Chain Termination Mechanism at Cool Flame Stage in Compression Ignition of DME and Straight Chain Alkanes

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Fuels capable of autoignition show two-stage or multi-stage ignition, where a partial heat release of cool flame is followed by the final complete combustion of thermal flame. It is notable that a cool flame once ends the heat release despite the remaining fuel and oxygen. Diesel fuels, low octane number hydrocarbon like n-haptane and dimethyl ether (DME) are such sort of fuels. Since the fuel dependent heat release rate of cool flame significantly influences the timing of thermal ignition, it is essential to elucidate the governing mechanism of cool flames in order to improve the knocking control and HCCI (homogeneous charge compression ignition) engine performance.

In this paper, compression ignition of DME and n-decane has been investigated experimentally in an externally motored single cylinder engine and the mechanism controlling the cool flames was analyzed by using a detailed chemical kinetics simulation.

The engine is a modified version of a commercial four-stroke IC engine (Subaru, EY15-B2, 150 cc). A 750 W electric motor drives the engine at a fixed rate of rotation irrespective of combustion in the cylinder. Intake fuel/air mixture and the homemade engine head were preheated up to 200 °C to attain the autoignition condition at this relatively low compression ratio of 6.8.

Laser induced fluorescence (LIF) was applied for the angle resolved *in situ* monitoring of

formaldehyde in DME compression. Transition of HCHO A-X 4¹₀ vibronic band at around 352.5 nm was selected for the excitation wavelength. Pressure dependent fluorescence lifetime and spectral linewidth were separately measured and used for the correction of perturbed fluorescence profiles.

Figure 1 shows corrected and uncorrected HCHO-LIF profiles in the case of single cool flame event and two-stage ignition. It is demonstrated that HCHO is promptly formed at the cool flame and rapidly consumed at the thermal flame, as anticipated by the detailed chemical model calculation. In a moderate condition that the thermal flame is suppressed, fraction of HCHO after cool flame remains constant until it is evacuated.

By the above aspect we recognized that exhaust gas analysis is a proper way to investigate the cool flame chemistry in such conditions. A quadrupole mass filter was used to selectively detect DME, HCHO, O₂, CO, CO₂ and H₂O in the DME exhaust. A gas chromatograph-mass spectrometer was used to measure aldehydes of various carbon numbers in the case of n-decane.

Figure 2 shows consumption of DME and formed HCHO amount relative to initial DME as a function of premix equivalence ratio. At above a certain equivalence ratio, the fuel consumption rapidly reaches 100 % owing to the onset of thermal flame. On the other hand, it is approximately constant around 30 % below this level. Similarly, HCHO formation per supplied DME is also around 30 % throughout the range of single cool flame ignition.

The above observation is satisfactorily reproduced by the SENKIN based homogeneous chemical kinetic calculation with given volume as a function of time, where Curran's detailed mechanism of DME oxidation was adopted as the reaction scheme, as superimposed in Fig. 2. The cool flame ignition is recognized as a consequence of degenerate chain branching mechanism, i.e., the chain carrier OH is growingly reproduced in a chain cycle in which O_2 addition to alkyl radical and hydroperoxyalkyl radical play important roles. Figure 4 shows the net branching factor, which is defined as the number of OH increase at one chain cycle. The temperature that this factor turns to negative is the upper limit for the chain growth. In the engine compression, however, the cool flame reaction ends below this point, depending on the equivalence ratio owing to another reason described below.

It was found that accumulated intermediate acts as a chain terminator. In the case of DME:

$CH_3OCH_3 + OH \rightarrow CH_3OCH_2 + H_2O$	(1)	[Initial step]
CH_3OCH_2 (via O_2 addition, isomerization, second O_2 addition and decomposition)		
$\rightarrow \alpha OH$ + $\beta HCHO$ + other products	(2)	[summarized chain cycle]
$\rm HCHO + OH \rightarrow CHO + H_2O$	(3)	[step leading to termination]

(α - 1) is the net branching factor of OH shown in Fig. 3. The effective branching to OH reproduction decreases by the competitive OH consumption of (3) as HCHO accumulates. The endpoint is denoted by the relation

$$[\text{HCHO}]/[\text{DME}] = (\alpha - 1)k_1/k_3$$

Since k_1/k_3 is a weak function of temperature, this accounts for the observed constant percentage fuel consumption against the equivalence ratio and preheat temperature.

Although the detail is further complicated and agreement with model is only qualitative, essentially the same mechanism is found to be applied for the n-dacane oxidation. In Fig. 4, measured and calculated amounts of C₂-C₈ aldehyde formed from n-dacane compression are shown as a function of equivalence ratio. Whereas most of decane is consumed in the cool flame, there remain intermediates of various carbon numbers and the partial heat release rate is less than that of DME.



Fig. 1 Crank angle resolved mole fraction of HCHO in cool flame (upper) and two-stage ignition (lower). Solid symbolas are raw LIF intensities and open symbols are corrected fractions. Dashed curves are from simulation.



Fig. 2 Consumed DME (a) and HCHO generation relative to initial DME. Symbols are experiment at 600 RPM and $T_0 = 414$ K.



Fig. 3 Net branching factor for OH reproduction per chain cycle. Calculated from Curran's DME model and modified LLNL n-heptane model.



Fig. 4 C2-C8 aldehyde formation relative to consumed n-decane. Symbols are experiments and lines are from the modified LLNL model.