

# Analysis of Transient Chemical Composition in HCCI and Mechanism Controlling Autoignition

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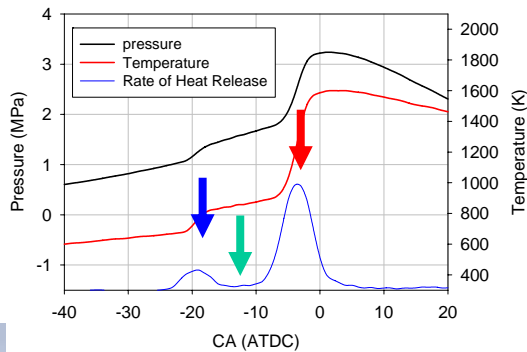


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## 1. Introduction: Characteristics of Each Stages in Compression Ignition



### Cool Flame/ Cool Ignition/ LTHR

- begins at ca. 700 K
- Partial combustion /HR influencing following temperature history

### Hot Flame/ Hot Ignition/ HTHR

- begins at over 1000 K
- Total combustion/ HR
- Common mechanism ( $H+O_2$ )

### Transient region

- Slow fuel consumption

Low temperature oxidation of alkyl peroxy radicals governs the cool flame behaviors. Intermediate species such as aldehydes and olefins are formed in this stage.

Hydrogen peroxide ( $H_2O_2$ ) is considered to be important in the transient region leading to the hot ignition. However, this part is not well characterized.

## Former studies detecting intermediates in HCCI

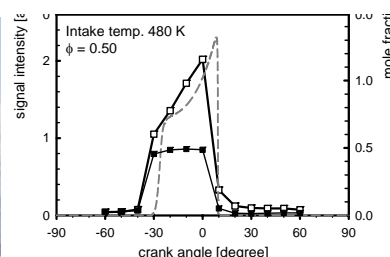
### Pulse valve sampling in DME fueled HCCI

- Gas sampling from inside the cylinder through an electrically actuated valve. Stored gas in a bag was analyzed by gas chromatography.
- ♦  $HCHO$  and  $CH_4$  were detected as intermediates, but the profiles and amounts were not in good agreement with predicted by a detailed oxidation model.
- ♦ Insufficient time resolution due to long valve open duration (10 CAD at 960 RPM)

### CA resolved LIF (Yamada et al., Combust. Flame 2005)

In situ monitoring of  $HCHO$  with pressure dependent sensitivity correction resulted in profiles consistent with models.

- Good time resolution
- ♦ Only applicable to limited species



## former study (cont'd)

### Exhaust Gas Analysis for Cool Flame Composition

Yamada et al., Proc. Comb. Inst 30 (2005)

- Exhaust of DME compression without hot flame was analyzed a Q-pole mass analyzer
- The role of formaldehyde controlling LTO chain reaction system was discussed.
- ♦ Some key species were undetectable with QMS, so that the model validation (Curran et al. 1998 vs. 2000) is insufficient

### Aim of This Study

Intermediate species detection in compression ignition of DME to discuss the ignition controlling mechanism

#### Method: 1. Improved Experiments

Time resolved mass sampling

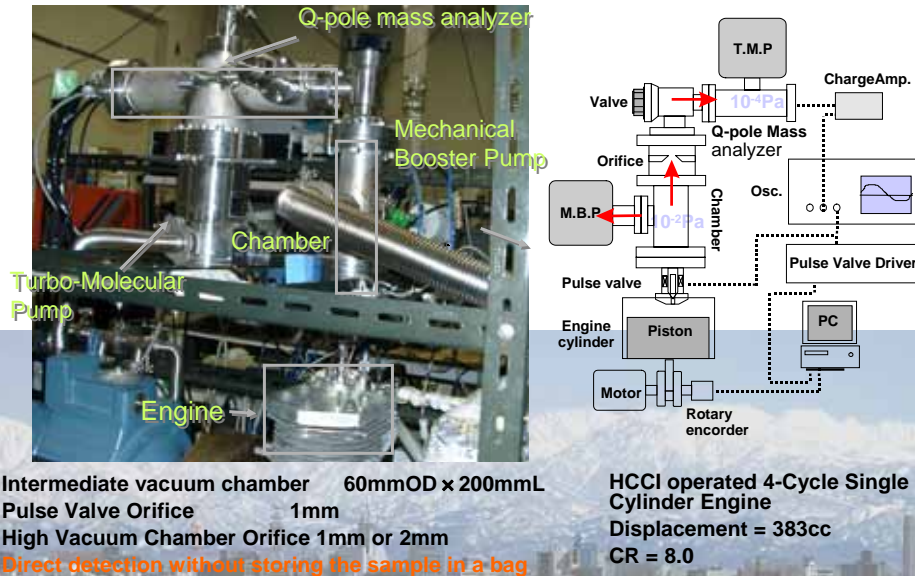
Exhaust gas analysis for cool ignition products Analysis

#### 2. Chemical Mechanistic Analysis

Role of chemical species formed during the ignition stages and added for the Ignition control

## Experiment 1: Pulse Valve Sampling

## Experimental Apparatus



## Normalized Mass Signal vs. Valve Open Duration

Fuel: DME,  $\phi = 0.39$ ,  $T_{\text{intake}} = 414\text{K}$

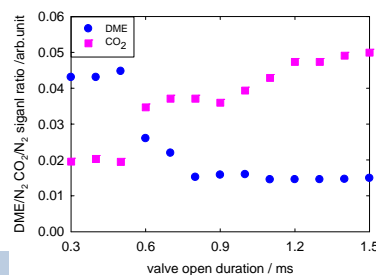
TDC +60deg (after combustion)

Fuel remains near to wall, while  $\text{CO}_2$  in the core volume is extracted after 0.6 ms of the valve open.

The core volume composition can be obtained by subtracting data of different open durations.

e.g.  $t_a = 0.6$  ms,  $t_b = 0.9 - 1.2$  ms

Effective time resolution is improved by this correction.





## Results: CA resolved sampling

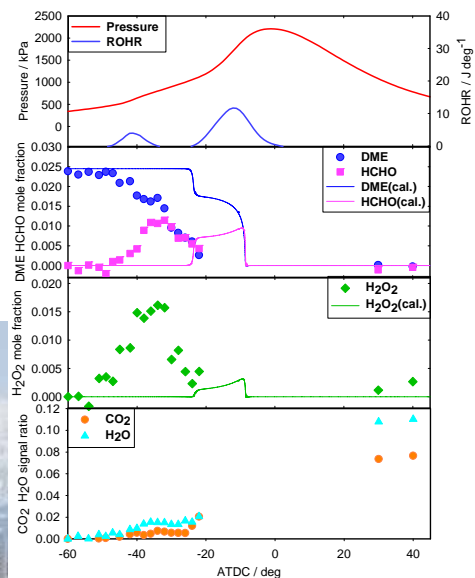
### Two-stage ignition

$\phi = 0.36$ , intake temp. = 410K

Fuel DME is partly consumed in the cool ignition and totally consumed in the hot ignition.

Intermediates (HCHO and  $\text{H}_2\text{O}_2$ ) are produced in the cool ignition and consumed in the hot ignition.

Amounts of final products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) at the cool ignition are considerably small



## Method 2: Exhaust Gas Analysis for Cool Flame Composition (in Hot Flame Suppressed Conditions)



## Intermediate Products in DME-LTO

- Modeled intermediates in cool ignition of DME

Curran et al. 1998 **HCHO, CO, CO<sub>2</sub>, H<sub>2</sub>O**

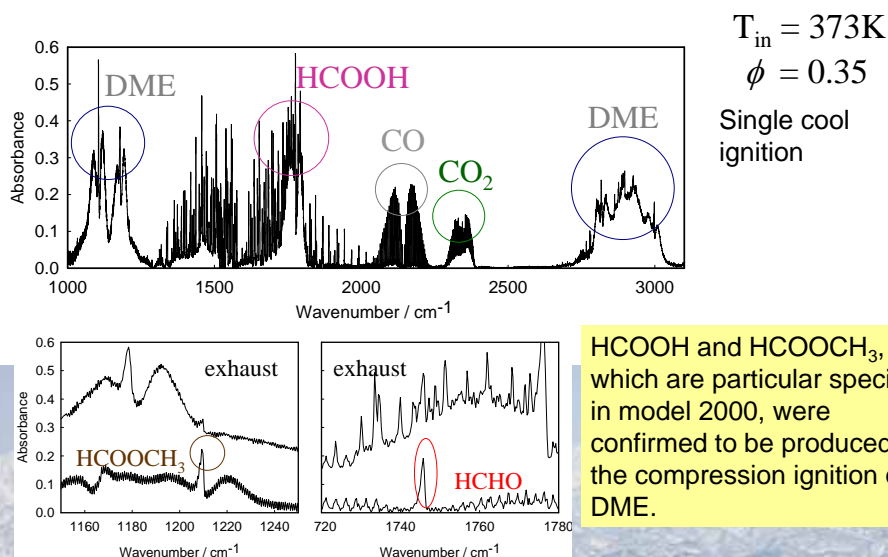
Curran et al. 2000 **HCHO, CO, CO<sub>2</sub>, HCOOH, HCOOCH<sub>3</sub>, H<sub>2</sub>O**

- Problem in Q-mass detection of CO(28), CO<sub>2</sub>(44) and HCOOH(46) due to the mass number overlap with N<sub>2</sub>(28), DME(46) and fragments

**Fourier Transform Infrared Spectrometer (FT-IR)** is used in this work:

Exhaust gas was introduced into a multi-path cell of 3m absorption length at reduced pressure of 0.1 atm to avoid water condensation. Tubing between the engine and the cell is heated above 50 °C.

## FT-IR Spectrum of Exhaust Gas



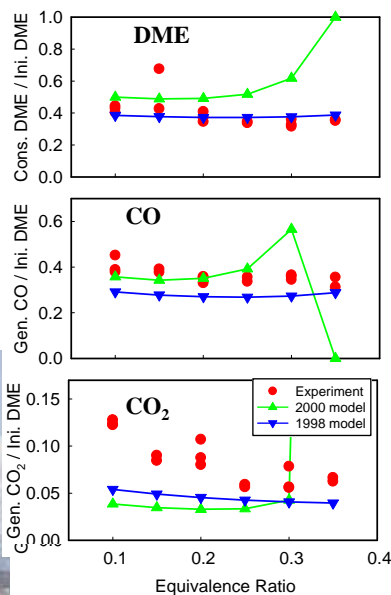
HCOOH and HCOOCH<sub>3</sub>, which are particular species in model 2000, were confirmed to be produced in the compression ignition of DME.

The single peak of HCHO is overlapped with the wider band of HCOOH

## Results and Analysis:



Results: Percentage Consumption/Production vs. Equivalence Ratio (1)



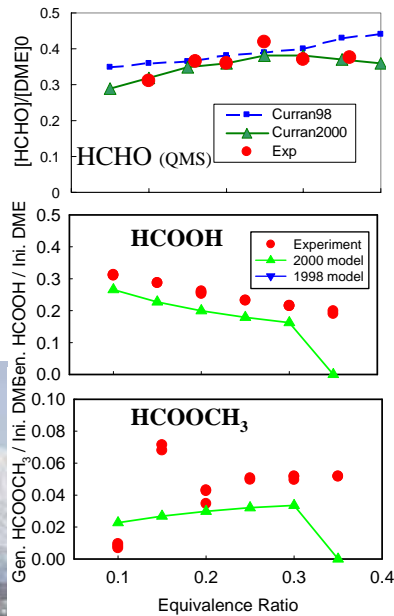
Ignitability is higher in model 2000, in which hot ignition occurs over  $\phi = 0.3$ .

CO and CO<sub>2</sub> are more accurately quantified by the use of FT-IR.

CO<sub>2</sub> is found to be produced than predicted by models, which may responsible for the LTO heat release.



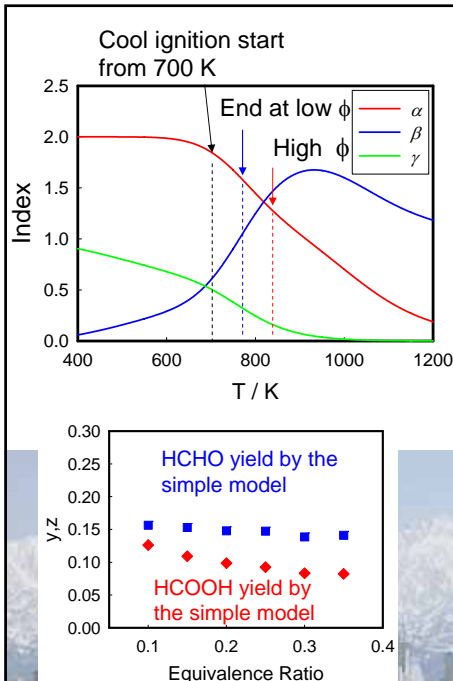
## Results: Percentage Consumption/Production (2)



Two HCHO yield shows slightly increasing trend with increasing equivalence ratio. Models and the experiment are consistent.

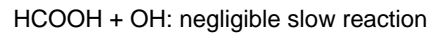
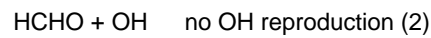
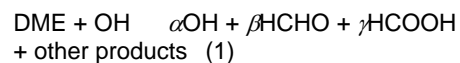
HCOOH formation is predicted only in model 2000. The decreasing trend with equivalence ratio is also represented.

The relative correctness of the model 2000 for DME oxidation is demonstrated.



## HCOOH yield vs. HCHO yield

LTO chain system of DME is simplified as:



The chain system terminates when  $d[OH]/dt = 0$ , corresponding to;

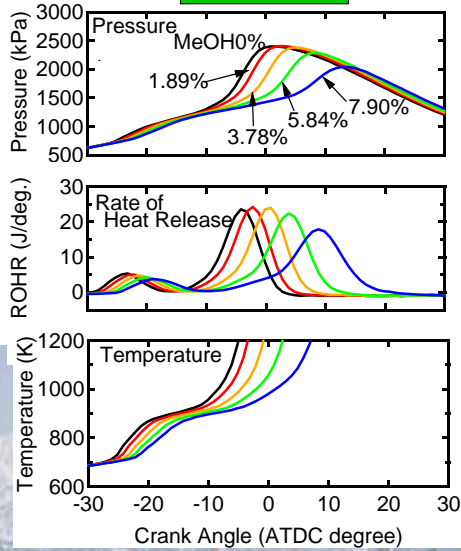
$$\frac{[HCHO]}{[DME]} = \frac{(\alpha - 1)k_1}{k_2} \quad (3)$$

Final temperature of cool ignition increases with increasing  $\phi$ , resulting in decreasing HCOOH yield.

On the other hand, final HCHO fraction is determined by (3), so that the effect of  $\beta$  increase is small, and partly compensated by the decrease of  $\alpha$ ,

## Methanol Addition (Pressure Profiles)

### Experiment



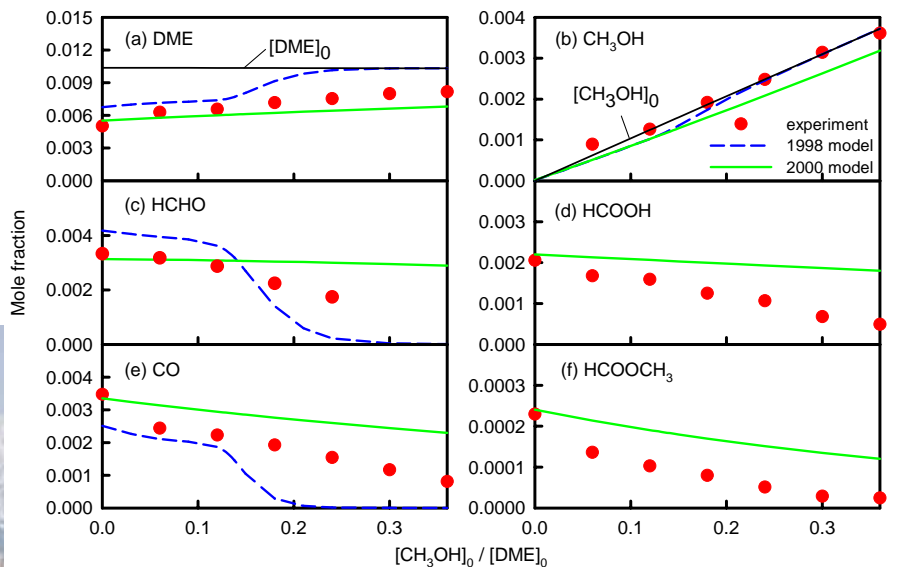
$$T_{\text{Intake}} = 383\text{K},$$

$$\phi_{\text{DME}} = 0.42.$$

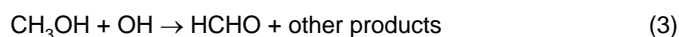
Ignition retardation is caused by reduction of cool flame HR with methanol addition



## Results: Exhaust Composition vs. Methanol Addition



## Simplified Formulation of Chain Reaction Mechanism for the Case of Methanol Addition



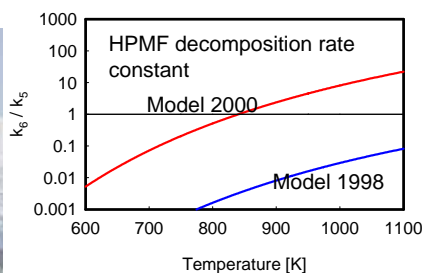
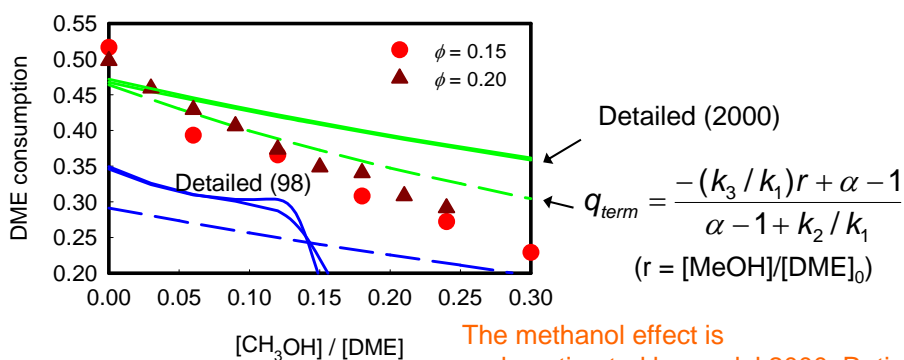
(Chain reaction mechanism reproducing OH is suppressed by HCHO and CH<sub>3</sub>OH reactions (2, 3))

The OH growth equation

$$G(\text{OH}) = k_1[\text{DME}] - k_2[\text{HCHO}] - k_3[\text{MeOH}]$$

Fuel consumption at the termination ( $G = 0$ )

$$q_{\text{term}} = \frac{-(k_3/k_1)r + \alpha - 1}{\alpha - 1 + k_2/k_1} \quad (r = [\text{MeOH}]/[\text{DME}]_0)$$



The methanol effect is underestimated by model 2000. Ratio of OH-methanol/ OH-DME rate constants is responsible

The irregular fall-off in model 1998 is caused by the slow decomposition rate of HPMF

# Conclusions

- Two different methods of intermediate species detection have been performed in engine compression cycles fueled with dimethyl ether to further validate the chemical mechanism of low temperature oxidation.
- Direct mass-spectrometric detection of the sampled species in the differential pumping system enabled detection of unstable  $\text{H}_2\text{O}_2$ .
- FT-IR analysis of exhaust gas composition enabled to detect  $\text{HCOOH}$  and  $\text{HCOOCH}_3$ , which are crucial to conclude the competition between new and old versions of detailed kinetics model.
- The trend of intermediate yield vs. equivalence ratio was reasonably predicted by a simplified formulation of the chain reaction mechanism. Effect of methanol addition suppressing ignition was also accounted for by this mechanism.

Future work

- Extension of this methodology to other fuels. (n-heptane investigation is going on)

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## ABSTRACT

The chemical mechanism responsible for controlling ignition timing by using additives in HCCI has been investigated. Dimethyl ether (DME) and methanol were used as the main fuel and the additive, respectively. Fuel consumption and intermediate formation in the first stage (cool ignition) were measured with crank angle resolved pulse-valve sampling and exhaust gas analysis, where HCHO, HCOOH, CO, H<sub>2</sub>O<sub>2</sub> and other species were detected as the intermediate. The effect of methanol addition retarding ignition is represented by an analytical model in which the growth rate of the chain reaction is reduced by the methanol addition.

## INTRODUCTION

A typical process of premixed compression ignition consists of two distinct stages of heat release. The first stage (cool ignition) is incomplete oxidation whose extent is considerably dependent on the fuel property such as octane number, whereas the latter stage (hot ignition) is total oxidation with the mechanism common to most hydrocarbons<sup>1)</sup>. Ignition timings can be controlled by using additives enhancing or depressing the activity of the cool ignition<sup>2-5)</sup>, where the combined effect of the additive and intermediate products influences the low temperature oxidation mechanism. In this regard, monitoring the formation of intermediate species during ignition is useful to validate the chemical mechanistic models and guide to better control HCCI.

As a method of the transient species detection, crank angle resolved in-cylinder sampling was conducted in dimethyl ether (DME) fueled HCCI<sup>6)</sup> and in butane based HCCI<sup>7)</sup>. By means of an electrically driven pulse valve equipped onto the cylinder, species like HCHO and CH<sub>4</sub> were recognized to be present between the stages of ignition; however, only qualitative correspondence with model calculations was obtained. Probably insufficient time resolution of the sampling and storage in sampling vessels caused significant errors. Typical valve open duration in the former studies is 1.5 ms, which is equivalent to 5 – 9

CA at 600 – 1000 RPM engine operation. This period is necessary for sufficient amount of sampling from the reacting volume in the cylinder over that from quenched volume near wall and in tubing.

Our previous work employed another approach; namely, exhaust gas analysis was conducted in the condition of hot ignition suppressed, single cool ignition<sup>8)</sup>. Through the observation that formaldehyde/ DME ratio after cool ignitions is constant within a range of equivalence ratio, the role of formaldehyde terminating the OH reproducing chain reaction system was elucidated. The same methodology was applied to a system controlling ignition timing by adding methanol and ozone<sup>5)</sup>. These experimental observations were reasonably reproduced by simulations using detailed chemical kinetic models of DME oxidation. However, the effective range of equivalence ratio applicable by this method alone is limited.

In this work, we employ an improved device for time resolved sampling measurement of in-cylinder species composition and apply it to DME fueled HCCI. As well, exhaust gas analysis with a Fourier transform IR spectrometer (FT-IR) is conducted to obtain further information of the intermediate behaviors in ignition.

In particular, methanol is used as an ignition suppressing additive and the chemical mechanism causing the effect is discussed in comparison with simulations using existing models of detailed DME oxidation mechanism<sup>9, 10)</sup>.

## EXPERIMENTAL SETUP

The base engine is a 4-stroke, side valve single cylinder type of bore × stroke = 84 × 70 [mm]. The compression ratio after modification is 8.0. The engine crank is externally driven by a 1500 W induction motor in order to rotate at a constant speed regardless of internal power generation. The standard speed was set at 600 RPM. DME is supplied from a commercial cylinder, regulated through a 2 SLPM mass flow controller, and mixed with air at the intake. The air is aspirated through a mass flow meter and a

surge tank, and preheated to around 400 K to meet the ignition condition at the current compression ratio. The engine head is also heated so that the mounted thermocouple equipped on engine head indicates the same temperature as the intake temperature during the steady state operation. The engine head was replaced to equip a pressure pickup and a pulse sampling system described in the next subsection.

## PULSE SAMPLING

The engine system equipped with a sampling system is schematically shown in Fig. 1. A solenoid-type pulse valve (General Valve, 0.8 mm orifice diameter) is screwed on the head plate of the engine. The outlet of the valve is directly connected to a vacuum chamber continuously pumped by a mechanical booster pump. The chamber has an orifice connected to a high vacuum chamber, in which a QMS detector (Anelva, M-400GA-DTS) is installed, pumped by a turbo-molecular pump. The orifice size of 1 mm was used in the current experiments.

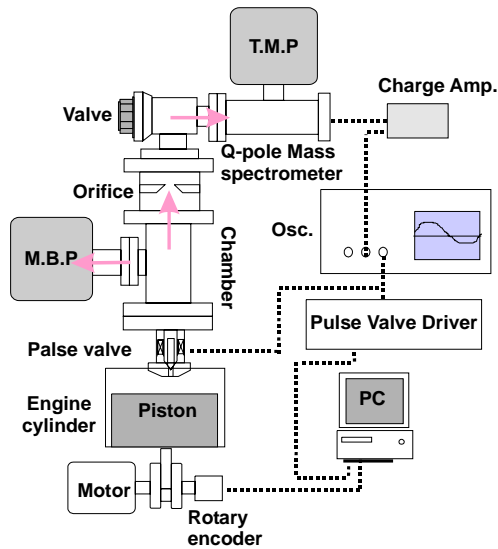


Fig. 1 Schematic of pulse sampling engine system.

In this setup, the direct QMS detection in the differential pumping system allows to set the valve open duration less than 0.5 ms with sufficient sensitivity, while 0.3 ms of the mechanical delay to actual open is present. However, simple sampling with short duration causes erroneous outcomes. As demonstrated in Fig.2, unburned DME is dominant in the sampling from DME-air compression cycles with valve open duration shorter than 0.5 ms, even though it is sampled at 60 deg ATDC, i.e., after complete combustion. On the other hand, CO<sub>2</sub> becomes dominant at longer sampling duration. This fact indicates that the valve at first samples out unreacted volume such as in dead volume of the valve and in boundary layer on the wall before extracting the reacted core volume.

According to the above observation, a correction scheme is established so as to extract the core volume signals as:

$$\text{Corrected signal} = \frac{S(X:t_b) - S(X:t_a)}{S(N_2:t_b) - S(N_2:t_a)}$$

where  $S$  is the raw QMS signal,  $X$  is the detecting species, and  $t_a$  and  $t_b$  are two different sampling durations. When  $t_a$  was set at 0.6 ms and  $t_b$  was varied over 0.7 and 1.0 ms, the corrected signals were confirmed to be constant. Finally we set  $t_a$  and  $t_b$  as 0.6 - 0.7ms and 1.2 - 1.3ms, respectively, considering the trade-off between S/N ratio and time resolution. The sampling amount at 1 ms of open duration was estimated to be 0.06 cm<sup>3</sup> as a volume at the in-cylinder pressure.

DME (mass-charge ratio  $m/e = 46$ ), HCHO (30), H<sub>2</sub>O<sub>2</sub> (34), CO<sub>2</sub> (44) and H<sub>2</sub>O (18) are measured in this method of CA resolved sampling. N<sub>2</sub> (28) is monitored as the standard signal representing total sampled amount. In the QMS setting, the electron impact ionization energy is set at 20 eV for species except H<sub>2</sub>O<sub>2</sub>. This is lower than the normal ionization energy of 70 eV, but the undesirable fragmentation is avoided without losing sensitivity. For H<sub>2</sub>O<sub>2</sub>, higher energy of 45 eV is applied to compensate the weak signals. It was confirmed that no fragment ion was detected at  $m/e = 34$  from standard samples of heavier mass including the above species, HCOOH and HCOOCH<sub>3</sub>.

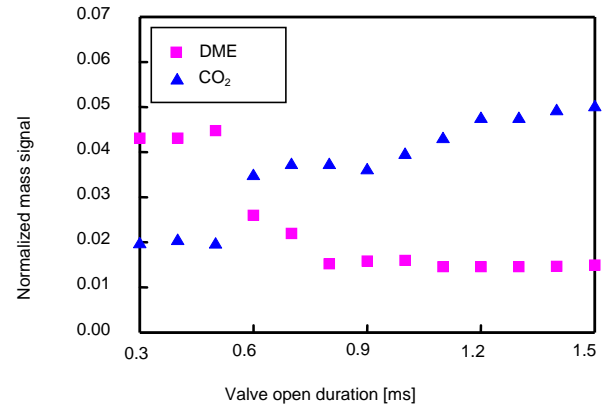


Fig. 2 Mass signals sampled through the pulse valve and normalized by N<sub>2</sub> signal, as a function of valve open duration in the compression of DME-air mixture at fixed CA of 60° ATDC.

## EXHAUST GAS ANALYSIS

A Fourier transform IR spectrometer (FTIR: IR Prestige-21 from Shimadzu) is used as a detector in this study. A portion of exhaust gas is fed into a 10 cm single path IR cell or a 3 m multi-path cell



mounted in the spectrometer. The 10 cm cell is heated to 323 K to avoid water condensation in the cell filled with the exhaust gas at atmospheric pressure. In the case of 3 m cell, exhaust gas is filled at 10 kPa and used without heating. Tubing between exhaust port and the cell is also heated above 323 K. Usually an IR spectrum is obtained as an average of 30 scans with a resolution of  $0.5\text{ cm}^{-1}$ .

DME, HCOOH, CO and  $\text{CO}_2$  are detected with sufficient sensitivity and selectivity in exhaust of DME-air compression in which a single cool ignition is established at equivalence ratio over 0.1. Their mole fractions are calibrated using standard samples. Usually a standard sample contains 0.2 % of the calibrating species.  $\text{HCOOCH}_3$  and HCHO are also identified. However, notable peaks in the IR range are limited and are superimposed by other spectra; consequently the quantitative accuracy is marginal.

## RESULTS AND ANALYSIS

### CRANK ANGLE RESOLVED SAMPLING

Figures 3 and 4 show profiles of species fractions obtained by the current sampling method together with pressure and rate of heat release (ROHR). On the species profiles, calibrations using standard gas of known concentration were conducted for DME, HCHO and  $\text{H}_2\text{O}_2$ , so that they are expressed in mole fractions. For  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , QMS signals normalized by that of  $\text{N}_2$  are indicated. At lower equivalence ratio of 0.25 shown in Fig. 3, the single peak of ROHR corresponds to cool ignition while hot ignition is suppressed. Consumption of DME and formation of intermediates begin at a close timing to the onset of the heat release. The species fractions change only gradually after the end of the cool ignition heat release. It is convincing that the observed final composition conserves in the expansion period until the exhaust valve to open. At higher equivalence ratio of 0.36, the two-stage ignition of distinct cool and hot stages appeared as shown in Fig. 4. The high temperature of the hot ignition is beyond the pulse valve operational range (513 K); therefore sampling was not conducted between -20 and 30 ATDC. It is recognized that the fuel DME is partly consumed at the cool ignition and totally consumed at the hot ignition. On the other hand, the intermediate, HCHO and  $\text{H}_2\text{O}_2$  are produced at the cool ignition and consumed at the hot ignition. Amounts of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  after the cool ignition are small fractions of the final ones after the hot ignition. The small deviations in the timing between heat release and species profiles are probably due to the difference in the nature that ROHR is volume averaged and the sampling is from a point of the volume; although timing shift during a course of experiment may be partly responsible. It

should be noted that the specific time of the species concentration change is shorter than that of ROHR, which demonstrates the good resolution of the current sampling method.

The detection of  $\text{H}_2\text{O}_2$  is a notable result of the direct *in vacuo* detection. Although the importance of  $\text{H}_2\text{O}_2$  as a triggering agent for hot ignition has been pointed out in many modeling studies, the unstable and low vapor pressure species was not detected in former sampling studies with storage bags.

The 2000 model predicts hot ignition at equivalence ratio 0.25 and the 1998 model predicts no hot ignition at equivalence ratio 0.36, both of which are contrary to the experimental results. Considering that the simulation neglects wall heat loss, It is unlikely that the overestimate of ignition is due to an error of the 2000 model kinetics, whereas the underestimate of the model 1998 is obvious.

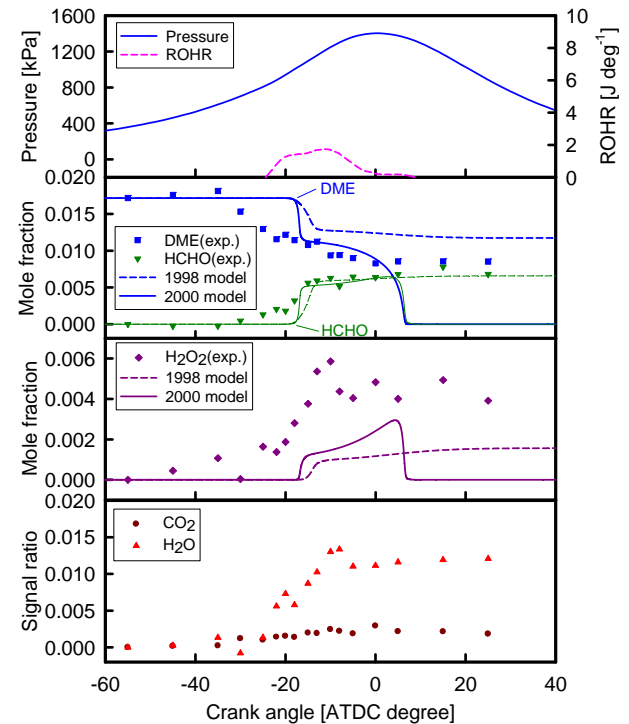


Fig. 3 Crank angle resolved profiles of pressure and heat release rate and species mole fractions. Equivalence ratio = 0.25, intake temperature = 410 K. 1998 model and 2000 model indicate the models in ref. 9 and 10, respectively.

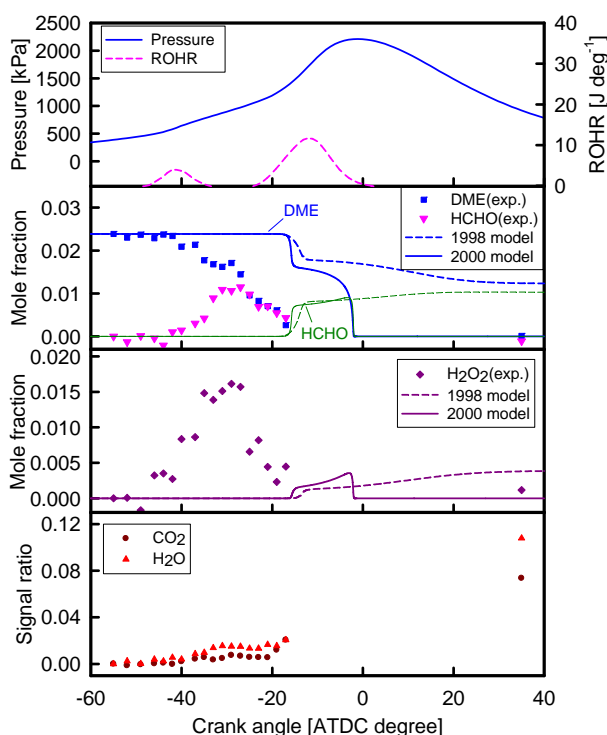


Fig. 4 Crank angle resolve profiles at equivalence ratio = 0.36, intake temperature = 410 K.

#### EXHAUST GAS ANALYSIS OF COOL IGNITION

Figure 5 shows DME consumption and product emissions at the exhaust as a function of equivalence ratio. Vertical scales are normalized by that of initial DME fraction. In experiment and the model 1998<sup>9)</sup>, single cool ignition condition is maintained throughout the range of equivalence ratio. The percentage DME consumption is a very weak function of equivalence ratio lying around 40%. In contrast, hot ignition occurs at equivalence ratio over 0.3 in model 2000,<sup>10)</sup> so that the fuel and intermediates are totally consumed in this region.

HCOOH yield shows a decreasing trend with increasing equivalence ratio, whereas HCOOCH<sub>3</sub> yield shows opposite, increasing trend. These trends of intermediates that are not included in the model 1998 are reproduced by the model 2000 within the range of single cool ignition. These behaviors are considered to be related with temperature dependence of product yields. Namely, the low temperature heat release starts at approximately constant temperature (~700 K) and terminates at constant percentage fuel consumption, which means the average temperature through the process increases with increasing equivalence ratio. According to the reaction model, the dominant pathway switches with temperature between 700 K and 850 K from that via second O<sub>2</sub> addition (A) to decomposition after single O<sub>2</sub>

addition (B). HCHO is produced by both pathways, but HCOOH is produced by only pathway A; consequently the yield of HCOOH decreases with increasing equivalence ratio. On the other hand, HCOOCH<sub>3</sub> is a minor decomposition product branched from the pathway B, hence the yield is an increasing function of temperature.

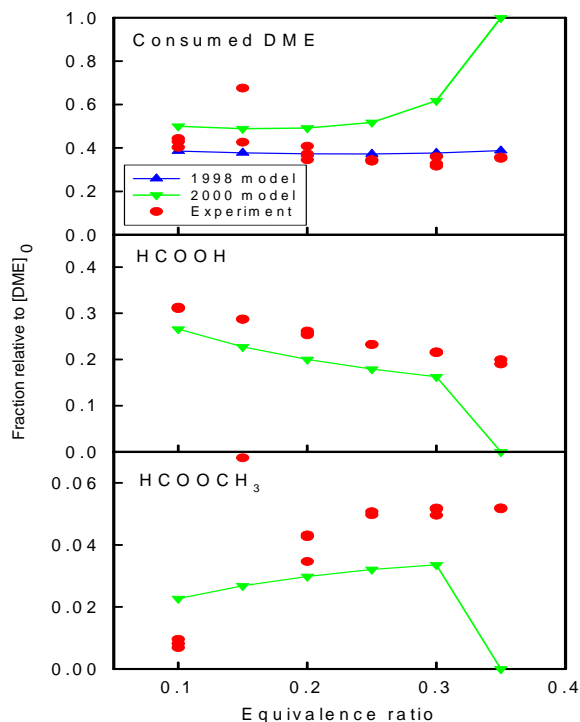


Fig. 5 (a) DME consumption, (b) HCOOH and (c) HCOOCH<sub>3</sub> formation relative to initial amount of DME as a function of equivalence ratio. Intake temperature = 373 K.

#### EFFECT OF METHANOL ADDITION

Methanol was added in the compression of DME-air mixture and the exhaust was analyzed by FT-IR in the 3 m cell. Figure 6 compares the measured species mole fractions with those simulated. DME fraction increases with increasing methanol addition towards the level of no consumption, whereas HCOOH and CO fractions decrease with methanol addition. The DME and CO results over the range of methanol addition are well reproduced by the model 1998, although only the model shows change of slope at 12 % addition. In contrast, the methanol effect is considerably less in the model 2000. In the case of HCOOH, only the model 2000 represents the formation, though, the model still underestimates the methanol effect reducing the HCOOH formation.

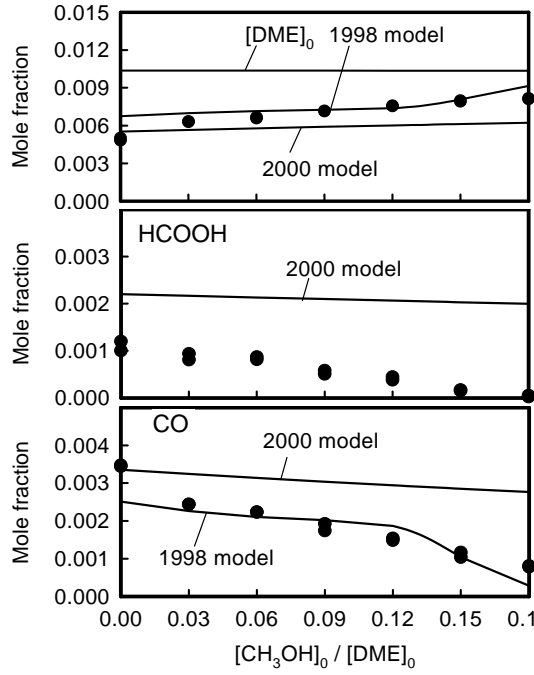


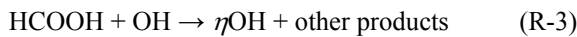
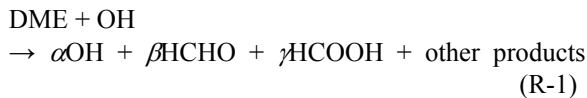
Fig. 6 Effect of methanol addition in species mole fractions in exhaust of DME-air compression. DME equivalence ratio = 0.15, intake temperature = 383 K.

#### LOW TEMPERATURE OXIDATION MECHANISM OF DME

In our former paper<sup>8)</sup>, we proposed a simplified formulation for the cool ignition of DME compression by extracting essential reaction processes from the detailed model 1998 and it was successful to represent the extent of partial oxidation in a range of equivalence ratio. Here we modify the former formulation to adapt the model 2000 mechanism and the effect of methanol addition.

Among the newly confirmed intermediates,  $\text{HCOOCH}_3$  is a small yield secondary product and negligible in the overall kinetics, but  $\text{HCOOH}$  is a significant product in low-temperature oxidation comparable to  $\text{HCHO}$  and should be properly treated.

The essential chemical kinetics of DME oxidation in the cool ignition regime is described as below:



The major chain branching is summarized in (R-1), where the OH reproduction index  $\alpha$  larger than unity assures the initial growth of the chain carrier (OH) concentration. When the intermediates are formed in

considerable concentration, they also react with OH to modify the OH reproduction coefficient. Differential equations for concentrations of OH and relevant species are derived from the kinetic relationship in the above reactions. A set of equations in terms of extent of reaction,  $q$ , is:

$$\frac{dy}{dq} = \beta - \frac{k_2}{k_1} \frac{y}{1-q}$$

$$\frac{dz}{dq} = \gamma + \varepsilon \frac{k_2}{k_1} \frac{y}{1-q} - \frac{k_3}{k_1} \frac{z}{1-q}$$

where  $k_i$  is the rate constant of  $i$  th reaction,

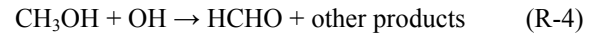
$$q = \frac{[\text{DME}]_0 - [\text{DME}]}{[\text{DME}]_0} \quad y = \frac{[\text{HCHO}]}{[\text{DME}]_0} \quad z = \frac{[\text{HCOOH}]}{[\text{DME}]_0}$$

and  $[\text{DME}]_0$  is the initial concentration of DME. The growth of chain carrier OH is given as:

$$\frac{d[\text{OH}]}{dt} = \{(\alpha-1)k_1[\text{DME}] - k_2[\text{HCHO}] + (\eta-1)k_3[\text{HCOOH}]\}[\text{OH}] = g[\text{OH}]$$

The chain system terminates when the factor  $g$  falls down to zero, thus the end of cool ignition is determined. Integrating  $y$  and  $z$  deriving  $g$  along  $q$  until  $g = 0$  gives the extent of fuel consumption and product yields in a cool ignition, where kinetic parameters can be extracted from a detailed reaction mechanism.

In the case of methanol addition, the reaction of methanol with OH should be included:



so that the  $y$  and  $g$  equations are modified as:

$$\frac{dy}{dq} = \beta - \frac{k_2}{k_1} \frac{y}{1-q} + \frac{k_2}{k_1} w(1-q)^{(k_4/k_1-1)}$$

$$g = (\alpha-1)k_1[\text{DME}] - k_2[\text{HCHO}] + (\eta-1)k_3[\text{HCOOH}] - k_4[\text{CH}_3\text{OH}]$$

where  $w = [\text{CH}_3\text{OH}]_0/[\text{DME}]_0$  and

$$\frac{d[\text{CH}_3\text{OH}]}{d[\text{DME}]} = \frac{k_4[\text{CH}_3\text{OH}]}{k_1[\text{DME}]}$$

Figure 7 shows calculated results of the cool ignition fuel consumption as a function of methanol addition. In the comparison of detailed and the simplified formulation with original parameters extracted from the detailed model shows basically good agreement except of the small discrepancy of the methanol dependence and the abrupt slope change in the detailed model 1998 at 13 % of methanol addition.

With the original set of parameters, the model 2000 tends to overestimate the DME consumption whereas the model 1998 shows the opposite trend. Both models underestimate the dependence on methanol addition. According to the recent evaluation of the above rate parameters<sup>11)</sup>,  $k_1$  is 40% smaller,  $k_2$  is 16% smaller and  $k_4$  is 5% smaller than those used in the model 2000 at 700 K. These changes enhance the calculated methanol addition effect toward better agreement with experiment.

It was found the DME consumption is sensitive to the OH reproduction index  $\alpha$ . Modification of  $\alpha$  from the original value of 1.52 to 1.80 in the case of the model 1998, and 1.82 to 1.60 in the case of the model 2000 exhibit better agreement with experimentally observed, as also shown in Fig. 8. However, the slope against the methanol addition is not changed by the  $\alpha$  modification.

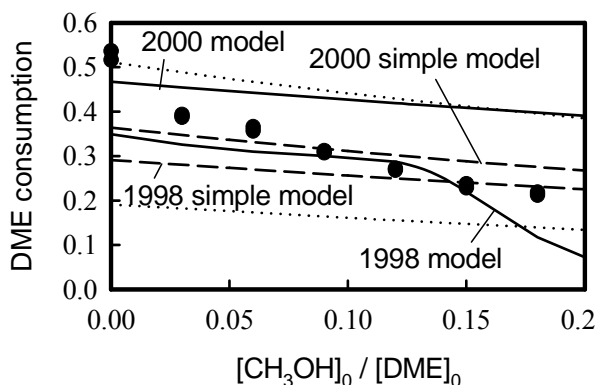


Fig. 7 Fuel consumption at cool ignitions dependent on methanol addition calculated by detailed and simplified models. Solid lines are detailed models, dotted lines are simplified models without parameter modification and dashed lines are simplified models with modification of  $\alpha$ . (see text)

## CONCLUSIONS

Two methodologies of Intermediate species detection have been applied to premixed compression ignition of dimethyl ether in a motored engine. The results are summarized as:

The direct mass-spectrometric detection without sample storage enabled detection of unstable hydrogen peroxide appearing in the short period between cool and hot ignitions. By a correction extracting signals of reactive core volume in the

cylinder using samples of different valve open durations, effective resolution of 2 CA has been achieved.

Detection of HCOOH and HCOOCH<sub>3</sub> in the exhaust gas analysis for cool ignition composition using IR spectrometer has validated the advantage in the newer version of Curran et al. DME oxidation model, while the issue of the version overestimating the extent of cool ignition is indicated.

The essential part of the mechanism determining partial oxidation of cool ignition can be approximated as a chain reaction system yielding certain amounts of OH, HCHO and HCOOH, in which HCHO acts as a major agent for the chain termination. The effect of methanol addition is also included in the scheme to represent the ignition depressing property caused by the OH consumption in the low temperature chain reaction system.

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