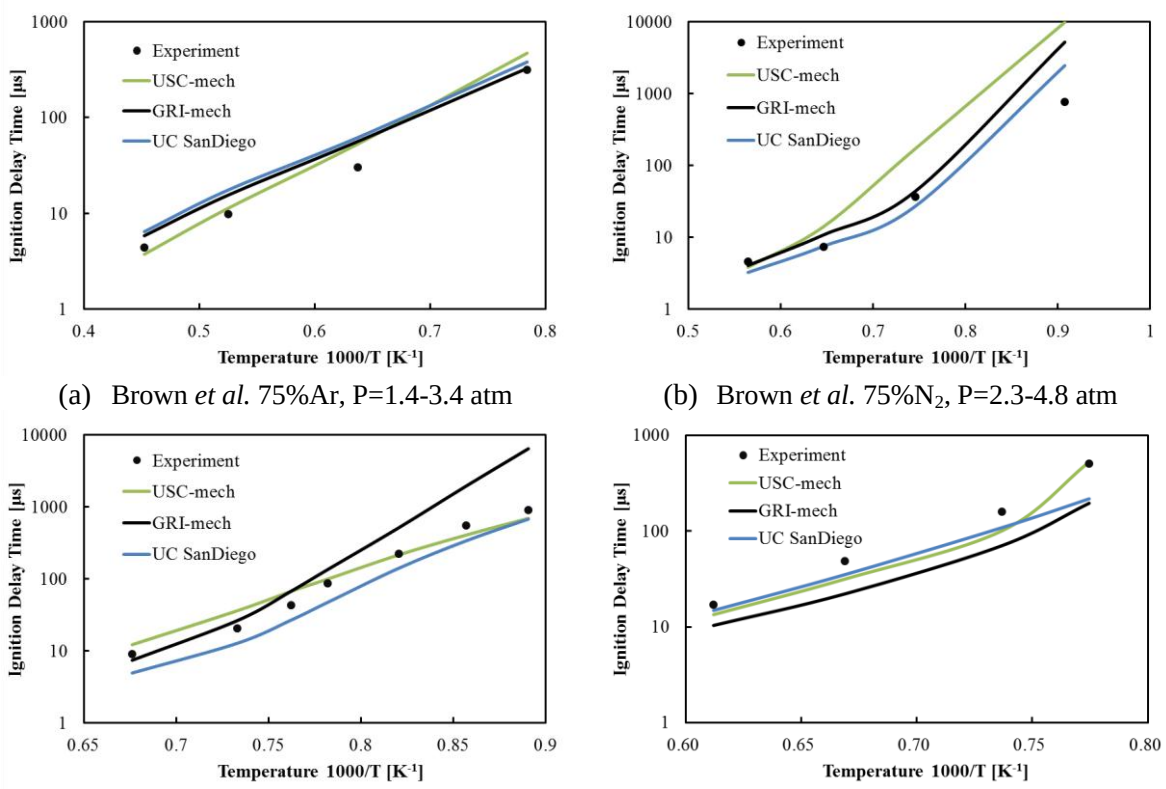
Reaction model	Species	Elementary reactions	Authors
USC-mech II [1]	112	784	Wang (2007)
GRI-mech 3.0 [2]	53	325	Serauskas (1999)
UC San Diego model [3]	50	235	Williams (2012)
VWmodel34 [4]	34	148	Varatharajan (2002)
VWmodel23 [5]	23	38	Varatharajan (2002)
Li model [6]	20	36	Li (2000)

3 Validation of detailed models

First, the former three detailed models in Table 1 were evaluated in experimental conditions. These models were compared to experiments by calculation of ignition delay times with CHEMKIN-II. The ignition time criterion was set to CH onset, as well as the experimental definition.
Then, the following experimental data which are shown in Table 2 were selected in this work. These experiments conducted in high pressure conditions are especially important for validating reaction models for application to detonation analysis.
The results of comparison are shown in Figs.1. Only four data are shown on the figures because we had many results in the present study. The others resulted similar to these representatives. In each graph, the *x*-axis indicates 1000 times the inverse of post-shock temperature. The ignition delay time τ is shown in logarithm at *y*-axis. In Figs.1, GRI-mech (black line) gives good agreement in high temperature, but not in low temperature. On the other hand, the USC-mech (green line) and the UC San Diego model (blue line) gives good agreement especially in high temperature range. As a result, USC-mech II and UC San Diego model seem to be applicable to detonation analysis because they indicate reasonable agreements in high temperature conditions. Additionally, the USC-mech and GRI-mech include much species. This causes increase of calculating cost when it is adopted in analyses of detonations, hence it is not practical to use these complicated models. As summary, UC San Diego model, which includes less species and keeps high accuracy is reasonable to be used for analyses of the ethylene detonations.

Table 2 Summary of experimental conditions.

Researchers	Test gas composition	Equivalence ratio	Pressure range [atm]	Temperature range [K]	Ignition time criteria
Brown *et al.* [8]	Ethylene/Oxygen/ 96%Argon	1.0	1.3-3.0	1276-2211	CH onset
	Ethylene/Oxygen/ 75%Argon		1.4-3.4	1102-1771	
	Ethylene/Oxygen/ 75%Nitrogen		2.3-4.8	1073-1565	
Penyazkov *et al.* [9]	Ethylene/air	1.0	6.28-8.01	1123-1479	CH onset, or OH onset
		0.5	6.83-8.24	1168-1430	
		2.0	6.67-7.89	1166-1519	
		1.0	13.1-15.2	1130-1372	
		0.5	13.42-15.5	1149-1385	
		2.0	12.7-16.5	1120-1460	
Saxena *et al.* [10]	Ethylene/Oxygen/ 93%Argon	3.0	1.9-2.6	1106-1539	Visible light, CH onset, or OH onset
			9.2-10.3	1063-1579	
			16.2-20.2	1000-1592	
		1.0	1.9-2.1	1106-1561	
			7.6-9.8	1034-1645	
	Ethylene/Oxygen/ 96%Argon	1.0	2.0-2.1	1198-1690	
			9.4-10.1	1197-1641	
			17.2-18.4	1109-1583	
	Ethylene/Oxygen/ 98%Argon	1.0	2.0-2.2	1223-1529	
			9.6-10.0	1223-1719	
			17.9-18.4	1291-1634	



(a) Brown *et al.* 75%Ar, P=1.4-3.4 atm (b) Brown *et al.* 75%N_2, P=2.3-4.8 atm

(c) Penyazkov *et al.* 73.8%N_2, P=6.3-8.0 atm (d) Saxena *et al.* 98%Ar, P=18 atm

Figs.1 Comparisons with experiments.

4 Effect of reduction

In this section, some reduced models from UC San Diego were selected to compare between them and to validate the reduced model. If these reduced models keep accuracy in detonation condition, it is suitable to be used in this works. Assuming a detonation under 0.1, 0.5, and 1.0 atm and 300 K, they were compared by ignition delay under the behind-shock conditions in ZND detonations. The initial gas composition was ethylene/oxygen=1/3 at volume ratio. The ignition time criterion was set to the OH onset.

The comparison graph is shown in Fig.2, and the each reduced model is validated by the differences from the detailed model (UC San Diego). The *y*-axis on the graph is the percentage of the difference. In case of a detonation under 0.1 atm, the VWmodel34 and VWmodel23 show good agreement with the detailed model. Therefore, it is found the VWmodel23 is better for simulating detonations under 0.1 atm with high accuracy and low cost.

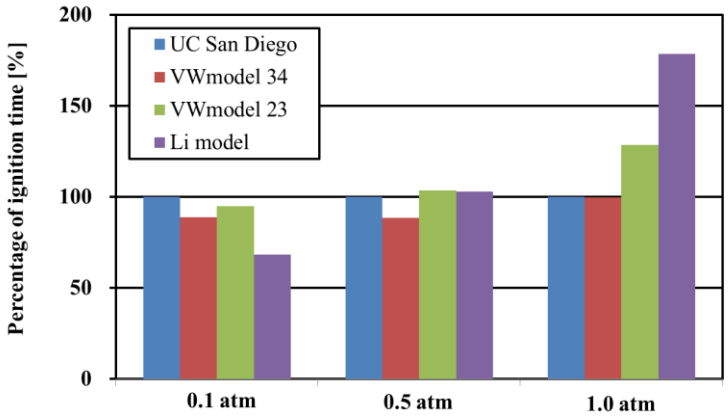
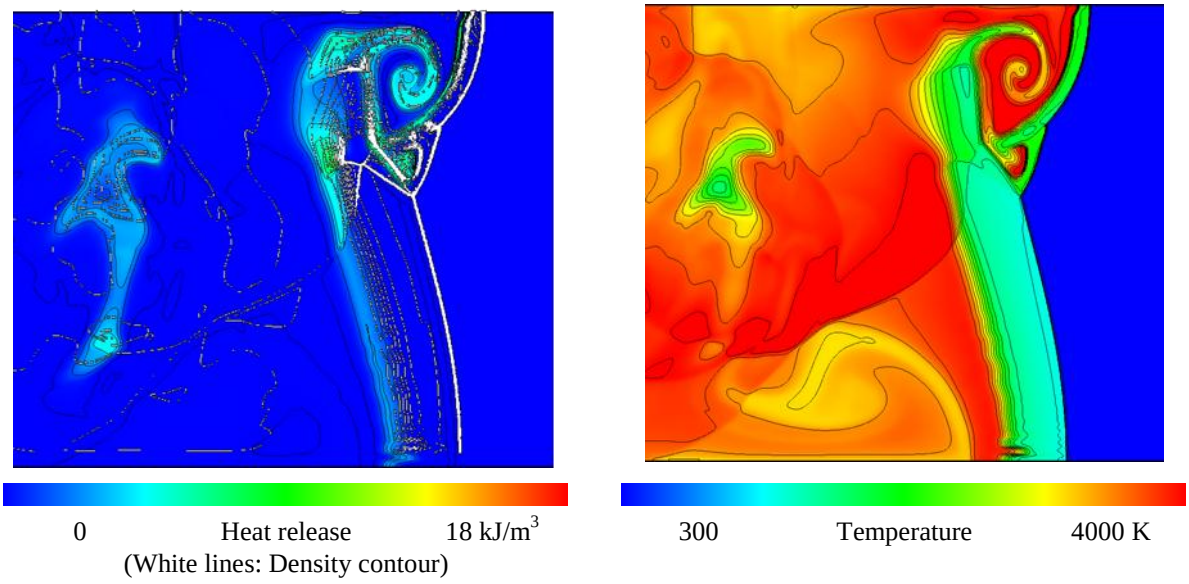


Fig.2 Comparison between reduced models and a detailed model.

5 Detonation analysis

The two-dimensional numerical simulation of the ethylene/oxygen detonation which propagates in narrow channel is carried out. In this simulation, the VWmodel23 was selected as the chemical reaction model. The governing equations are the Euler equations which include mass conservation laws of 23 species, and the equations are explicitly integrated using 3rd order TVD Runge-Kutta method, and the source term is integrated by VODE stiff solver. The AUSMDV scheme with 2nd order MUSCL and minmod limiter was used for the convection term. This simulation code was developed by Morii *et al.*[11] to show the ability to simulate for hydrocarbon detonation. The initial conditions were ethylene/oxygen stoichiometric mixture at 0.1 atm and 298 K. The grid width was set to 3.0 μm, which is the resolution of 30 points in the half reaction length. Assuming a detonation wave propagating in a 1 mm channel, we have some results of the calculation, and the structure when the wave is propagating steady is shown in Fig.3.
The contour of density (white lines in Fig.3 (a)) shows the structure of the detonation wave, and contour surface of the heat release shows the heating zone, *i.e.* the combustion wave front. In this figure, the typical structure of detonation wave, which is called the triplet point, is observed, and the double-Mach reflection is formed in the wave front. The induction length of a detonation wave is derived as the length from the shock wave to the combustion front. The length behind the Mach stem is shorter compared to that of leading shock wave. On the other hand, in the distribution of temperature (Fig.3 (b)), a circulation is clearly observed behind the Mach stem. This circulation causes by the influence of pressure differences in the backward region. . This strong circulation rolls up the unburned gas layer behind the Mach stem. This phenomenon is not observed in case of the hydrogen; therefore it is possibly due to the influence of characteristics of the ethylene combustion. This figure also shows an unburned gas pocket in the burnt gas. When the transverse shock wave propagates over the pocket, the chemical reactions are induced and the unburned gas disappears. The generation of the pocket is responsible for the activation energy of the chemical reactions, but, this phenomenon is not observed in case of the hydrogen/oxygen.
As the results, we can investigate about the two-dimensional structure of the detonation wave in the ethylene/oxygen mixture, and obtain the characteristic structures of ethylene detonations.



(a) Heat release and Density (b) Temperature

Figs.3 Instantaneous profiles in detonation front (t = 4.10 μsec).

6 Conclusion

In the present study, several reaction models for hydrocarbon were evaluated, and a numerical simulation of a detonation in a two-dimensional channel was carried out. As the results, the following results were obtained.

(a) The UC San Diego model, which includes small number of species, gives good accuracy for ignition in high temperature conditions.
(b) The VWmodel23 keeps accuracy in detonation condition in 0.1 atm, and is applicable for detonation analysis because of its accuracy and the calculating cost.
(c) A triple point, which is well-known as a typical structure in detonation wave, is investigated at the detonation wave front.
(d) The unburned gas pocket was observed in the detonation wave, and it disappears when the transverse shock wave runs over the pocket.
(e) The strong circulation appears behind the Mach stem, and it rolls up the unburned layer to backward.

In summary, numerical simulations of detonations in the ethylene/oxygen mixture were successfully conducted, and then its structures and mechanisms were found out in detail by using the reduced chemical reaction model. The characteristic structures which were obtained in the present study are necessary to be verified in other conditions.

Acknowledgements

The numerical simulations on this research were carried out on the Large-Scale Computing System of the Cyber Media Centre in Osaka University.

References

[1] Wang, H., *et al.* (2007). USC Mech Version II. High-Temperature Combustion Reaction Model of H2/CO/C1-C4 Compounds. http://ignis.usc.edu/USC_Mech_II.html

[2] Serauskas B. *et al.* (1999). http://www.me.berkeley.edu/gri_mech/index/html

[3] Williams, F. A. *et al.* (2011). http://web.eng.ucsd.edu/mae/groups/combustion/index/html

[4] Varatharajan, B., Williams F. A. (2002). Ethylene Ignition and Detonation Chemistry, Part 1: Detailed Modelling and Experimental Comparison. *Journal of Propulsion and Power* Vol.18, No.2, 344-351

[5] Varatharajan, B., Williams, F. A. (2002). Ethylene Ignition and Detonation Chemistry, Part 2: Ignition Histories and Reduced Mechanisms. *Journal of Propulsion and Power* Vol.18, No.2, 352-362

[6] Li, S. C., Varatharajan, B., Williams, F. A. (2000). The chemistry of ethylene ignition for application to pulse detonation engines. *AIAA paper* 2000-3475

[7] Yungstar, S., Radhakrishnan, K., (2005). Structure and stability of one-dimensional detonations in ethylene-air mixtures, *Shock Waves*, Vol.14, No.1-2, 61-72

[8] Brown, C. J., Thomas, G. O., (1999) Experimental Shock-Induced Ignition and Transition to Detonation in Ethylene and Propane Mixtures. *Combustion and Flame*, Vol.117, No.4, 755-776

[9] Penyazkov, O. G., Sovrouk, K. L., Tangirala, V., Joshi, N., (2009). High-pressure ethylene oxidation behind reflected shock waves. *Proceedings of the Combustion Institute* Vol.32, 2421-2428

[10] Saxena, S., Kahandawala, M.S.P., Sidhu, S.S., (2011). A Shock tube study of ignition delay in the combustion of ethylene. *Combustion and Flame*, Vol.158, 1019-1031

[11] Morii Y. Tsuboi N. *et al.* (2012). Numerical approach to one-dimensional CH4/O2 detonation with the reduced chemical kinetic model DRG30. *Science and Technology of Energetic Materials*, Vol. 73, No.6, 170-175