27 Fundamental Study on the Influence of Additives on Ignition Control of Natural Gas HCCI Engine

Mohamed H. MORSY[(1)] and Suk Ho CHUNG[(2)]

[(1)] Department of Engineering Sciences, Faculty of Petroleum and Mining Engineering

Suez Canal University, Suez, Egypt

[(2)] School of Mechanical and Aerospace Engineering, Seoul National University

Seoul 151-742, Korea

The influence of additives such as dimethyl ether (DME), formaldehyde (CH_2O) and hydrogen peroxide (H_2O_2) for the control of ignition in natural gas HCCI engines have been investigated numerically by adopting a single-zone zero-dimensional model. Computations were first carried out in a constant volume bomb to demonstrate variations in ignition delay times with the additives by varying initial temperature, pressure, equivalence ratio, and composition. The effect of H_2O_2 addition in reducing the ignition delay was most pronounced as compared to the other two additives of DME and CH_2O for all conditions examined. With engine-like conditions, calculations were done at a fixed equivalence ratio of 0.3 and initial mixture pressure of 1.5 bar. It was found that an additive-free mixture did not ignite for the intake temperature of 400 K. A mixture containing a small quantity of additives at the same temperature was ignited. For a fixed quantity of additive, it was found that H_2O_2 addition was effective in advancing the ignition timing as compared to the other two additives, which is consistent with the constant volume calculations. Furthermore, the addition of even 2.5% by volume of H_2O_2 could ignite a mixture at an intake temperature of 350 K, while at least the fractions of 10% and 15% by volume were needed for DME and CH_2O, respectively.

***Keywords*: Natural Gas, Ignition Control, Ignition Improvers, HCCI Engines**

1. INTRODUCTION

A homogeneous charge compression ignition (HCCI) is currently under widespread investigation due to its potential in reducing the emissions of nitrogen oxides (NO_x) and particulate matter (PM), while maintaining high thermal efficiency [1-7]. It is a promising alternative to the existing spark ignition (SI) and compression ignition (CI) engines. The HCCI engine concept promises to combine the advantages of both CI and SI engines, while minimizing their drawbacks. As in an SI engine, the charge is well mixed and then introduced into the cylinder which minimizes particulate emissions. As in a diesel engine, it adopts compression ignition and has no throttling losses, which leads to high efficiency. However, unlike either of these conventional engines, combustion occurs simultaneously throughout the cylinder volume rather than forming a flame front.

The homogeneous lean burn operation associated with HCCI engines will yield lower gas temperatures and hence NO_x, as compared to both SI and CI counterparts [1]. Furthermore, unthrottled part load operation eliminates pumping losses leading to improved fuel economy over SI engines. As the HCCI concept operates on the premise of autoignition, this allows the use of elevated compression ratios of approximately 20-25.

Conventional diesel fuel for HCCI could pose several problems arising from inherent physical and chemical characteristics. For example, in order to achieve a homogeneous diesel/air mixture, early injection timings are required, because the vaporization of diesel fuel is poor. Early fuel injection tends to splash the spray at the wall of the cylinder. This aggravates the formation of a homogeneous mixture, thus, emissions of THC, CO, and PM will be increased and the engine thermal efficiency will be decreased [2].

A natural gas fuel is an alternative than diesel fuel as it easily forms a uniform mixture. The application of natural gas to an internal combustion engine should be by way of compression ignition if high thermal efficiency and low NO_x emission are expected. However, the auto-ignition of natural gas under diesel-like conditions requires temperatures as high as 1100-1200 K [8]. This high temperature requirement mandates that either a high compression ratio or a high intake air temperature be used, both of which have negative effects on engine

performance and durability.

Although recent investigations on HCCI combustion appear promising, several problems can appear. The ignition timing is very difficult to control and is considered as one of the barriers in realizing the engine. Therefore, controlling the ignition timing over a wide range of conditions is challenging. Several methods have been proposed to control HCCI combustion: varying the amount of exhaust gas recirculation (EGR) so that the autoignition temperature of the fuel is reached during the compression stroke. This can be done by closing the exhaust valve early [9-12] using variable valve timing to change the amount of hot exhaust gases retained in the cylinder. Variable valve timing technology is particularly attractive because its time response could be made sufficiently fast to handle rapid transients. Although this technology has shown strong potential, performance is not yet fully proven, and cost and reliability issues must be addressed. The control of ignition timing could be also achieved either by addition of promoters [3, 13-15] (additives reducing ignition delay time) or blending low cetane number fuels (such as natural gas and methanol) with high cetane number fuels [2, 5].

The aim of the present work is to investigate the effect of several potential additives on the ignition timing of a natural gas HCCI engine. The effect of additives such as formaldehyde (CH_2O) and hydrogen peroxide (H_2O_2) and high cetane number fuel such as DME on the ignition timing is investigated numerically. As the HCCI ignition process is mainly controlled by chemistry, the numerical study adopted detailed chemical kinetics, while neglected effects from transport phenomena.

2. REACTION SCHEMES AND NUMERICAL SIMULATION

It is generally accepted that an HCCI process with its auto-ignition characteristics is controlled primarily by chemical kinetics. In this regards, extensive works has been carried out in HCCI modeling to implement detailed reaction mechanisms to accurately predict autoignition. In the present study, two chemical kinetics schemes for natural gas and DME have been utilized. The natural gas chemistry was described by the GRI-3.0 mechanism [17] that considers 53 species and 325 reactions, including NO_x chemistry and was used to study the effect of both CH_2O and H_2O_2 addition. The DME reaction scheme consisting of 79 species and 351 reactions proposed by Curran *et al.* [16] was adopted to study the effect of DME addition. The combustion event has been modeled using the single-zone zero-dimensional SENKIN code [18] from the Chemkin-III package [19]. Computations were carried out at two conditions; constant volume adiabatic condition and engine-like condition accounting the compression and expansion processes. The model for engine-like condition described below is based on the assumptions that the mixture is a perfect gas, heat loss from the cylinder walls is neglected (adiabatic walls), and temperature and species concentrations are uniformly distributed.

Formulas describing the piston motion are not included in the SENKIN code. Therefore, the volume was treated as a function of time given by a user-made routine to fit the experimental compression cycle with the following formula [20]

$$\frac{V}{V_c} = 1 + \frac{1}{2}(r_c - 1)\left[R + 1 - \cos\theta - (R^2 - \sin^2\theta)^{1/2} \right]$$

where V_c is the clearance volume, r_c is the compression ratio, R is the ratio of connecting rod length to crank radius, and θ is the crank angle. A transition from time to crank angle and vise versa could be made as:

$$\theta = \frac{2\pi N}{60} t + \theta_{IVC}$$

where N is the engine speed in rpm and θ_{IVC} is the crank angle at intake valve close (IVC) in radians.

The engine specifications assumed in this research are shown in Table 1.

Table 1 Specifications of model engine

Displacement	1132 cm^3
Bore x Stroke	112 x 115 mm
Connecting Rod Length	250 mm
Compression Ratio	18.0
Intake Valve Close	ABDC 48^o
Exhaust Valve Open	BBDC 48^o

The simulation is started at IVC where fresh charge at specified pressure, temperature and equivalence ratio is inducted into the cylinder and stopped at the end of the expansion stroke.

The present analysis considers a single zone model that ignores spatial variations in the combustion chamber. Due to the assumed temperature uniformity, our estimates of burn duration and the heat release processes will be shorter than in experiments. That is, the boundary layer and crevices will always react last and extend the heat release rate compared to this simulation.

Peak cylinder pressure and rate of pressure rise thus can be over-predicted with the single-zone model, and the model cannot accurately predict CO and hydrocarbon emissions, which primarily depend on crevices. However, predictions of start of combustion and NO_x, which depend on the peak temperature of the core gases inside the cylinder, have been shown to be determined with reasonable accuracy [5]. Since the aim of this study is basically to investigate the effect of different additives on the ignition timing of a natural gas HCCI engine, the single zone model can reasonably capture the relative effectiveness of various additives.

3. RESULTS AND DISCUSSION

Calculations have been first performed with the constant volume condition to compute the ignition delays for CH_4/air mixtures with several additives at various concentrations, pressures and temperatures. When ignition improvers are added, as reported by Golovichev *et al.* [21], the definitions of conventional ignition delay using H or OH maxima or the criterion for the ignition delay of [OH]

$= 10^{-9}$ moles/cm^3, are no longer valid. Thus, the ignition delay time in this study was defined as the time at which the temperature gradient picks up. An example of temperature variations with time used to define the ignition delay times are plotted in Fig. 1.

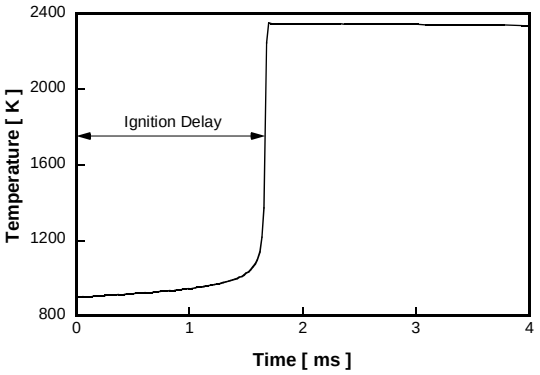

Fig. 1 Time history for temperature used to define ignition delay.

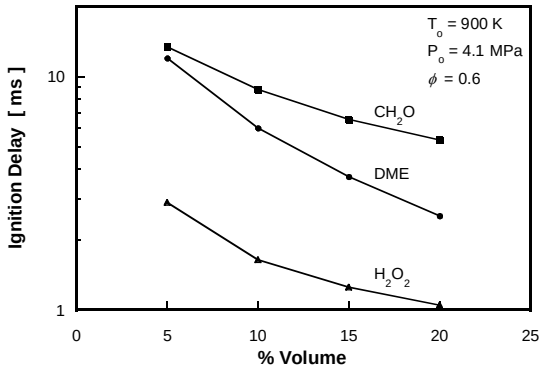

Fig. 2 Effect of additives concentration on the ignition delay of CH_4 / air mixture.

Figure 2 shows the effect of the volume fraction of additives on the ignition delay for a CH_4/air mixture with ϕ = 0.6 (this equivalence ratio is actually for the base condition of CH_4/air and then methane was replaced by the desired percentage of additives) at an ambient pressure and temperature of 4.1 MPa and 900 K, respectively. It is to be noted that a CH_4/air mixture with ϕ = 0.6 could be ignited but with a very long ignition delay time of about 155 ms. As shown in Fig. 2, increasing the volume percentage of additives decreases the ignition delay time. It is clear that the addition of H_2O_2 has a pronounced effect in reducing the ignition delay compared with the other two additives.

The reason for the effectiveness of H_2O_2 as an ignition promoter compared with the other two additives can be explained with the aid of Fig. 3, where the variations of mole fractions of some important intermediate products such as H, OH, CH_3, HO_2, CH_2O, and H_2O_2 are plotted with time. The mass fraction behavior of the intermediate products is divided into a nearly three stages. At the first stage, a very quick formation of those products is seen clearly especially with H_2O_2 addition (O (1 μs)) and is slower with DME addition (O (1 ms)). At the end of the first stage, a value of 10^{-7} of the mass fraction of OH radical is reached with the H_2O_2 addition while a time of about 8 ms was required with the CH_2O addition to reach the same level. At the second stage, the mass fraction of the intermediate products is nearly constant with the H_2O_2 and DME addition but it increases slowly with the CH_2O addition. The mass fraction of the intermediate products is increased again at the third stage at which ignition occurred. The value of OH radical is nearly the same after ignition for all additives. It is clearly seen that CH_4 relatively rapidly decreases with the H_2O_2 addition through rapid increase in OH at the very initial stage.

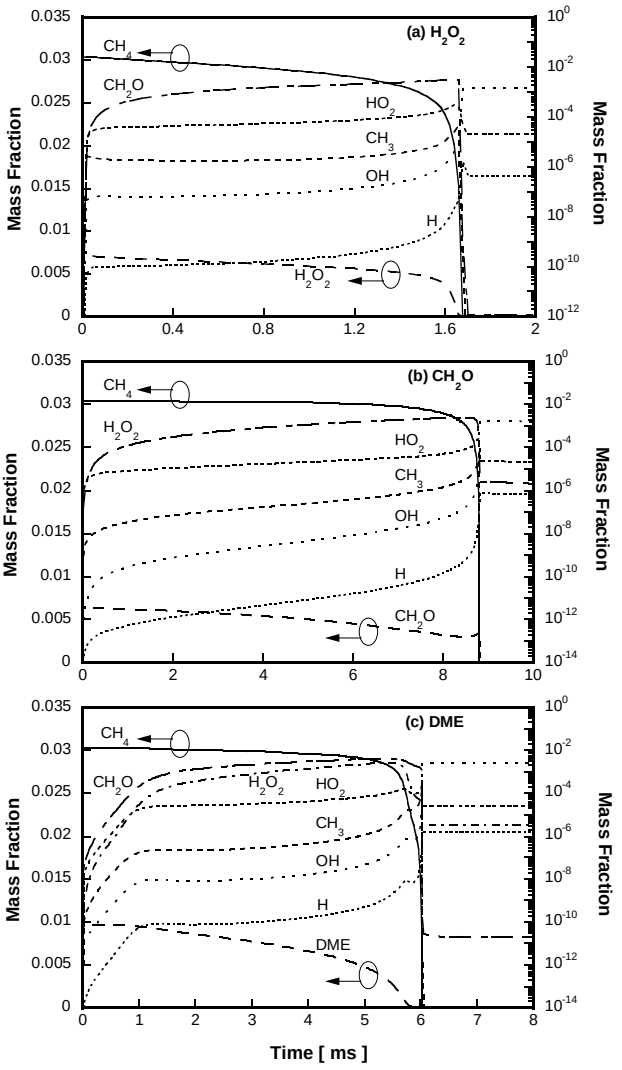

Fig. 3 Variations of mole fraction of intermediate products with time for the three additives examined.

Figure 4 shows a comparison of the ignition delay times, plotted in an Arrhenius diagram, for the mixture of CH_4/air (ϕ = 0.6) at which the fuel was substituted by 10% by volume of various additives at the initial pressure of 4.1 MPa. The addition of ignition improvers shows an

essentially monotonous reduction of ignition delay times at all initial temperatures examined and the effect of H_2O_2 addition is most pronounced compared with the other two additives. The effect of CH_2O is more pronounced at higher initial temperatures when compared with the DME additions. It seems that DME is becoming more effective at low initial temperature and the effectiveness of H_2O_2 mitigates with the decrease in temperature due to the reduction in the dissociation rate.

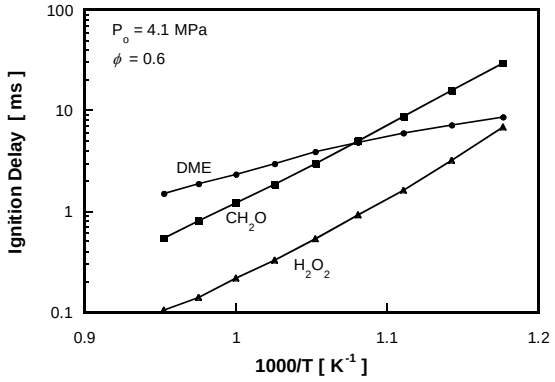

Fig. 4 Effect of initial temperature on the ignition delay of CH_4 / air mixture with 10% additives replacing CH_4.

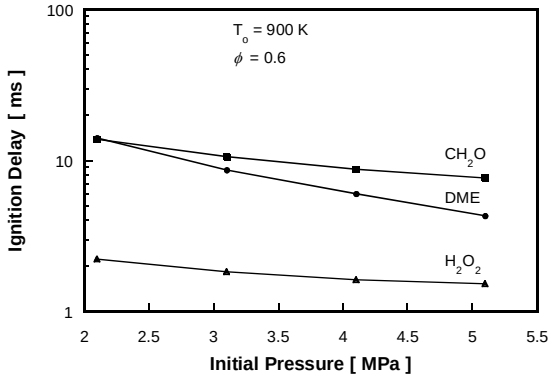

Fig. 5 Effect of initial pressure on the ignition delay of CH_4 / air mixture with 10% additives replacing CH_4.

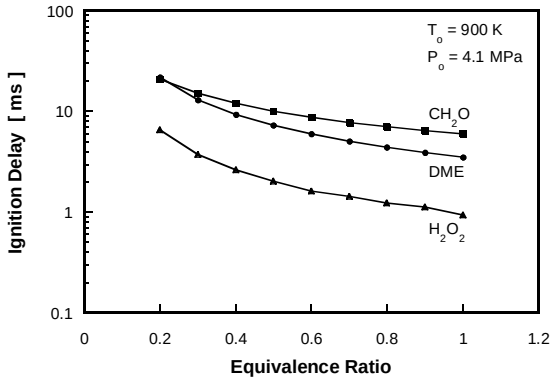

Fig. 6 Effect of equivalence ratio on the ignition delay of CH_4/air mixtures with 10% additives replacing CH_4.

The effect of initial pressure on ignition delay times has been also investigated as shown in Fig. 5. The ignition delay times decreases as pressure increases for all the additives with a more pronounced effect with H_2O_2 addition. The advantage of H_2O_2 addition is also clear as shown in Fig. 6 at various equivalence ratios.

For engine-like conditions, simulations have been performed to investigate the effect of additives on the combustion in a HCCI engine. The effects of DME, CH_2O and H_2O_2 addition have been evaluated with respect to the control of combustion timing. Computations were first carried out as the intake temperature of a CH_4/air mixture varied from 400 K to 600 K. The equivalence ratio was maintained at 0.3, and the initial mixture pressure was 1.5 atm. The resulting pressure traces are shown in Fig. 7. As the initial temperature increases, it advances the onset of ignition due to increased reaction rates. However, it is also important to note that increasing inlet manifold temperatures negatively affect indicated thermal efficiency, volumetric efficiency, and trapped mass, as reported by Fiveland *et al.* [1]. An increase in the inlet temperature reduces trapped mass and volumetric efficiency, which in turns adversely affects torque and power output. Advanced ignition, which increases compression effort, combined with reduced volumetric efficiencies leads to a reduction in net indicated thermal efficiency. It was further noted that methane did not ignite for an intake manifold temperature of 400 K, consistent with previous studies [1, 22].

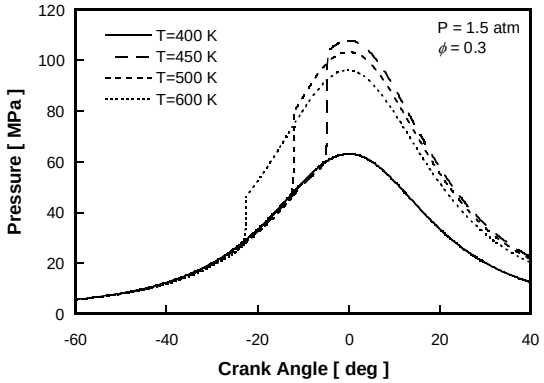

Fig. 7 Effect of initial temperature on ignition and pressure profile of CH_4 / air mixture in engine-like conditions.

The effect of additives such as DME, CH_2O and H_2O_2 on the ignition of a non-ignitable mixture of CH_4/air is then investigated. The comparisons were made at an equivalence ratio of 0.3, an inlet pressure of 1.5 atm, and an inlet temperature of 400 K. The pressure and temperature profiles are shown in Fig. 8. Clearly, the addition of H_2O_2 has a pronounced effect on advancing the ignition as compared to the other two additives, which is consistent with the constant volume calculations. Furthermore, the maximum pressure was greatly reduced with DME addition from which it can be concluded that the quantity of added DME needs to be increased to advance ignition. On the other hand, with H_2O_2 addition,

advancing the ignition timing before TDC will increase the compression effort and in turn result in a reduction in net indicated thermal efficiency.

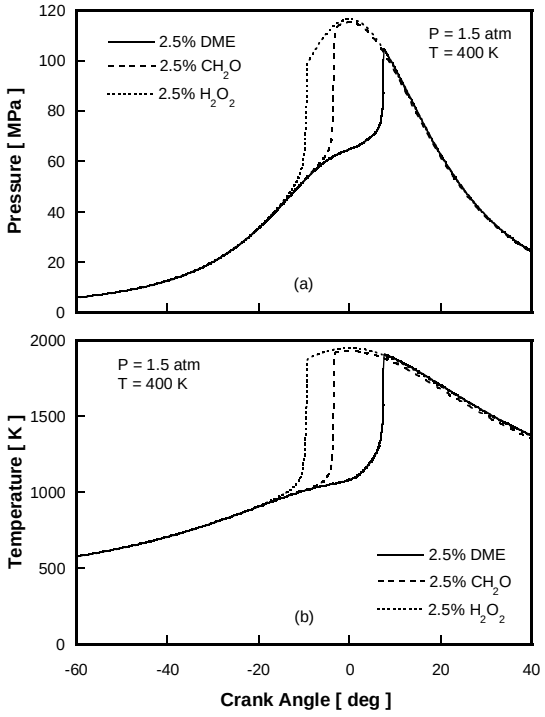

Fig. 8 (a) pressure and (b) temperature profiles with 2.5% addition of different ignition improvers.

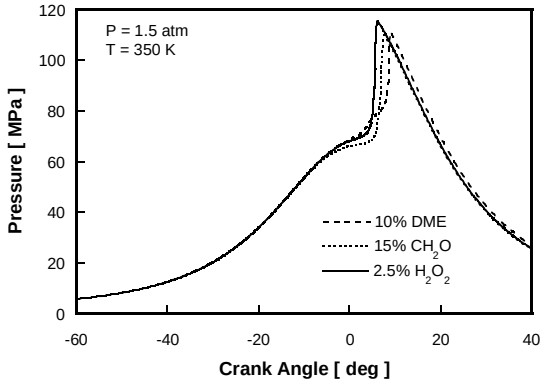

Fig. 9 Minimum concentration of different additives required to achieve ignition.

In order to decrease the required intake temperature, computations were done to examine the minimum percentage of additives to achieve combustion. The intake temperature was reduced to 350 K while the equivalence ratio and the initial mixture pressure were maintained at 0.3 and 1.5 atm, respectively. The resulting pressure traces are shown in Fig. 9. A large amount of DME (10%) and CH_2O (15%) is required to support combustion while adding only 2.5% of H_2O_2 was enough.

4. CONCLUDING REMARKS

The effect of additives such as DME, CH_2O and H_2O_2 on the ignition of natural gas has been studied numerically. The combustion event has been modeled using the single-zone zero-dimensional SENKIN code from the Chemkin-III package. Two chemical kinetics schemes describing natural gas and have been implemented in the code. Several parametric studies of additive concentrations, initial temperature, pressure, and equivalence ratio were first carried out using a constant volume bomb. The effect of H_2O_2 addition in reducing the ignition delay of methane/air mixtures is most pronounced as compared to the other two additives of DME and CH_2O for all conditions examined and CH_2O was more effective than DME when the initial temperature was more than 925 K. The H_2O_2 with the concentration of about 5% (by volume) in the fuel significantly reduce the ignition delay of CH_4/air mixtures in which it acts as a radical source.

The engine cycle simulation has been exercised to study the ignition control of natural gas fueled HCCI engines using additives. Calculations were performed at a fixed equivalence ratio of 0.3 and initial mixture pressure of 1.5 bar. It was found that an additive-free mixture did not ignite for an intake temperature of 400 K. A mixture containing a small quantity of additives at the same temperature was ignited. For a fixed quantity of additive, it was found that H_2O_2 addition was effective in advancing the ignition timing as compared to the other two additives. Furthermore, the addition of even 2.5% by volume of H_2O_2 could ignite a mixture at an intake temperature of 350 K while at least a fraction of 10% and 15% by volume was required for DME and CH_2O addition, respectively.

REFERENCES

1. Fiveland, S. B. and Assanis, D. N., “A Four-Stroke Homogeneous Charge Compression Ignition Engine Simulation for Combustion and Performance Studies” SAE Paper 2000-01-0332, 2000.

2. Chen, Z., Konno, M., Oguma, M., and Yanai, T., “Experimental Study of CI Natural-Gas/DME Homogeneous Charge Engine” SAE Paper 2000-01-0329, 2000.

3. Chen, Z., Konno, M., and Miki, K. “Computational and Experimental Study on the Influence of Formaldehyde on HCCI Combustion Fueled with Dimethyl Ether” SAE Paper 2003-01-1826, 2003.

4. Kim, K. O., Azetsu, A., and Oikawa, C., “A Study on the Control of Ignition and Combustion of Dimethyl Ether in Homogeneous Charge Compression Ignition Engine” The Fifth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines COMODIA, 2001.

5. Flowers, D., Aceves, S., Westbrook, C. K., Smith, J. R., and Dibble, R., "Detailed Chemical Kinetic Simulation of Natural Gas HCCI Combustion: Gas Composition Effects and Investigation of Control Strategies" Journal of Engineering for Gas Turbine and Power, Vol. 123, pp. 433-439, 2001.

6. Yamada, H., Suzaki, K., Sakanashi, H., Choi, N., and 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 140, pp. 24-33, 2005.

7. Amneus, P., Nilsson, D., mauss, F., Christensen, M., and Johansson, B., "Homogeneous Charge Compression Ignition Engine: Experiments and Detailed Chemical Kinetic Calculations" The Fourth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines COMODIA, 1998.

8. Agarwal, A. and Assanis, D. N., "Multi-Dimensional Modeling of Natural Gas Ignition under Compression Ignition Conditions using Detailed Chemistry," SAE Paper 980136, 1998.

9. Kontarakis, G., Collings, N., and Ma, T., Demonstration of HCCI Using a Single Cylinder Four-Stroke SI Engine with Modified Valve Timing" SAE Paper 2000-01-2870, 2000.

10. Koopmans, L. and Denbratt, I., "A Four Stroke Camless Engine, Operated in Homogeneous Charge Compression Ignition Mode with Commercial Gasoline" SAE Paper 2001-01-3610, 2001.

11. Law, D., Kemp, D., Allen, J., Kirkpatrick, G., and Copland, T., "Controlled Combustion in an IC Engine with a Fully Varialbe Valve Train" SAE Paper 2000-01-0251, 2000.

12. Koopmans, L., Ogink, R., and Denbratt, I., "Direct Gasoline Injection in the Negative Valve Overlap of a Homogeneous Charge Compression Ignition Engine" SAE Paper 2003-01-1854, 2003.

13. Yamaya, Y., Furutani, M., and Ohta, Y., "Advanced/Retarded Criterion on Ignition of Fuel/Air Mixtures with Formaldehyde Doping" The Sixth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines COMODIA, 2004.

14. Yamada, H., Yoshii, M., and Tezaki, A., "Controlling Mechanism of Ignition Enhancing and Suppressing Additives in Premixed Compression Ignition" The Sixth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines COMODIA, 2004.

15. Sato, S., Yamasaki, Y., Kawamura, H., and Iida, N., "Research on the Influence on Natural Gas HCCI Combustion of Hydrogen and Carbon Monoxide" The Sixth International Symposium on Diagnostics and Modeling of Combustion in Internal Combustion Engines COMODIA, 2004.

16. Curran, H. J., Fischer, S. L., and Dryer, F. L., "The Reaction Kinetics of Dimethyl Ether. II: Low-Temperature Oxidation in Flow Reactors", Int. J. Chem. Kinet: 32: 741–759, 2000.

17. Smith, G.P., G.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, T. Bowman, R. Hanson, S. Song, G.C. Gardiner Jr., V. Lissianski, and Z. Qin, GRI-MECH 3.0, http://www.me.bereley.edu/gri_mech/.

18. Lutz, A.E., Kee, R.J. and Miller, J.A., "SENKIN: A Fortran Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis" Sandia Report SAND 87-8248, UC-4, 1988.

19. Kee, R. J., Rupley, F. M., Meeks, E., and Miller, J. A., "Chemkin-III: a Fortran chemical kinetics package for the analysis of gas phase chemical and Plasma kinetics" Sandia National Laboratories Report No. SAND96-8216, 1996.

20. Heywood, J., *Internal Combustion Engine Fundamentals*, Singapore, McGraw- Hill, 1988.

21. Golovitchev, V. I., Pilia, M. L., and Bruno, C., "Autoignition of Methane Mixtures: The Effect of Hydrogen Peroxide," Journal of Propulsion and Power, Vol. 12, No. 4, pp. 699-707, 1996.

22. Agarwal, A. and D.N. Assanis, "Modeling the Effect of Natural Gas Composition on Ignition Delay under Compression Ignition Conditions" SAE Paper 971711, 1997.