

Transient Species Analysis in Homogeneous Charge Compression of Dimethyl Ether

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Introduction

The chemical mechanism of autoignition has been drawing growing attention as it is crucial in controlling HCCI (Homogeneous Charge Compression Ignition) engines, in addition to its relevance to conventional diesel ignition and engine knock. A typical autoignition process undergoes two distinct stages of heat release, in which low and high temperature oxidation mechanisms govern the first (cool) and final (hot) ignition stages, respectively. Low temperature oxidation (LTO) is particularly concerned because the complicated mechanism is less understood and considerably dependent on fuels.

Aiming at elucidating the mechanism controlling cool ignition, our previous study conducted *in situ* laser-induced fluorescence (LIF) measurement and exhaust gas analysis in HCCI of dimethyl ether (DME) (Yamada 2005). 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 discussed. The same methodology was applied to a system controlling ignition timing by adding methanol and ozone (Yamada 2004). However, the effective range of the exhaust analysis to assess the composition of cool ignition was limited in this time unresolved measurement. Furthermore, there remained undetected species that might be important in ignition like hydrogen peroxide and formic acid.

In this paper, we employed additional detection devices for both time resolved and unresolved measurements in order to expand the range of HCCI investigation. After introducing experimental detail and primary results, validity of the formerly proposed reaction mechanism is discussed.

Experimental

Overall system of the experimental engine with measurement devices is essentially the same as in our former paper (Yamada 2004). A single cylinder, side-valve type four-stroke engine of 80 x 70 mm bore – stroke, and compression ratio 8.0 was modified for HCCI operation and sampling measurements. The engine crank is externally driven by a 1500 W induction motor in order to rotate at a fixed rate (typically 600 RPM). Conventionally, exhaust gas was sampled at the exhaust port and the composition was measured using a quadrupole mass analyzer. Formation reactions of formic acid (HCOOH) is not present in the former version of the detailed DME oxidation model of Curran et al. (1998), but was additionally included in the latter version (Curran 2000). However, HCOOH was not detected in our QMS

measurement, because the mass number is same as that of DME and the sensitivity is two orders of magnitude less than that of DME. In this study, a Fourier-transform infrared spectrometer (FT-IR: Shimadzu Corp., IRPrestage-21) was employed to detect species not sensitive in QMS. The exhaust gas was introduced into a 10 cm optical cell equipped with water-resist IR windows at atmospheric pressure and analyzed by the FT-IR. HCOOH was detected at the broad absorption band around 1750 cm^{-1} without interruption from DME, CO, CO₂ and H₂O. A sharp band of HCHO is superimposed in the HCOOH band, but can be easily distinguished. It was found in the calibration that HCOOH is one order of magnitude more sensitive than HCHO. The detection limit for HCOOH is about 100 ppm.

Another notable modification in the current study is a pulse sampling system. A solenoid-type pulse valve (General Valve, 0.8 mm orifice diameter) was equipped on the headplate of the engine with a ring adaptor capable of water cooling. 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 is installed, pumped by a turbo-molecular pump. The orifice size is 1 - 2 mm and is changed according to experimental condition.

Formerly gas collection to a sampling bag was conducted for this type of sampling and a typical valve open duration was 1.5 ms, which is equivalent to 5 CA at 600 RPM and much longer than required even in this low engine speed. In this study, the direct QMS detection in the differential pumping system allowed to set the valve open duration less than 0.5 ms with sufficient sensitivity, while 0.3 ms of the mechanical delay to actually open is present. However, shorter duration tends to have greater fraction from dead volume in the valve and boundary volume close to the cylinder wall. Therefore, a scheme to correct the unnecessary contribution was developed. Figure 1 shows profiles of signal intensity vs. valve open duration, sampled from the engine cylinder, in which cool ignition of DME takes place. The signals normalized by N₂ signal show that HCHO fraction increases with increasing duration, whereas DME shows gradual decrease. The opposite trend indicates that HCHO is formed in the core volume, while much DME remains unreacted in the wall boundary. When the sampling trigger was set at a CA before the cool ignition, no HCHO was detected and DME/N₂ signal ratio was independent of open duration. According to the above observation, we made a correction extracting core volume signals as:

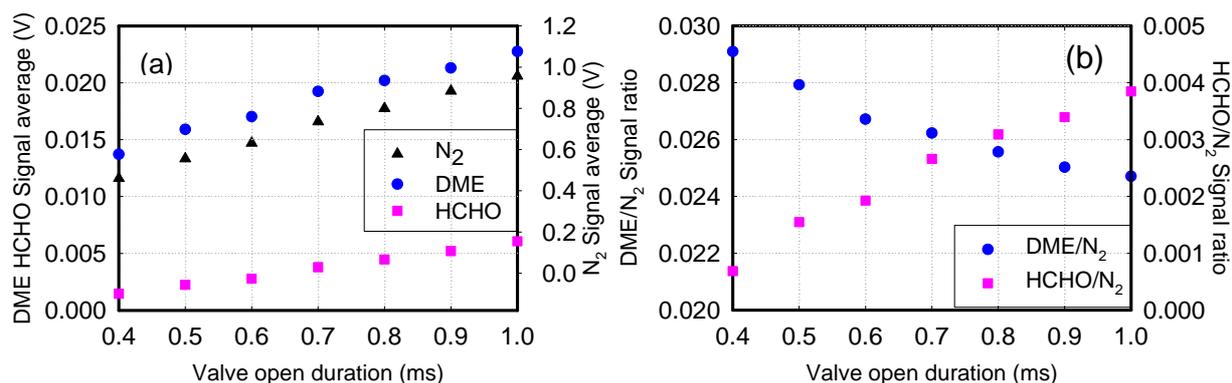


Figure 1. (a) Pulse-valve sampled QMS signals in compression ignition of DME-air mixture as a function of valve open duration. (b) DME and HCHO signals normalized by N₂ signals. Equivalence ratio is 0.21, intake temperature is 383 K, sampling time is ATDC 20 deg, where cool ignition takes place before valve open.

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

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 0.4 ms and t_b was varied between 0.7 and 1.0 ms, both DME and HCHO corrected signals were confirmed to be constant.

Experimental Results

Figure 2 shows a result of crank angle resolved sampling in a DME-air compression cycle together with pressure and rate of heat release taken from a pressure transducer. The heat release profile shows the onset of cool ignition centered at -10 deg CA and the species profiles show corresponding changes, i.e., DME is partially consumed and HCHO and other products are formed at the cool ignition. After the cool ignition, the species composition remains constant at this hot ignition suppressed condition. For DME and HCHO profiles, superimposed lines are non-dimensional numerical simulation using 1998 version of Curran et al. model. The yield of HCHO and DME consumption are in good agreement. Note that the experimentally observed fraction was not fitted to the simulation but separately calibrated. On the time constant at the cool ignition, the experimental profile shows longer duration in the species fraction shift than that of simulation, which is common when the simulation is homogeneous. The sampling profile, however, has still shorter time constant than that of heat release profile. This indicates that the sampling result reflects local species concentration with sufficient resolution, whereas the heat release derived from pressure history data corresponds to a volume average in the cylinder.

Hydrogen peroxide (H_2O_2) was also detected as shown in Fig. 2 (c). Because of the relatively low sensitivity in QMS and the low yield, the ionization energy was set at 45 eV and valve open duration was 1.5 ms. It was confirmed that fragmentation from DME and other stable products is negligible at $m/e = 34$, and logically, only possible source of fragment ion at this mass number is peroxides. There has been no published study detecting H_2O_2 as an intermediate product in homogeneous compression within our search.

In FT-IR measurement of exhaust gas at the condition of single cool flame event, HCOOH was unambiguously detected. HCOOH is a co-product with HCHO in unimolecular decomposition of CH_2OCH_2OOH (QOOH) species arrived in 2000 version of Curran et al. model, but not included in 1998 version. Precise calibration of HCOOH is under way, but a rough estimate of the yield is 10 – 20 % relative to HCHO, which is consistent with simulation using the 2000 version model.

Mechanism Controlling LTO Chain Reaction

In the previous study (Yamada 2005), the role of formaldehyde terminating LTO chain system was discussed in the assumption that formaldehyde is the only reactive intermediate. Here we observed formic acid as prospected with the latest version of the detailed reaction model. It was argued that the effect of intermediate comes from the reaction rate with OH competing with that of DME. As the OH-HCOOH rate constant is one order of magnitude less than that of OH-HCHO and the HCOOH yield is only a fraction of HCHO, the effect of HCOOH in the LTO chain can be considered as negligible. The HCHO yield observed in this study is consistent with that in the previous study.

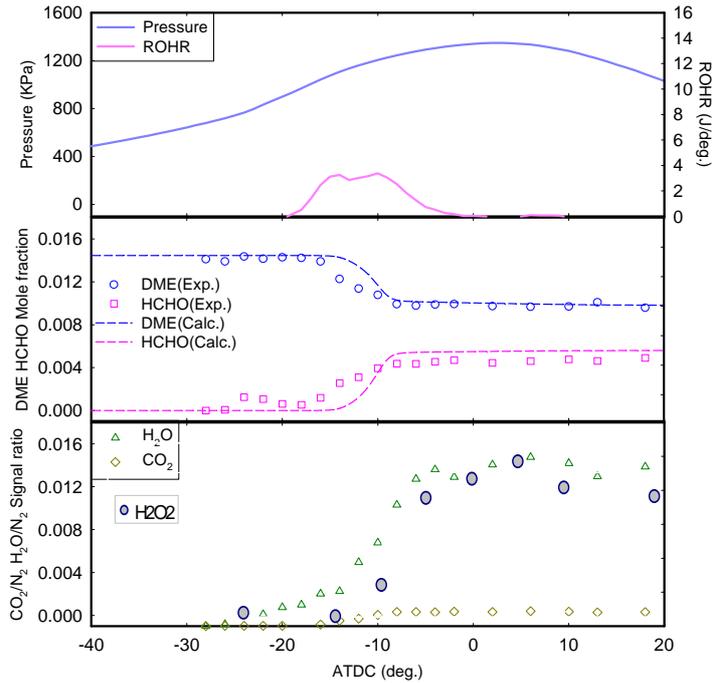
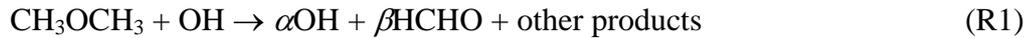


Figure 2. Crank angle resolved profiles of (a) pressure and rate of heat release, (b) corrected DME and HCHO fractions obtained in the pulse valve sampling, and (c) corrected H₂O, CO₂ and H₂O₂ signals. Equivalence ratio is 0.21, intake temperature is 383 K. The signal intensity of H₂O₂ is not in scale.

The LTO chemical mechanism of DME oxidation can be summarized as:



where α is the index of OH reproduction, and β is the number of formaldehyde produced in a cycle. OH growth can be represented by $G = \{(\alpha - 1)k_1[\text{DME}] - k_9[\text{HCHO}]\}$ and the chain system is active while the G factor is positive. This factor tends to decrease with increasing HCHO and the chain terminates at $[\text{HCHO}]/[\text{DME}] = (\alpha - 1)k_1/k_9$. The parameters can be estimated from rate constants in the detailed model and the $[\text{HCHO}]/[\text{DME}]$ ratio at termination is given as 0.22 irrespective of equivalence ratio using values at 700 K, which is consistent with the experimental observation.

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