



HOKKAIDO UNIVERSITY

Title	Hydrogen as an ignition-controlling agent for HCCI combustion engine by suppressing the low-temperature oxidation
Author(s)	Shudo, Toshio; Yamada, Hiroyuki
Citation	International Journal of Hydrogen Energy, 32(14), 3066-3072 https://doi.org/10.1016/j.ijhydene.2006.12.002
Issue Date	2007-09
Doc URL	https://hdl.handle.net/2115/30292
Type	journal article
File Information	IJHE32-14.pdf



Hydrogen as an ignition controlling agent for HCCI combustion engine by suppressing the low-temperature oxidation

Toshio SHUDO

Applied Energy System Group, Division of Energy and Environmental Systems, Hokkaido University

N13 W8, Kita-ward, Sapporo, 060-8628, JAPAN

Email: shudo@eng.hokudai.ac.jp

Tel/Fax: +81-11-706-6402

Hiroyuki YAMADA

Environment Research Department, National Traffic Safety and Environment Laboratory, JAPAN

Abstract

Homogeneous charge compression ignition (HCCI) combustion enables internal combustion engines to achieve higher thermal efficiency and lower NO_x emission than with conventional combustion systems. To control the ignition timing in accordance with the operating conditions is crucial for utilizing HCCI combustion engines. Adding hydrogen-containing gas is known to retard the autoignition of dimethyl ether (DME) considerably. The effective ignition control by hydrogen can expand the operation range of equivalence ratios and engine loads in HCCI combustion. This research investigated the mechanisms in the ignition control by the chemical kinetics analysis. The results show that the retarded ignition can be attributed to a consumption of OH by hydrogen during low-temperature oxidation of DME. The decreased OH concentration leads to retarded heat release and delays the onset of the high-temperature oxidation.

Keywords: Internal combustion engine, HCCI, Ignition control, low-temperature oxidation, DME

Nomenclature

ε	Compression ratio
ϕ	Equivalence ratio
θ	Crank angle
P	In-cylinder pressure
$dQ/d\theta$	Apparent rate of heat release
Q	Cumulative apparent heat release
η_i	Indicated thermal efficiency
T_g	In-cylinder gas mean temperature
LTR	Low-temperature reactions
HTR	High-temperature reactions
T_{LTR}	T_g at the beginning of LTR
T_{HTR}	T_g at the beginning of HTR
θ_{LTR}	Crank angle at the beginning of LTR
θ_{HTR}	Crank angle at the beginning of HTR
HCCI	Homogeneous charge compression ignition
DME	Dimethyl ether
MRG	Methanol-reformed gas
MeOH	Methanol
MFC	Mass flow controller
EGR	Exhaust gas recirculation
IMEP	Indicated mean effective pressure
THC	Total hydrocarbon
CA	Crank angle
ATDC	After top dead center

1. Introduction

It is expected that the use of homogeneous charge compression ignition (HCCI) combustion in internal combustion engines will result in higher thermal efficiency and lower NO_x emissions than with conventional combustion systems. However, difficulties in controlling the ignition timing in accordance with the engine load are preventing HCCI combustion from practical application in vehicle engines. Adjusting the proportion of two fuels with different ignition properties has

been reported as an effective technique to control the ignition timing and load in HCCI combustion [1]. However, this technique has not been practically used in vehicles because of the inconvenience of carrying two kinds of fuels.

Dimethyl ether (DME) has been studied as a clean alternative to diesel fuel due to its high cetane number and smokeless combustion characteristics [2–4], and DME can be easily produced from methanol by the dehydration reaction [5]. There is a report of an idea to use a small amount of DME produced from methanol as an ignition promoter in a methanol direct-injection diesel engine [2]. Methanol can also be thermally decomposed into methanol reformed gas (MRG) which consists of hydrogen and carbon monoxide. Since both hydrogen and carbon monoxide have good anti-knocking properties [6], MRG has been studied as a fuel for spark-ignition engines [7, 8].

With this background, an HCCI combustion engine system that was fuelled with DME and MRG has been proposed [9–11]. Because the ignition properties of DME and MRG are very different, adjusting the proportion of the two fuels can control the ignition timing in an HCCI combustion engine fueled with the two. In addition to ignition control, production of DME and MRG by onboard reformers utilizing the exhaust gas heat of the engine has also been proposed, with an outline of the arrangement as shown in Figure 1. Because the reactions to produce DME and MRG from methanol are endothermic, the heating values of the produced DME and MRG can be higher than the primary fuel. Therefore, methanol reformation using the engine exhaust gas heat could be utilized to recover waste heat from the engine. By combining efficient HCCI operation and waste heat recovery a system based on these processes can achieve a good overall thermal efficiency. The use of a single liquid fuel, methanol, also eliminates the inconvenience of having to carry two fuels and makes the HCCI combustion practically possible in vehicles. It is crucial to avoid a too early ignition to achieve higher load operation in HCCI engines, and hydrogen retards the autoignition of DME considerably [10–11]. The ignition control effect by MRG is attributed to the hydrogen in MRG. Therefore, DME-reformed gases, which contain hydrogen, are also effective to control autoignition of DME [12]. This report investigates the reaction mechanisms in the ignition control of hydrogen by using chemical kinetics analysis.

2. Experiments and Calculations

The test engine used was a four stroke cycle single cylinder engine with a bore of 85mm, a stroke of 88mm and a compression ratio of 9.7. The fuel gases, dimethyl ether (DME; CH_3OCH_3) and hydrogen (H_2), were stored in high-pressure cylinders and continuously supplied to the intake manifold of the engine as shown in Figure 2. Fuel flow rates were separately controlled using needle valves and measured by mass flow meters (Oval). The in-cylinder pressure was measured with a piezoelectric pressure transducer (AVL GM12D) installed in the cylinder head. For each experimental condition, the pressure data for 100 cycles were averaged and used to calculate the mean in-cylinder gas temperature, the indicated mean effective pressure, the indicated thermal efficiency and the apparent rate of heat-release. Concentrations of CO and THC in the exhaust gas were measured with an NDIR analyzer and an FID analyzer respectively. The engine speed was set at 1000 rpm for all the experiments. The volumetric efficiency was controlled at 75% including fuel gases. The intake air was at room temperature without heating.

A chemical kinetics analysis using CHEMKIN II was performed to analyze the reaction mechanisms in the ignition control effect of hydrogen. The detailed reaction mechanism for DME oxidation reported by Curran et al. [13–14] was employed in SENKIN adiabatic calculations. Volume changes and initial conditions for the calculation were determined according to the engine experiments.

3. Results and Discussions

3.1. Experimental results of ignition control by hydrogen in HCCI combustion

Previous research [9] has shown that MRG, which consists of hydrogen and carbon monoxide, has a large ignition control effect in HCCI combustion of DME. Figure 3 shows the effects of hydrogen and carbon monoxide on HCCI combustion of DME. The DME amount was fixed at a value that gives the equivalence ratio of 0.27 without the addition of hydrogen or carbon monoxide. The mole fraction of hydrogen or carbon monoxide to DME was varied from 0 to 1.5. Equivalence ratios which increase by the addition of hydrogen or carbon monoxide as indicated in the figures were calculated by the totally supplied fuels. Figure 4 shows a comparison of results with hydrogen and carbon monoxide at a 40% DME fraction. Figure 5 shows crank angles at the onset of heat release by the low- and high-temperature oxidation reactions (θ_{LTR} , θ_{HTR}), the in-cylinder gas mean temperatures at the timings (T_{LTR} , T_{HTR}) and cumulative apparent heat-release during the low- and high-temperature oxidation reactions (Q_{LTR} , Q_{HTR}). These values are derived from the experimental results shown in Figure 3.

The figures show that the addition of hydrogen or carbon monoxide retards the combustion phase in spite of the increased equivalence ratio, and the effect is clearly larger in the hydrogen addition. Though the hydrogen addition retards the timing of the second heat-release considerably, there is no remarkable change in the temperature at the timing. Hydrogen makes the first heat-release slower and effectively delays the temperature rise during the low-temperature oxidation of DME. Because of the delayed temperature-rise, the starting crank angle of the second heat-release is considerably retarded in spite of the absence of any remarkable change in the starting temperature of the high-temperature oxidation reactions. There is almost no change in the cumulative apparent heat release during the low-temperature oxidation Q_{LTR} , while the heat release during the high-temperature oxidation Q_{HTR} increases with the equivalence ratio.

3.2. Reaction mechanism in the ignition control effect of hydrogen

Figure 6 shows the in-cylinder pressure and the temperature for HCCI combustion of DME and hydrogen that were calculated using CHEMKIN II with the DME oxidation reaction kinetics model by Curran et al. [12, 13]. The calculated trends of the combustion phase retardation by the hydrogen addition are similar to the experimental results in Figure 3. The DME oxidation model by Curran et al is qualitatively consistent with the experimental results in HCCI engines. The first step in the model is the production of CH_3OCH_2 from DME. Though hydrogen abstraction from DME by oxygen is the initiation reaction, the largest part of the CH_3OCH_2 is produced by the following hydrogen abstraction reaction with OH in the low-temperature oxidation of DME [14].



The CH_3OCH_2 reacts with O_2 or a third body to produce HCHO, OH, and other species. The produced HCHO consumes OH in the following reaction.



Here OH is a chain carrier in the low-temperature oxidation. As a result of the production and consumption of OH, when $d[\text{OH}]/dt$ becomes negative the chain branching terminates. When hydrogen and carbon monoxide are introduced to this low-temperature oxidation process of DME, they consume OH in the following reactions and suppress the consumption of CH_3OCH_3 .



Reaction (3) occurs at a 3 to 6 times higher rate than Reaction (4) in the temperature range from 700 to 1000K where the low-temperature oxidation reactions occur, as shown in Figure 7. This causes the differences in the ignition control effect of hydrogen and carbon monoxide. The hydrogen produced from the reactions quickly combines with O_2 to produce HO_2 and the HO_2 reacts with H to produce H_2O_2 .

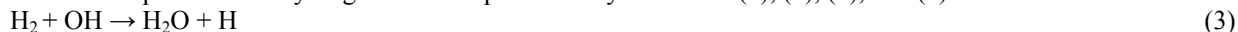


However, HO_2 and H_2O_2 are much less reactive than OH during the low-temperature oxidation process, while H_2O_2 dissociates to OH in the high temperature oxidation process. There is another reaction between H and O_2 to produce OH and O.



If this reaction is dominant, the increased OH promotes the low-temperature oxidation. Figure 8 shows the rate constants for the two reactions between H and O_2 versus temperature. Reaction (5), producing HO_2 , is dominant over Reaction (7), producing OH and O, in the low-temperature oxidation regime. Therefore, H radicals produced in Reactions (3) and (4) do not increase the OH concentration. Overall, the introduced hydrogen converts the highly reactive OH into the less reactive HO_2 and H_2O_2 .

Figures 9 and 10 show the influence of hydrogen addition on the mol fractions of chemical species and temperature against crank angle in HCCI combustion of DME. The calculations are for H_2/DME mol fractions of 0, 0.67, 1.0, and 1.5 with a constant DME amount which brings an equivalence ratio of $\phi=0.27$ in the neat DME case. The increase in hydrogen decreases the OH concentration remarkably and retards the first peak of the OH concentration, and this subsequently retards consumption of CH_3OCH_3 and formation of HCHO. An increase in the hydrogen fraction increases the peak concentrations of HO_2 and H_2O_2 just before the high-temperature oxidation. The high-temperature oxidation starts with the dissociation of H_2O_2 to 2OH and oxidizes intermittent species to H_2O and CO_2 . The H_2O_2 decreases and OH increases rapidly at around 1000K regardless of the hydrogen fraction; along with the abrupt increase in the OH concentration, CH_3OCH_3 , CO, and H_2 are rapidly consumed producing H_2O and CO_2 here. The cases with higher hydrogen fraction tend to have more OH during the high-temperature oxidation. This is because of the higher concentration of H_2O_2 during the low-temperature oxidation and combustion process of hydrogen itself. Almost all the introduced hydrogen is consumed during the high-temperature oxidation, and the consumption of it during the low-temperature oxidation is quite small. Here, the combustion processes of hydrogen can be represented by Reactions (3), (5), (7), and (8).



Reaction (7) producing OH and O is slower than Reactions (3) and (8), and is the rate-determining process. However, Reaction (5), another reaction between H and O_2 , is dominant over Reaction (7) in the temperature range below 1250K as shown in Figure 8, and the combustion process of hydrogen does not proceed during the low-temperature oxidation of DME.

The strongly retarded low-temperature oxidation brought about by the addition of hydrogen in the experiments can be attributed to the consumption of OH by hydrogen. The reduced OH concentration retards the H abstraction from CH_3OCH_3 by OH and subsequent exothermic reactions during the low-temperature oxidation. While hydrogen does not affect the starting-temperature of the high-temperature oxidation, the onset of the second heat-release is retarded due to the delayed rise in temperature.

4. Conclusions

- (1) Hydrogen is an effective ignition controller for HCCI combustion of DME. Hydrogen makes the first heat-release slower and delays the rise in temperature during the low-temperature oxidation of DME. Because of the delayed rise in temperature, the starting crank angle of the second heat release is greatly delayed. There is no large change in the starting-temperature of the high-temperature oxidation. Hydrogen addition prevents a too early ignition and enables higher load operation in HCCI engines.
- (2) The first step in the low-temperature oxidation of DME is hydrogen abstraction from DME, producing CH_3OCH_2 . The largest part of CH_3OCH_2 is produced in reaction with OH. When hydrogen is introduced to the low-temperature oxidation of DME, it reduces the OH concentration and retards the CH_3OCH_3 consumption.
- (3) Both hydrogen and carbon monoxide consume OH and retard H abstraction from DME by OH. The reaction of H_2 and OH is faster than the reaction of CO and OH, and hydrogen has a stronger effect of retarding autoignition of DME than carbon monoxide.
- (4) The reaction of H_2 and OH produces H_2O and H. The H reacts with O_2 to produce HO_2 which reacts with H to produce H_2O_2 . Though there is another reaction between H_2 and OH producing the highly reactive OH and O, the production of the less-reactive HO_2 is dominant during the low-temperature oxidation of DME.
- (5) Because the introduced hydrogen converts the highly reactive OH into less-reactive HO_2 and H_2O_2 , the oxidation process and the heat release are retarded during the low-temperature oxidation of DME.
- (6) The retarded heat release delays the temperature-rise starting the high-temperature oxidation, while the starting temperature for the high-temperature oxidation is not influenced by hydrogen.
- (7) The combustion process of hydrogen is controlled by the reaction of H and O_2 producing OH and O. However, the reaction producing the less-reactive HO_2 is dominant in the temperature range of the low-temperature oxidation. Therefore, hydrogen combustion does not proceed during the low-temperature oxidation of DME.

Acknowledgments

The authors express gratitude to Mr. Yoshitaka Ono and Mr. Takehiro Takahashi, former students of Musashi Institute of Technology, for their help in this research. This research was financially supported by RC210 of the Japan Society of Mechanical Engineers.

References

1. Furutani, M., Ohta, Y., Kono, M., Hasegawa, M. An ultra-lean premixed compression-ignition engine concept and its characteristics. Proceedings of COMODIA 98 1998.
2. Murayama, T., Chikahisa, T., Guo, J., Miyano, M. A study of compression ignition methanol engine with converted dimethyl ether as an ignition improver. SAE Technical Paper 1992;922212.
3. Sorenson, SC., Mikkelsen, SE. Performance and emissions of a 0.273 liter direct injection diesel engine fuelled with neat dimethyl ether. SAE Technical Paper 1995;950064.
4. Kajitani, S., Chen, Z., Konno, M., Rhee, KT. Engine performance and exhaust characteristics of direct-injection diesel engine operated with DME. SAE Technical Paper 1997;972973.
5. Bercic, G., Levec, J. Catalytic dehydration of methanol to dimethyl ether kinetic investigation and reactor simulation. Industrial & Engineering Chemistry Research 1993;32.
6. Obert, E.F. Internal combustion engines and air pollution. New York NY: Harper & Row, 1973.
7. Hirota, T. Study of methanol-reformed gas engine. Journal of Society of Automotive Engineers of Japan (in Japanese) 1980;34(10).
8. Shudo, T., Tsuga, K., Nakajima, Y. Combustion characteristics of H_2 -CO- CO_2 mixture in an IC engine. SAE Transactions Journal of Engines 2002;110(3).
9. Shudo, T., Ono, Y. HCCI combustion of hydrogen, carbon monoxide and dimethyl ether. SAE Transactions Journal of Engines 2003;111(3).
10. Shudo, T., Ono, Y., Takahashi, T. Influence of hydrogen and carbon monoxide on HCCI combustion of dimethyl ether. SAE Transactions Journal of Fuels & Lubricants 2003;111(4).
11. Shudo, T., Takahashi, T. Influence of reformed gas composition on HCCI combustion of onboard methanol-reformed gases. SAE Technical Paper 2004;2004-01-1908.
12. Shudo, T., Ono, Y., Takahashi, T. Ignition control by DME-reformed gas in HCCI combustion of DME. SAE Transactions Journal of Fuels & Lubricants 2004;112(4).
13. Fischer, S. L., Dryer, F. L., and Curran, H. J. The Reaction kinetics of dimethyl ether I: High-temperature pyrolysis and oxidation in flow reactors. International Journal of Chemical Kinetics 2000;32:.
14. Curran, H. J., Fischer, S. L., and Dryer, F. L., The Reaction kinetics of dimethyl ether II: Low-temperature oxidation in flow reactors. International Journal of Chemical Kinetics 2000;32:.
15. Yamada, H., Suzuki, K., Sakanashi, H., Choi, N., Tezaki, A. Kinetic measurements in homogeneous charge compression of dimethyl ether: Role of intermediate formaldehyde controlling chain branching in the low temperature oxidation mechanism. Combustion and Flame 2005;140(24).

16. Eng, JA., Leppard, WR., Sloane, TM. The effect of POx on the autoignition chemistry of n-heptane in an HCCI engine. Proceedings of Society of Automotive Engineers of Japan 2002;25(02).
17. Shudo, T., An HCCI combustion engine system fueled with onboard-reformed gases of methanol: Ignition control by hydrogen, Journal of Society of Automotive Engineers of Japan (in Japanese) 2004;58(9).
18. Shudo, T., Nabetani, S., Nakajima, Y. Analysis of the degree of constant volume and cooling loss in a spark ignition engine fuelled with hydrogen. International Journal of Engine Research 2001;2(1).

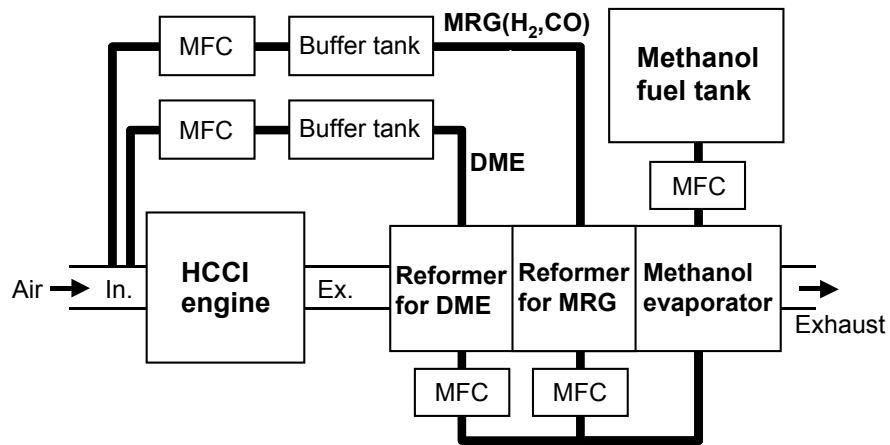


Fig. 1 Concept of HCCI combustion engine system fueled with DME and MRG onboard-reformed from methanol

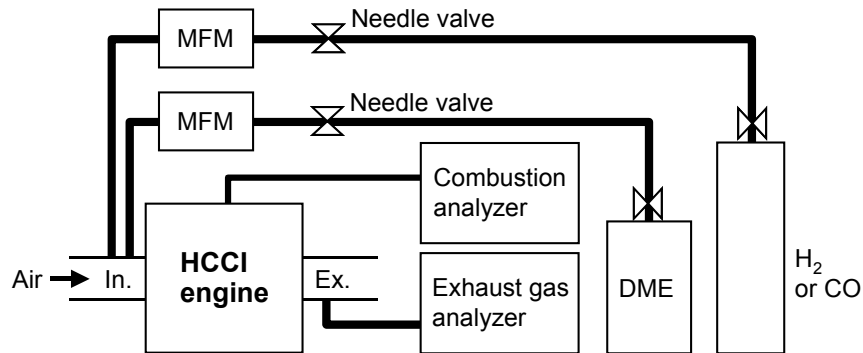


Fig. 2 Schematic diagram of experimental system

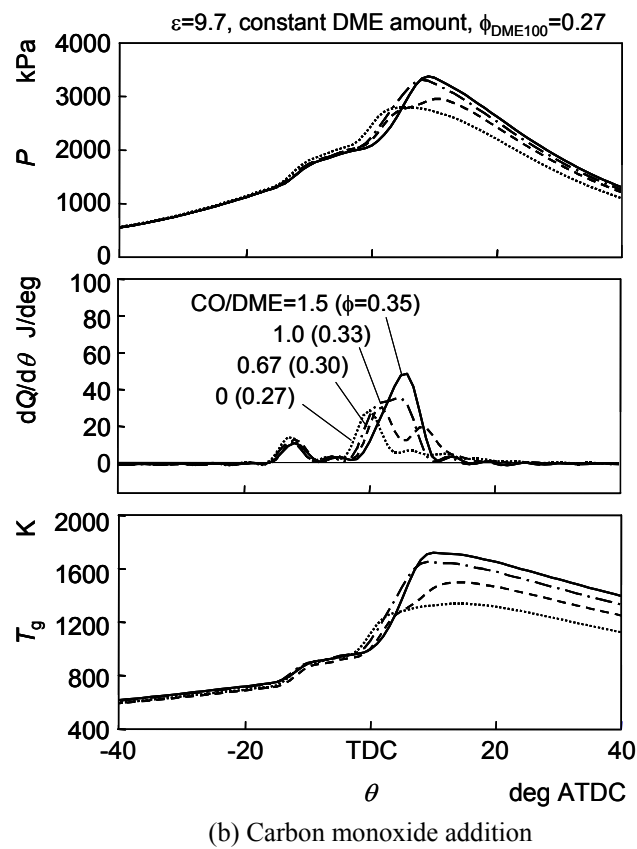
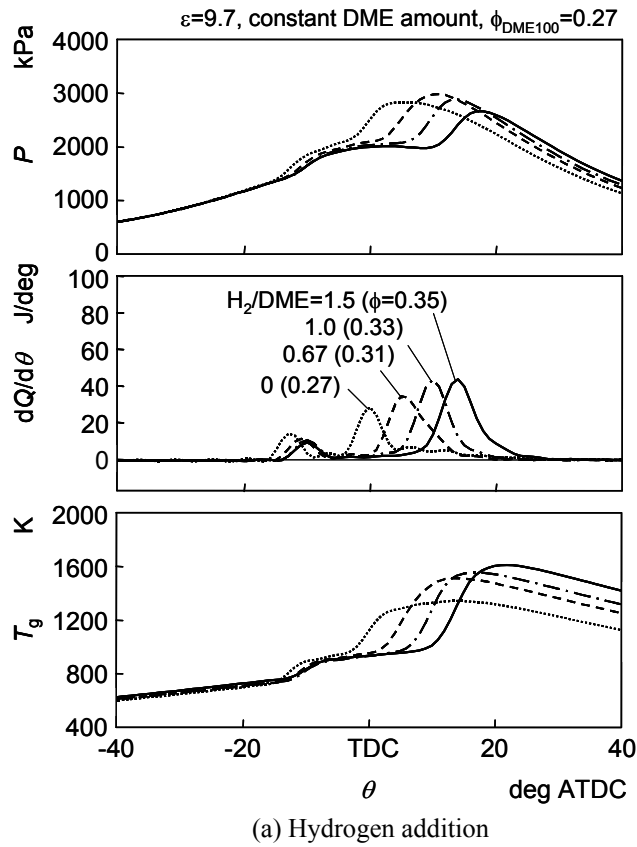


Fig. 3 Effects of hydrogen on autoignition of DME

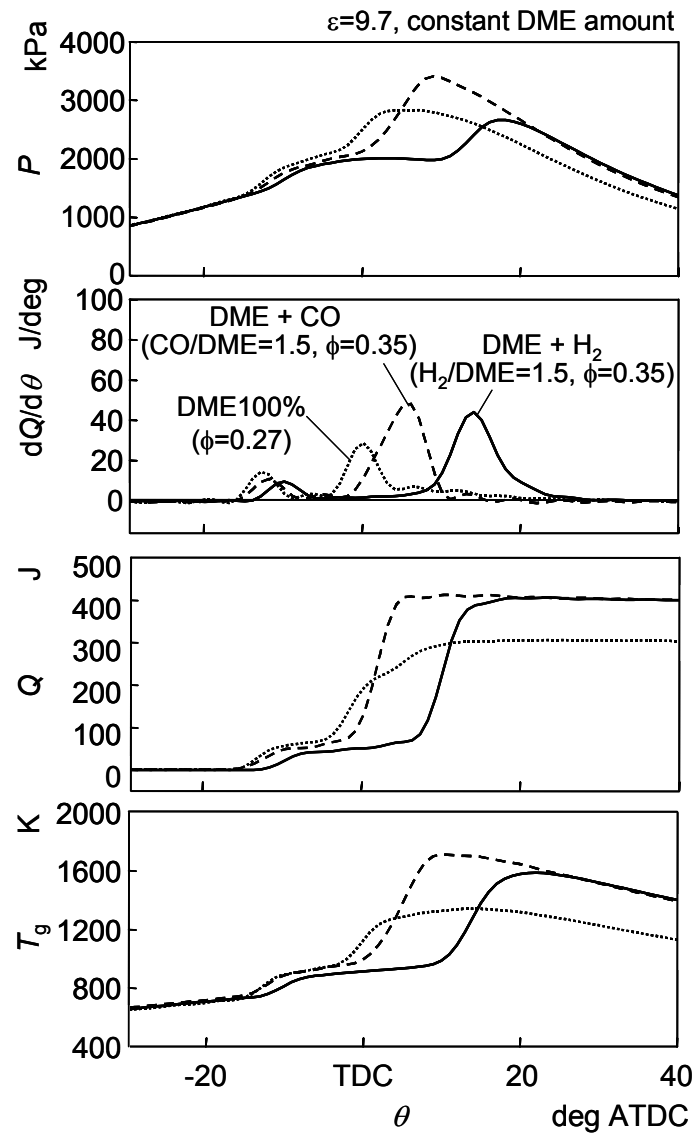


Fig. 4 Ignition control effects by hydrogen and carbon monoxide

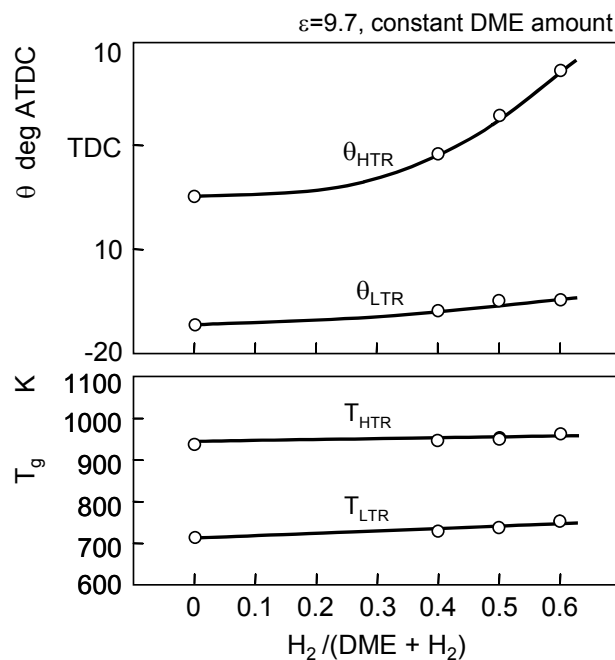


Fig. 5 Crank angles and in-cylinder gas mean temperature at the onset of the low- and high-temperature reactions

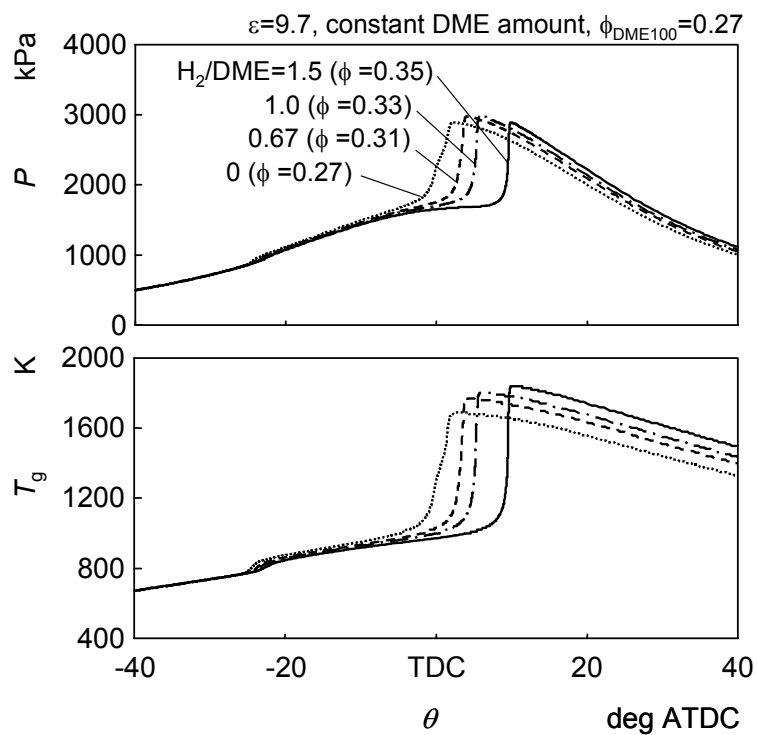


Fig. 6 Calculated effect of hydrogen on autoignition of DME

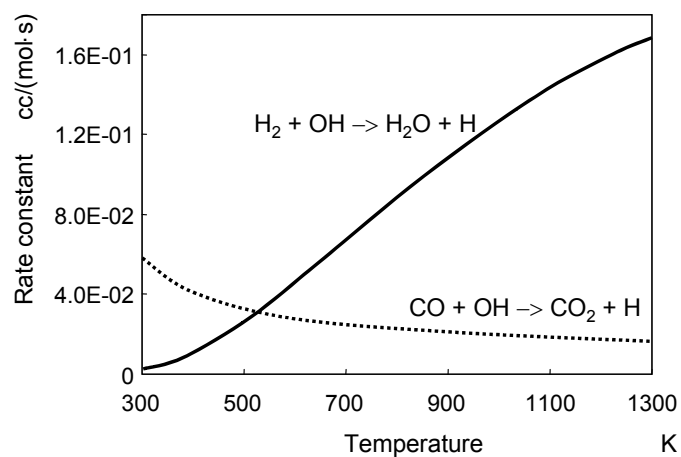


Fig. 7 Rate constants for OH consumption by hydrogen and carbon monoxide

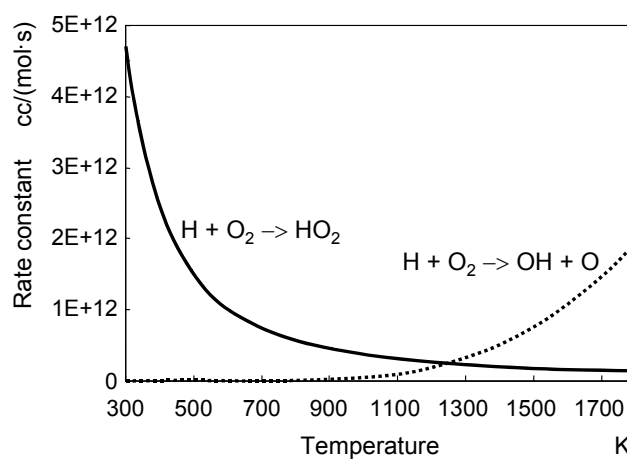


Fig. 8 Rate constants for reactions of H and O_2

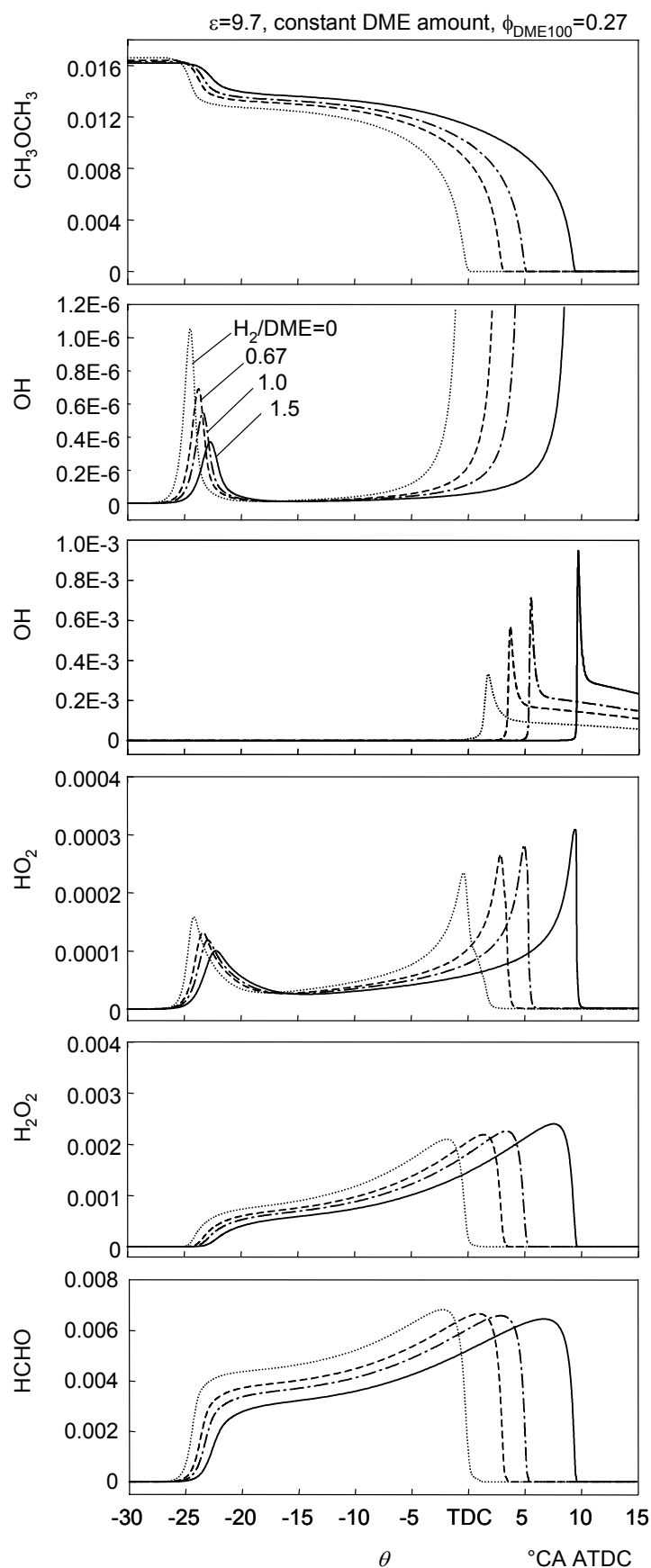


Fig. 9 Calculated mole fraction of species in DME oxidation with different hydrogen fractions

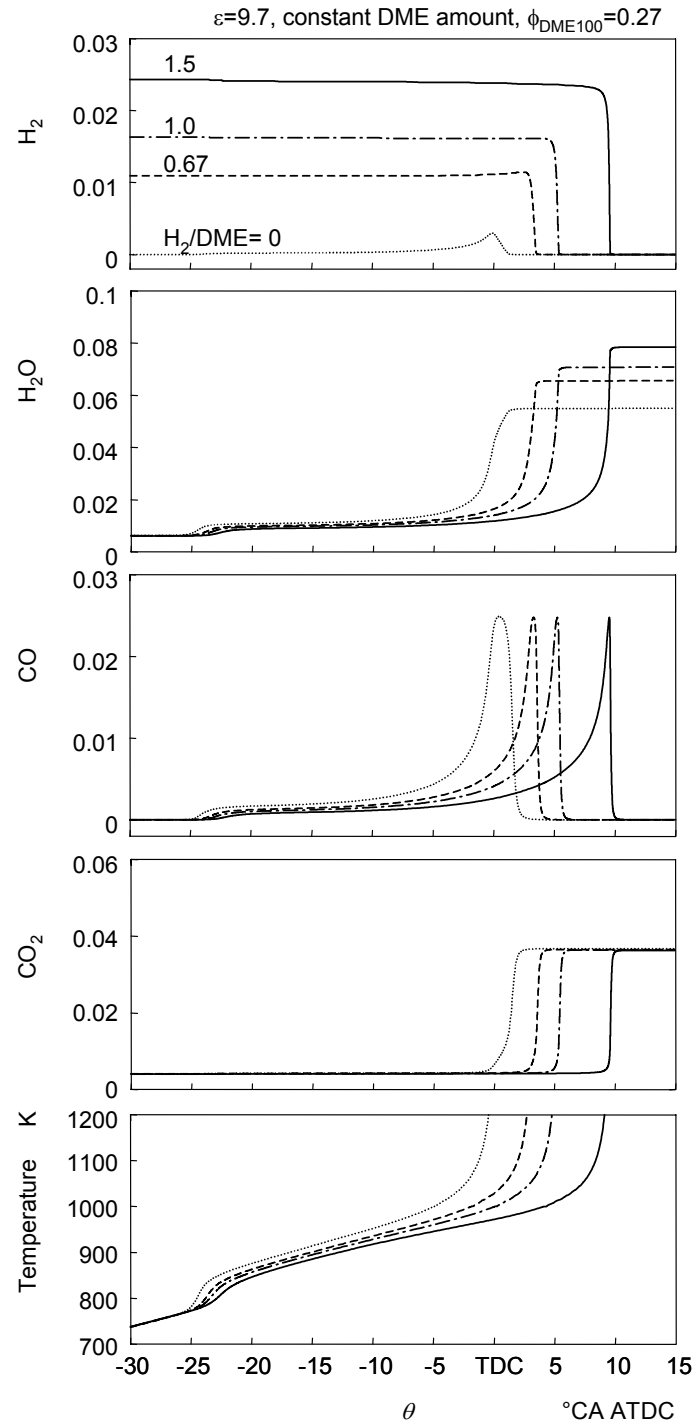


Fig. 10 Calculated mole fraction of species in DME oxidation with different hydrogen fractions