Time-Domain Mixing, the Key to Combustion Control for Future Internal Combustion Engines, and Its Impact on Low-Temperature Oxidation Chemistry

Hiromitsu Ando and Kazunari Kuwahara

Mitsubishi Motors Corporation
ando-hiromitsu@pde.mitsubishi-motors.co.jp
1, Nakashinkiri, Hashime, Okazaki, Aichi 444-8501 Japan

Keywords: Internal Combustion Engine, Combustion, Low-Temperature Oxidation

Next Target of Combustion Control

In these ten years, the authors presented several combustion control technologies for gasoline engines. Combustion control for a premixed leanburn gasoline engine was achieved by the intensification of a bulk flow in the cylinder, and its conversion into turbulence immediately before combustion to increase a turbulent burning rate, that is, by turbulence control(1). Combustion control for a direct injection gasoline engine was achieved basically by the formation of both a uniform air fuel mixture at a high load, and a stratified mixture with a moderate concentration at a low load, that is, by mixing control(2). By utilizing the freedom of mixture formation with the direct injection, combustion control technologies with two-stage fuel injection was also realized: one with a stratified mixture within a lean uniform mixture beyond the lean combustion limit to suppress knocking(3), and another with a fuel injection into the burned gas of a stratified mixture to promote the warm-up of a catalyst(4).

The level of unburned HC emissions of a gasoline engine is much higher than that of a diesel engine. About 2 % of fuel in a gasoline engine are discharged out of the exhaust pipe. Including another part of fuel burned during the exhaust stroke, the total part of fuel which cannot contribute to the piston work, is estimated to be several times as much as the unburned fuel out of the exhaust pipe. The high HC level of a gasoline engine is caused by the high octane number of gasoline. Gasoline is normally ignited with spark discharge, and burned with flame propagation. Part of fuel in an adjacent layer to the wall where a flame cannot propagate, is left from combustion. On the other hand, diesel oil with the high cetane number can be self-ignited in the compression stroke. Even a fuel droplet straying from a flame, can be burned up. In point of the advantage of gasoline, however, it can easily prepare various kinds of mixtures between uniform and stratified ones. On the other hand, a mixture with diesel oil is limited generally to stratified one, because the ignition of uniform one can be hardly controlled.

The authors have kicked off discussing of ignition control as a next target of combustion control(5). The following idea could be the ultimate combustion control: from a microscopic point of view, it targets the same combustion characteristics as those when a fuel with a high cetane number is dispersed uniformly at the minimum concentration for self-ignition, to complete combustion. From a macroscopic point of view, on the other hand, it targets the same as those using a fuel with a high octane number, to maintain the combustion under control. In order to achieve these conflicting requirements at the same time, it expects controlling the cetane and octane numbers independently. A relationship between these numbers of typical hydrocarbon fuels where the sum of the numbers is approximately 110, implies that it is impossible to control the numbers independently. However, with consideration that each number demonstrates its own effect on combustion at different timing from that of the other, or their effects take different lifetimes, and that fuel changes its characteristics during the compression stroke by experiencing low-temperature oxidation such as isomerization and peroxidation, it is not necessarily unreasonable.

Mixture Experiencing Low-temperature Oxidation

When a typical hydrocarbon fuel of which ignition exhibits negative temperature dependence, is ignited through temperatures below 900 K, the ignition is characterized by two-stage heat release: the first one in the initial stage of low-temperature oxidation, and the second one at thermal ignition. **Figure 1** shows a result of the ignition in an engine condition from a detailed kinetic model of propane oxidation(6). Several kinds of peroxide and aldehyde are in a state of partial equilibrium, and have a relatively long lifetime, before they are decomposed at thermal ignition.

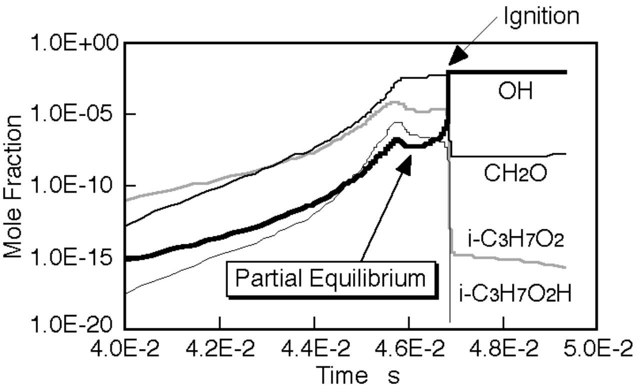

Fig. 1. In-Cylinder Self-Ignition of Air Propane Mixture with Low-Temperature Oxidation

Table 1. Typical ingredients of Mixture including Products of Low-Temperature Oxidation

N2	0.759	CH3OH	4.85e-5
O2	0.189	CH4	1.26e-5
H2O	0.014	HO2	5.77e-6
CH3OCH3	0.00859	HO2CH2OCHO	1.42e-6
CH2O	0.00791	HCO3	9.76e-7
CO	0.00759	HCO2	1.67e-7
H2O2	0.00302	HCO3H	1.12e-7
CO2	0.00129	OH	2.07e-10
H2	0.000185	Units: Mole Fraction	

Initial Equivalence Ratio: 0.28,
Press.: 1.0 MPa, Temp.: 730 K

In order to understand basic characteristics of a mixture experiencing the partial equilibrium, non-dimensional calculation was performed with Curran's detailed model of dimethyl ether (CH3OCH3) oxidation(7). Dimethyl ether is convenient for tracking paths of low-temperature oxidation, because it is the simplest fuel with negative temperature dependence of ignition, and then has the most limited paths of low-temperature oxidation, that is, an only main path toward each of chain propagation, chain branching, and termination(7). First, an air fuel mixture was compressed and expanded in engine conditions where low-temperature oxidation appeared, but thermal ignition couldn't, and products of the low-temperature oxidation were frozen in the expansion stroke, for example at compression ratio: 10, rotation speed: 833 min^{-1}, equivalence ratio: 0.28, initial temperature: 300 K, and initial pressure: 0.075 MPa, for preparation of mixtures having experienced low-temperature oxidation. Then, these mixtures were self-ignited in constant-volume conditions. **Table 1** shows typical contents of a mixture including products of low-temperature oxidation. **Figure 2** compares temperature profiles of the mixtures with those of a fresh air fuel mixture. While the fresh-mixture ignition exhibits a two-stage temperature rise with an initial temperature lower than about 830 K, the mixtures including the low-temperature oxidation products at the beginning, reach thermal ignition after a gradual temperature rise alone, in other words, without the first one

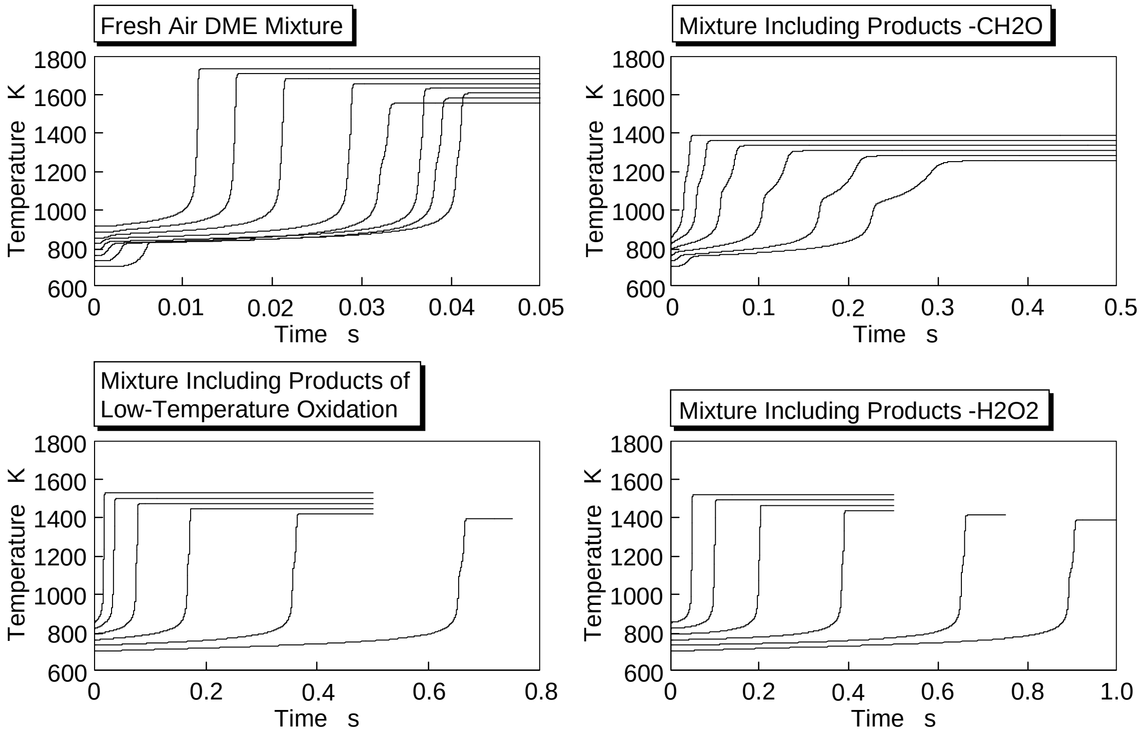

Fig. 2. Temperature Profiles of Self-Ignited Mixtures with Low-Temperature Oxidation in Constant-Volume Condition (Initial Equivalence Ratio: 0.28, Initial Pressure: 1.0 MPa)

of a two-stage temperature rise. As shown in **Fig. 3**, when the initial temperature is much lower than 830 K, the ignition delay with the products is much longer than that of the fresh mixture. With an initial temperature higher than 830 K, however, the delay with the products is shorter than that of the fresh mixture. About 820 K is the boundary below which OH is generated in a cycle of the main paths of low-temperature oxidation, but above which OH is consumed.

Mixtures including the low-temperature oxidation products, but from which one out of the products was removed, were also self-ignited. Figures 2 and 3 includes meaningful results. When CH2O is removed, the ignition tends to regain a two-stage temperature rise, and the ignition delay is shorter than that when the CH2O is included. When H2O2 is removed, the ignition delay is longer than that with the H2O2.

Therefore, CH2O is one of major reasons for the longer ignition delay with the low-temperature oxidation products. According to OH generation rates with an initial temperature of 730 K shown in **Fig. 4**, when CH2O is included in advance, CH2O+OH=HCO+H2O competes against CH3OCH3+OH=CH3OCH2+H2O from the beginning, which interferes with chain propagation and branching beginning with CH3OCH2 generation. On the other hand, H2O2 mainly causes the shorter delay with the products, because it can promote OH generation with H2O2(+M)=OH+OH(+M) as the trigger of thermal ignition.

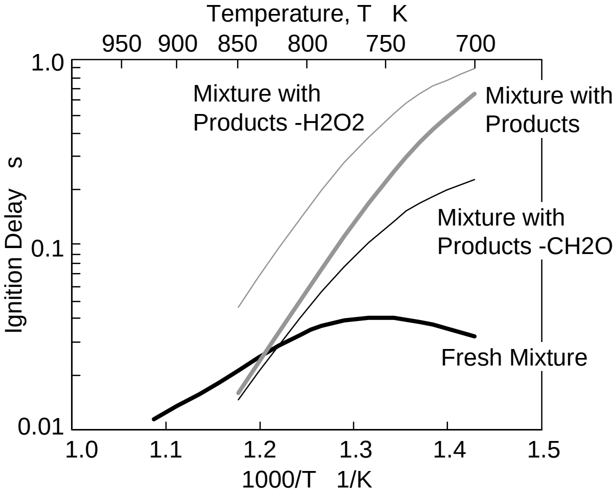

Fig. 3. Ignition Delays

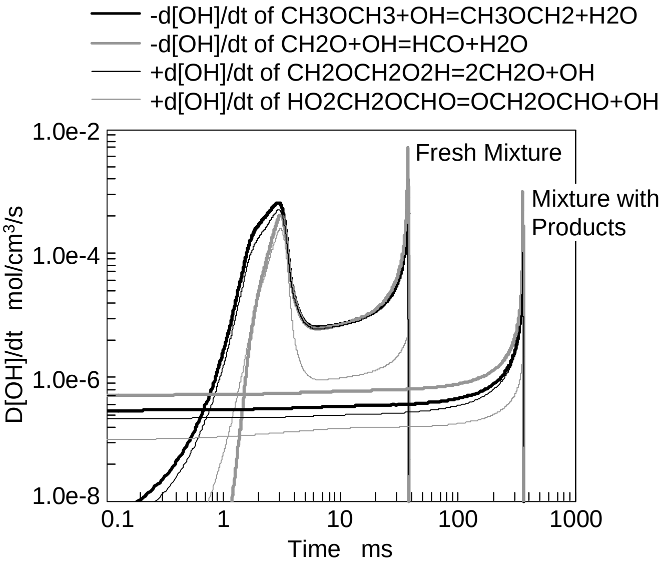

Fig. 4. OH Generation rates of Typical Reactions
(Initial Temperature: 730 K)

Time-Domain Mixing

Tracking normal process in a simple combustion system along by time, stages such as fuel vaporization, air fuel mixing, low-temperature oxidation, thermal ignition, reactions toward thermal equilibrium, and burn-up of products as soot, proceed in this sequence. Products in one stage are separated from those in other stages time- and space-wise. In the cylinder, on the other hand, inhomogeneity of local concentrations and temperatures causes the sequential stages in a local area to proceed at different rates from those in other areas. Various products in different stages exist at the same time. In an enclosed space of the cylinder filled and stirred with a lot of eddies, products in one stage have chances to meet those in other stages, and be mixed with them. **Figure 5** illustrates the phenomenon. Along the sequential stages, for example, when it is now that soot is generated, its precursors were generated in the past, and the soot will be burned up in the future. In this sense, products at the present can be mixed with those in the past or future. The authors dubbed this kind of mixing “time-domain mixing.”(5) It is considered essential for describing combustion in the cylinder.

In a premixed leanburn gasoline engine, a flame with reacting zones widely spread behind the flame front, is observed(5), (8). Assumedly, the laminar burning rate of a mixture with an equivalence ratio approaching 0.6, decreases to several-ten cm/s. The turbulence intensity has to be increased to several to 10 m/s, to acquire a turbulent burning rate for completing combustion. In such a condition, although according to the present turbulent combustion theory, it is no wonder that a local flame is quenched, combustion can be completed as if nothing had happened. In order to explain the combustion, the authors proposed an idea that in the cylinder, local quenching usually takes place, but quenching zones have chances to be entrained into reacting zones, and restart combustion(5).

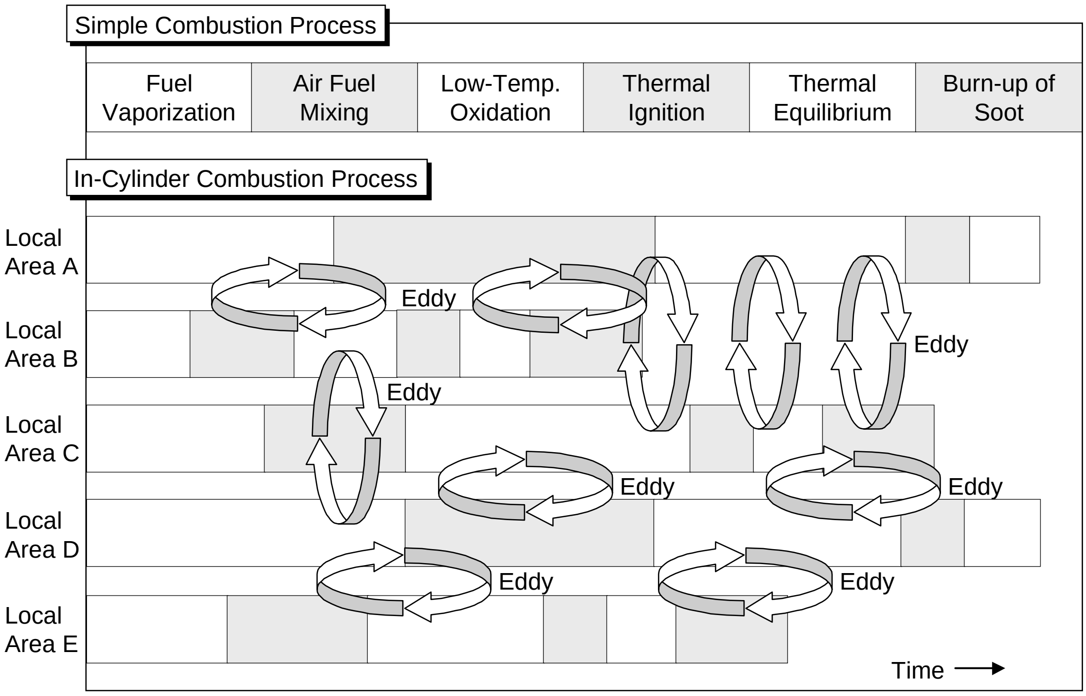

Fig. 5. Idea of Describing In-Cylinder Combustion, Time-Domain Mixing

In a direct injection gasoline engine operating with stratified-mixture combustion, first, a flame with chemiluminescence from OH, CH, and C2, together with CO-O recombination emission, rapidly propagates throughout the combustion chamber, and then, a luminous flame with thermal radiation from soot generated in local rich zones, propagates into an area behind the first flame front filled with products of the first flame(3), (5). From a microscopic point of view, in a usual gasoline engine, a flame propagates into an air fuel mixture, and in a direct injection diesel engine, a thermal flame propagates into the air surrounding a fuel spray. In a direct injection gasoline engine, on the other hand, the thermal flame propagates into the area filled with not only air and fuel, but also various kinds of radicals and CO. The soot in the thermal flame is burned up within the activated area.

Impact of Time-Domain Mixing on Low-Temperature Oxidation

The above examples show time-domain mixing at very high temperatures. For ignition control, time-domain mixing at temperatures below 900 K is considered more important. Time-domain mixing interacting with low-temperature oxidation, was simply modeled with the detailed model of dimethyl ether oxidation in the following way: a fresh air fuel mixture was mixed with a mixture having experienced low-temperature oxidation, and the mixed one was self-ignited in a constant-volume condition. **Figure 6** shows temperature profiles of both a fresh mixture and the mixed one, in other words, mixtures with and without time-domain mixing, with an initial temperature of 730 K. 25 % time-domain mixing is a case when the part with experience of low-temperature oxidation accounts for 25 % of the mixed one in mole fraction, that is, the fresh part of 75 %. With time-domain mixing, as expected, the first one of a two-stage temperature rise is depressed, and the ignition delay is longer than that without time-domain mixing. **Figure 7** shows OH generation rates. CH2O carried by time-domain mixing, consumes OH at the beginning. In conditions where ignition must exhibit a two-stage temperature rise, time-domain mixing plays a role in prolonging a period of low-temperature oxidation, and retarding the ignition. This means that even when a fuel additive exhibits its effect on ignition promotion in a quiescent field, unfortunately, the effect is weakened in the cylinder, as CH2O scavenges radicals generated from the

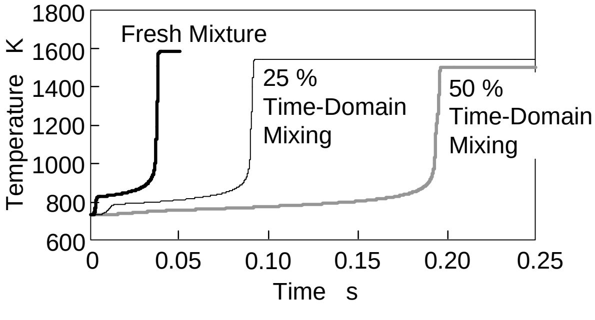

Fig. 6. Temperature Profile with Time-Domain Mixing
(Initial Equivalence Ratio: 0.28,
Initial Pressure: 1.0 MPa)

additive.

However, dimethyl ether exaggerates this impact of time-domain mixing on low-temperature oxidation, because it generates CH2O with a much higher concentration than that using gasoline or diesel oil.

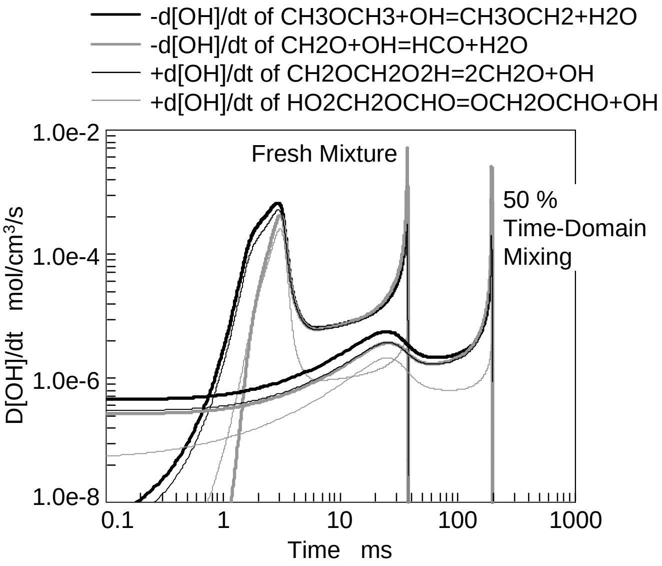

Fig. 7. OH Generation rates with Time-Domain Mixing

References

(1) Kuwahara, K., Watanabe, T., Takemura, J., Omori, S., Kume, T., and Ando, H., “Optimization of In-Cylinder Flow and Mixing for a Center-Spark Four-Valve Engine Employing the Concept of Barrel-Stratification,” SAE Paper, 940986, 1994
(2) Kume, T., Iwamoto, Y., Iida, K., Murakami, M., Akishino, K., and Ando, H., “Combustion Control Technologies for Direct Injection SI Engine,” SAE Paper, 960600, 1996
(3) Kuwahara, K., Ueda, K., and Ando, H., “Mixing Control Strategy for Engine Performance Inprovement in a Gasoline Direct Injection Engine,” SAE Paper, 980158, 1998
(4) Kuwahara, K., Yamamoto, S., Iwachidou, K., and Ando, H., “Two-Stage Combustion for Quick Catalyst Warm-up in Gasoline Direct Injection Engine,” COMODIA 98, pp. 293-298, 1998
(5) Ando, H., and Kuwahara, K., “A Keynote on Future Combustion Engines,” SAE Paper, 2001-01-0248, 2001
(6) Koshi, M., Department of Chemical System Engineering, The University of Tokyo
(7) Curran, H. J., Pitz, W. J., Westbrook, C. K., Dagaut, P., Boetter, J-C., and Cathonnet, M., “A Wide Range Modeling Study of Dimethyl Ether Oxidation,” 26th International Symposium on Combustion, pp. 627-632, 1996
(8) Kuwahara, K., Kawai, T., and Ando, H., “Influence of Flow Field Structure after the Distortion of Tumble on Lean-Burn Flame Structure,” COMODIA 94, pp. 89-94, 1994