

# Effect of Mixture Dilution or EGR on Low-Temperature Autoignition under Piston Compression

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## ABSTRACT

We have studied the effects of initial-charge dilution and chemical preconditioning of the recycled residual products of combustion on the autoignition process through the observations of the process of compression ignition.

Elevated temperature and pressure of the charge resulting from a supplement of recycled products make the ignition delay usually shorter, except in the negative temperature-coefficient region.

When mixture is diluted by argon or nitrogen, the cool-flame delay  $\tau_1$  is not changing, and only the blue-flame onset retards; i. e. the  $\tau_2$  is elongated, almost due to the increase of mixture heat capacity per unit mass of fuel caused by inert gas enhancement.

Carbon dioxide or water vapor dilution makes cool-flame delay  $\tau_1$  slightly longer. And the addition of water vapor results in an extreme retardation of blue flame appearance in the high temperature side of the negative temperature-coefficient regime.

Residual products carried over by an exhaust gas recirculation and mixed with the fresh charge, which give a possibility that chemically-active species could be recycled and dispense with initiation reaction for autoignitions, scarcely have other effects on the chemistry preceding the autoignition under the real engine conditions than the ones of stable species dilution.

## INTRODUCTION

In modern spark ignition engines, exhaust gas recirculation (EGR) systems are installed to eliminate NO<sub>x</sub> emission. Hot recycled products derived from the combustion of previous cycle, when introduced to an intake port and mixed with the incoming charge, raise temperature and pressure of the mixture during the compression stroke in the cycle. The preignition reactions accelerate due to the higher pressure and temperature of the charge in which the recycled products are added to. This situation would give an effect to promote autoignitions in the end gas, and put at a disadvantage to the engine knock.

Residual products of combustion mixed into the fresh charge, on the contrary, would act as diluent of inert or reactive gases on the autoignition processes. Because of their chain-thermal nature of the reactions, low-temperature oxidations carried out in the end gas exothermically up to the autoignitions

would elongate ignition delays of diluted mixtures which have more heat capacities.

These two directly-opposed effects of EGR would compete against another; the result would settle upon whether the engine knock will occur or not. Chemically-active species included in residual products, if they could come back alive in the intake port, might give some significant influences on the end-gas ignition processes.

Empirically obtained temperature and pressure dependence of the fuel-air mixtures have been reported by the authors<sup>(1,2)</sup>. Experimental investigations of the temperature dependence associated with the influence of dilutions of stable species on the low-temperature autoignition driven by piston compressions will be first described.

Comprehensive chemical kinetics calculations will be performed to estimate the ignition delays in the case of acetaldehyde as a fuel. Because of the limited establishment of mechanism on the low-temperature oxidation reactions, modelings can be done only for the restricted conditions higher than 750K.

The effect of the recycled chemically-active species on the chemistry preceding the autoignition under the real engine conditions will be examined taking account of the experimental results of other papers<sup>(3,4)</sup>, and the conclusion will be derived deductively.

## EXPERIMENTAL TECHNIQUE

n-Butane (C<sub>4</sub>H<sub>10</sub>) or acetaldehyde (CH<sub>3</sub>CHO) was used as a fuel, and synthetic airs composed of argon (Ar) and oxygen (O<sub>2</sub>) as oxidizers. Argon (Ar), nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) or water vapor (H<sub>2</sub>O) was adopted as an individual diluent of stable species.

n-Butane was adopted as a fuel which has a similar characteristics to commercial gasolines on the low-temperature flame appearances<sup>(2)</sup>. Acetaldehyde is one of the most familiar fuels on which low-temperature oxidation kinetics are somewhat known, though not quite satisfactorily.

In the n-butane case the mixture strength was always stoichiometric: the equivalence ratio  $\phi=1$ . The composition of reference mixture as the non-diluted original is C<sub>4</sub>H<sub>10</sub> / O<sub>2</sub> / Ar = 2.67 / 17.33 / 80.00, which is called "80%Ar mixture". When diluted, C<sub>4</sub>H<sub>10</sub> / O<sub>2</sub> / Ar / Diluent = 2.34 / 15.16 / 80.00 / 2.50.

In the acetaldehyde case mixture is always lean: the

equivalence ratio  $\phi=0.5$ . The reference composition is  $\text{CH}_3\text{CHO} / \text{O}_2 / \text{Ar} = 2.43 / 12.20 / 85.37$ , called "85.4% Ar mixture". When diluted by argon or carbon dioxide,  $\text{CH}_3\text{CHO} / \text{O}_2 / \text{Ar} / (\text{Ar} \text{ or } \text{CO}_2) = 2.22 / 11.11 / 77.78 / 8.89$ , and when water vapor is the diluent,  $\text{CH}_3\text{CHO} / \text{O}_2 / \text{Ar} / \text{H}_2\text{O} = 2.38 / 11.91 / 83.33 / 2.38$ . Owing to practical restrictions of equipment for compression, mixture compositions listed above were selected in order to put the ignition delays between several and hundreds of millisecond for the temperature and pressure conditions mentioned below.

A rapid-compression machine was used to obtain ignition delays of the well premixed charge. Details about the rapid-compression machine used (cylinder bore: 65mm, stroke: 140mm) are described elsewhere (2). Quartz windows were mounted at the sidewalls of the cylinder of the rapid-compression machine, and a strain-gauge type pressure transducer (Kyowa PE30KF) on the head of cylinder. Two photomultipliers (RCA 1P28) were used to detect radiant emissions. A blue and a red glass filter (Toshiba V-42; 320~510nm, R-62; 620nm~) were laid ahead of the photomultipliers to detect low-temperature or hot flame onset separately (5).

Mixtures were compressed and lights emitted from low-

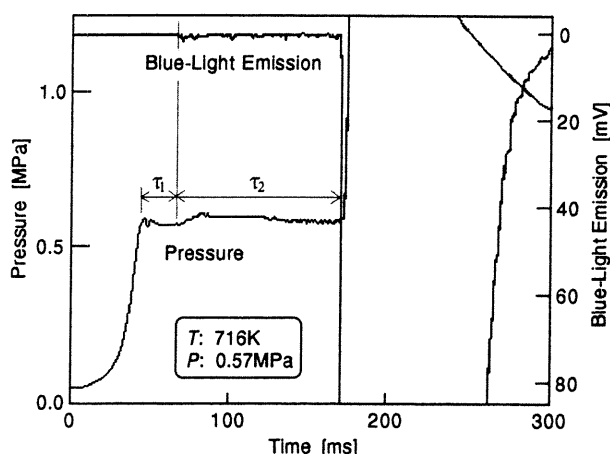


Fig. 1, Typical pressure and blue-light emission records of n-butane autoignition in rapid-compression machine.  $\phi=1$ , 716K, 0.57MPa.

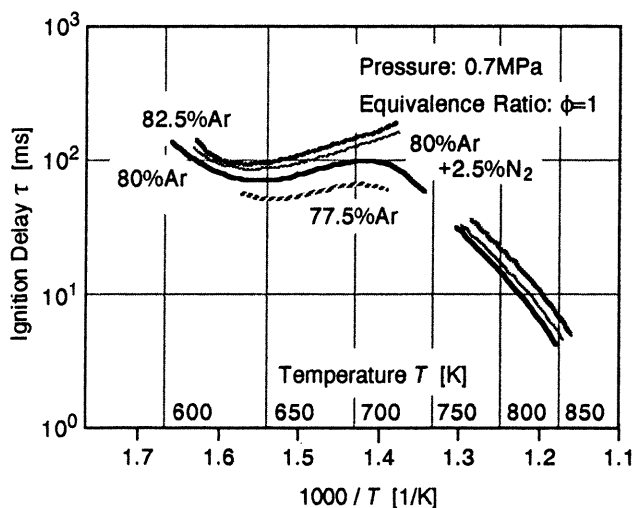


Fig. 2, Total ignition delay up to hot ignition of n-butane mixture diluted with Ar or  $\text{N}_2$ .

temperature flames and hot-flame were observed during the induction periods. Temperatures prepared for autoignition were ranging from 600 to 950 K under pressure conditions of 0.5 to 0.7 MPa, which include the end-gas conditions in the preflame periods in practical engines. This temperature range contains cool-flame-dominant ignition regime, negative temperature-coefficient regime and blue-flame-dominant ignition regime. The latter two regimes are important for spark ignition engines.

## CHEMICAL KINETICS MODELING

Comprehensive chemical kinetics calculations were carried out to estimate the ignition delays only in the acetaldehyde case. Reactions and heat release were calculated during and after the compression where the piston was arrested. Only during the piston compression stroke, temperature and pressure histories were given according to the experiment. Low-temperature oxidation mechanism of acetaldehyde used here was the one which has been developed by the authors (6).

## RESULTS AND DISCUSSION

Pressure dependence was not examined strictly. Pressure was not scattered widely, because the pressure dependence can be estimated by the knowledge in our previous work (1).

Fig. 1 shows typical pressure and blue-light emission records of the n-butane case. Light emission record swings downward. Light emission during the preflame region of the n-butane can be seen to be quite faint, even though the pressure rise due to the cool-flame appearance is remarkably clear.

The total ignition delay is the induction period up to the hot ignition from the end of compression at which the piston is arrested. Fig. 2 shows the cases argon or nitrogen is a diluent in the Arrhenius plots. The abscissa is measured in reverse direction to the reciprocal temperature, decreasing from left to right as the temperature rises. Fig. 3 is the delay for the cool-flame appearance,  $\tau_1$ . Ignition delay is changing in similar fashion for both diluents. In these figures the case the diluent is reduced by 2.5% is also indicated as the 77.5% Ar.

When mixture is diluted by argon or nitrogen, the cool-flame delay  $\tau_1$  is hardly changing, and only the blue-flame onset retards; i. e. the  $\tau_2$  is elongated. The change of the total

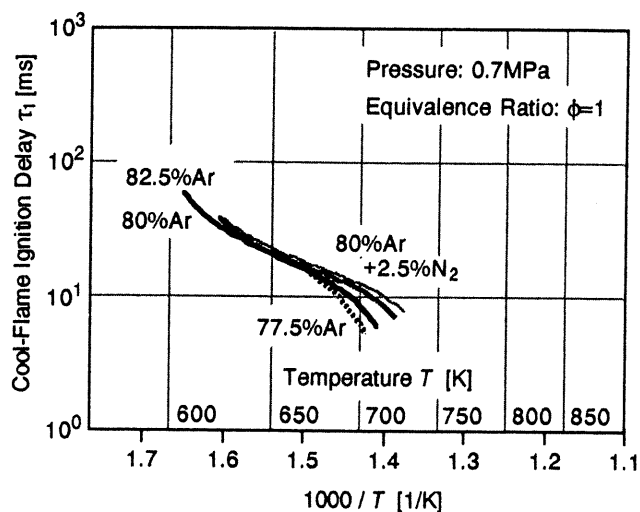


Fig. 3, Ignition delay up to cool-flame appearance of n-butane mixture diluted with Ar or  $\text{N}_2$ .

delay is caused by blue-flame delay  $\tau_2$ . This is the same manner lead-alkyl additives give the anti-knock properties to fuel gasolines.

Mixture heat capacity per unit mass of fuel is compared in Figs. 4. It is well known that the low-temperature ignition reactions have the "chain thermal" nature. It can be recognized that the ignition delay elongation is caused in the  $\tau_2$  period almost due to the increase of mixture heat capacity per unit mass of fuel caused by inert gas enhancement. In high-temperature thermal ignition occurring at higher temperatures above 1000K or so, the power of the concentration of inert Ar in the empirical equation expressing ignition delay is always zero (e.g. 7); the increase of the Ar concentration by dilution only acts relatively to decrease reactants concentration. However here, in the blue-flame-dominant ignition regime inert gas dilution has an effect to retard the blue-flame onset. In the low-temperature ignition, including blue-flame dominant regime, temperature field prepared is not satisfactorily high, compared to the high-temperature thermal ignition. The preflame reaction in the low-temperature ignition should raise the mixture temperature by itself to achieve the ignition.

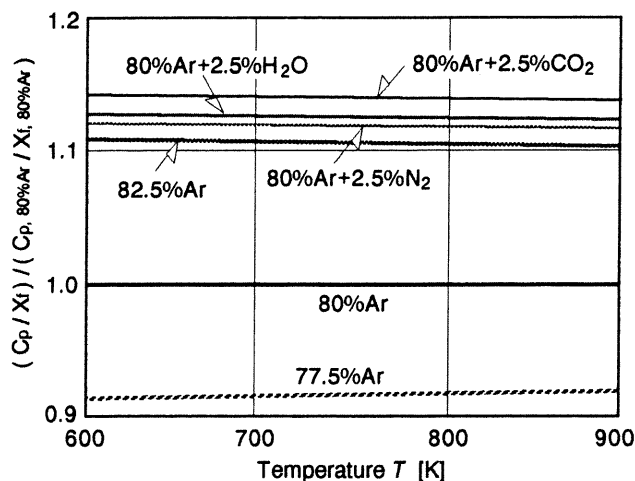


Fig. 4, Heat capacity of mixture per unit mass of fuel compared.

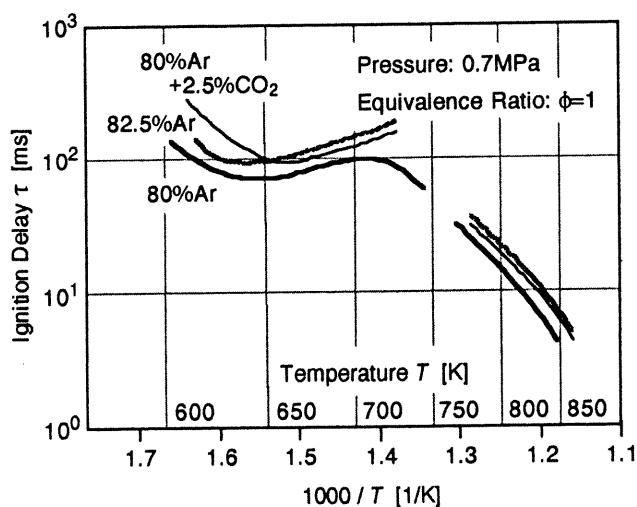


Fig. 5, Total ignition delay up to hot ignition of n-butane mixture diluted with  $\text{CO}_2$ , compared with a case Ar is a diluent.

The effects of dilution by carbon dioxide in the case of n-butane as a fuel are demonstrated in Figs. 5 to 7, compared with a case where the argon is the diluent. Pressure at the end of compression is arranged to be 0.7MPa. In the n-butane case, when charges are diluted above the reference mixture, the ignition delay becomes too long to measure in the temperature regime where the negative temperature-coefficient and the blue-flame-dominant regimes come into contact with.

The total delay is presented in Fig. 5. The delay for cool-flame appearance  $\tau_1$  is shown in Fig. 6. And the delay for the blue-flame onset thereafter the cool flame appears,  $\tau_2$  is indicated in Fig. 7; the nature of negative temperature-coefficient is typically seen.

Water vapor case as a diluent with n-butane as a fuel is presented in Figs. 8, 9 and 10. The total delay, delay for cool-flame appearance  $\tau_1$ , and the delay for the blue-flame onset  $\tau_2$  are indicated respectively.

Carbon dioxide or water vapor dilution makes cool-flame delay  $\tau_1$  longer in the cool-flame dominant regime. And the addition of water vapor results in an extreme retardation of blue

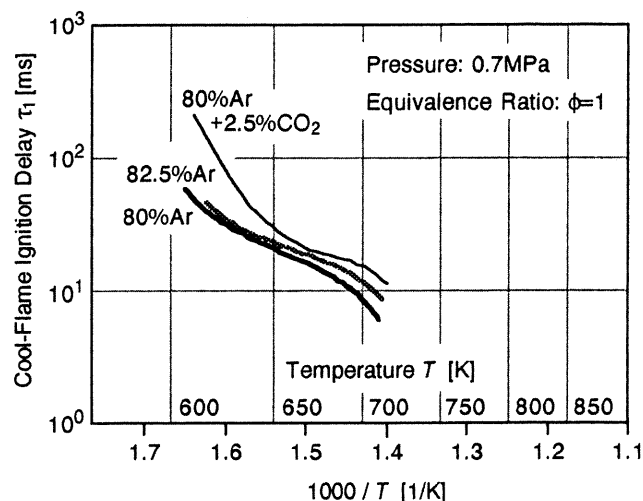


Fig. 6, The delay for cool-flame appearance,  $\tau_1$  of n-butane mixture diluted with  $\text{CO}_2$ , compared with a case Ar is a diluent.

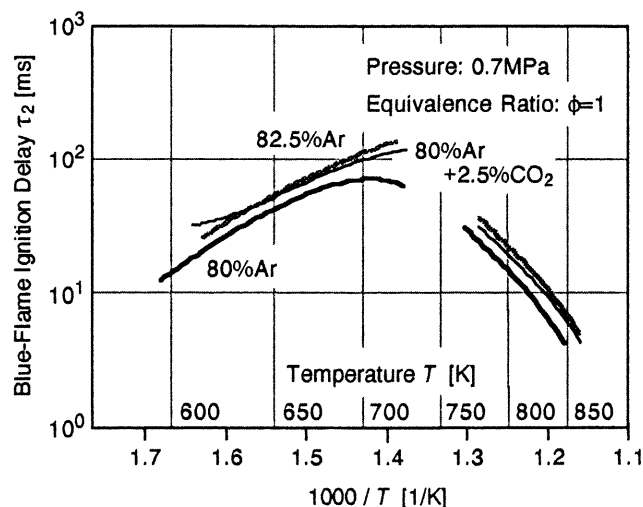


Fig. 7, The delay for blue-flame onset,  $\tau_2$  of n-butane mixture diluted with  $\text{CO}_2$ , compared with a case Ar is a diluent.

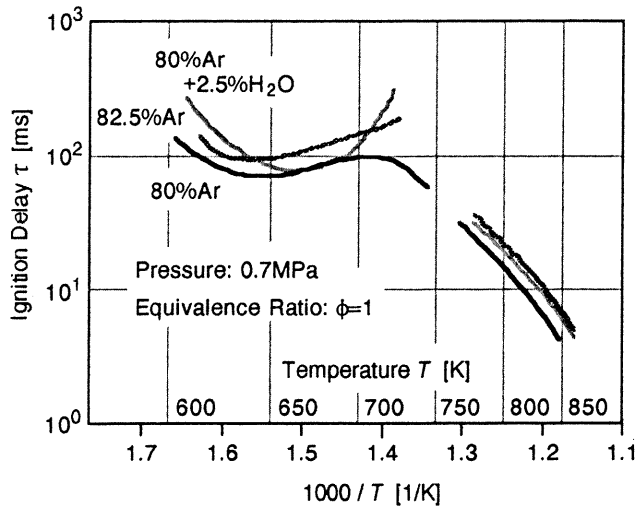


Fig. 8, Total ignition delay up to hot ignition of n-butane mixture diluted with  $\text{H}_2\text{O}$ , compared with a case Ar is a diluent.

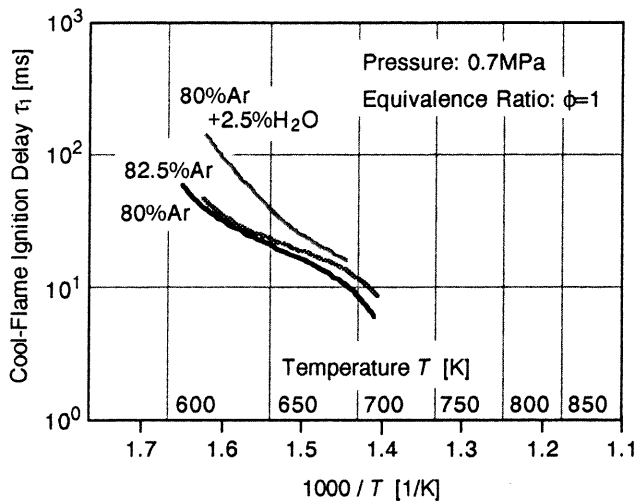


Fig. 9, The delay for cool-flame appearance,  $\tau_1$  of n-butane mixture diluted with  $\text{H}_2\text{O}$ , compared with a case Ar is a diluent.

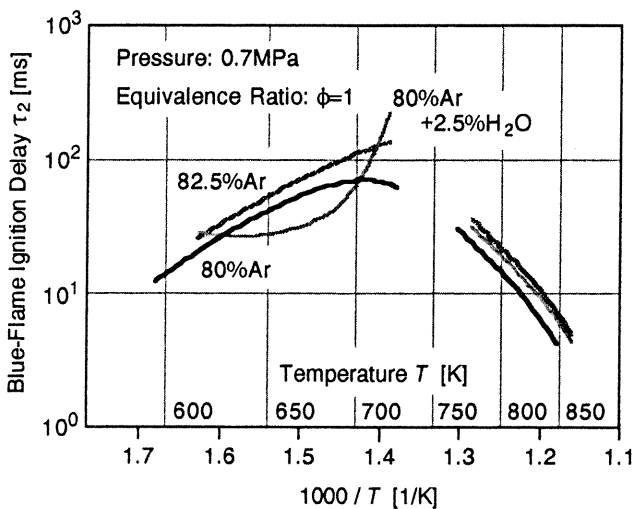


Fig. 10, The delay for blue-flame onset,  $\tau_2$  of n-butane mixture diluted with  $\text{H}_2\text{O}$ , compared with a case Ar is a diluent.

flame appearance in the high temperature side of the negative temperature-coefficient regime. We recognize as an empirical knowledge that engine knock is eliminated in humid rainy days. In the higher temperature side of the negative temperature-coefficient regime,  $\text{HO}_2$  is the most dominant radical which is controlling the  $\text{H}_2\text{O}_2$  branching. Addition of  $\text{H}_2\text{O}$  would change the ratio between  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$ , or retard consumption of peroxides. Increase of  $\text{CO}_2$  is considered to retard production, decomposition and oxidation of formaldehyde.

The experimental results in the case of acetaldehyde as a fuel are summarized in Fig. 11. Acetaldehyde is a fuel very easy to be resolved. Also in this experiment, early during the compression stroke decomposition reaction is proceeding and just after the piston compression finishes, remarkable cool flame will appear; this situation will be shown in Fig. 12. Total delay counted from the end of compression is shown in the figure. Owing to the remarkable development of the pre-cool-flame reactions in the compression stroke, the activation energies are apparently small. The effect of dilutions seems to be similar to the n-butane case

Modelings were done only for the restricted conditions higher than 750K and acetaldehyde as a fuel. Applicability of the comprehensive mechanism to the lower temperature range is uncertain. Ignition delay of the reference mixture under the condition at the end of compression; temperature 763K and pressure 0.5MPa is estimated to be two and a half times longer than the experimental result as shown in Fig. 12. In the case of carbon dioxide as a diluent, this factor is two. These discrepancies between the calculation and experiment are not peculiar because the calculations are carried out under the assumption of homogeneity in species and temperature. In practical cases the appearances of low-temperature flames are heterogeneous spatiotemporally<sup>(8)</sup>. They usually appear from ignition kernels.

How does the diluent act on the chemistry and the difference between the diluents in the negative temperature-coefficient regime are the most interesting and desirable to examine, but they are not clear, because the temperature range in which the simulation is available is the blue-flame dominant regime, and there the dilution hardly show other effects on the

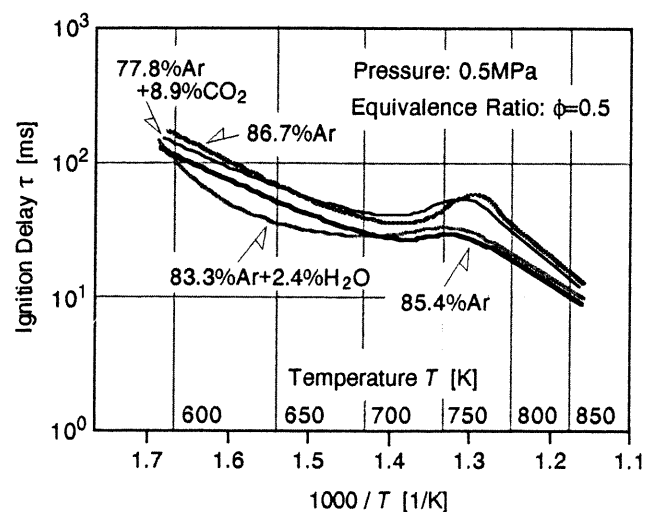


Fig. 11, Total ignition delay up to hot ignition of acetaldehyde mixture diluted with Ar,  $\text{CO}_2$  or  $\text{H}_2\text{O}$ .

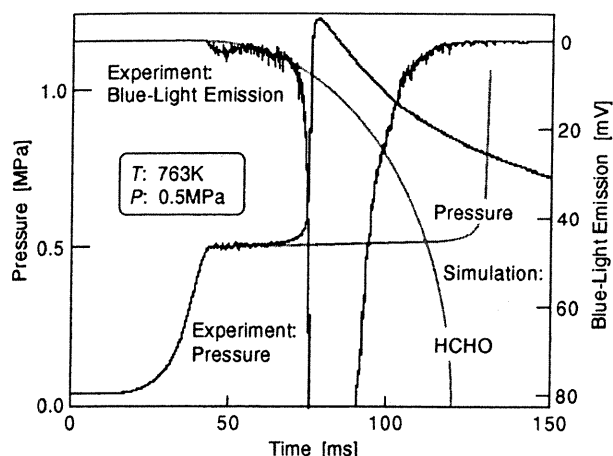


Fig. 12, Comparison between simulation using kinetics mechanism and experimental result of acetaldehyde autoignition.  $\phi=0.5$ , 763K, 0.5MPa.

chemistry preceding the autoignition than the thermal heat-capacity effect of stable species dilution. Comprehensive kinetics calculation could estimate the effect of dilution on the ignition delays as for the blue-flame dominant regime.

Authors has shown that the ignition system of the fresh mixture injected into and heated up by the hot combustion products will present a very small activation energy for preflame reactions<sup>(3)</sup>. Ignition occurs on the contact surface of a fresh mixture jet and surrounding hot combustion products. Chemically-active species contained in the combustion gases are considered to make the initiation reaction dispensable for autoignition. This is an extreme case for the present matter of mixtures diluted by recycled products in engine cylinders. However, it implies the possibility of the recycled products taking part in the chemistry preceding the autoignition.

Green et al.<sup>(4)</sup> showed an interesting experiment in relation to an autoignition in an engine cylinder, relevant to the matter we are considering about: a three-cycle sequence; the first fired cycle initiated by a conventional spark, associated with end-gas autoignition; the second skip cycle with neither spark ignition nor autoignition; the final cycle in which the charge autoignites by compression ignition. Compression ignition occurs only on a skip cycle that follows another skip cycle.

They thought that recycled intermediates resulting from partial oxidation of the fuel carried over from the second cycle and mixed with the fresh incoming charge of the final cycle have a significant influence on the end-gas reaction. However, this result should be interpreted that the charge in the second cycle is so diluted by the recycled products of combustion as no hot ignition could be induced, and the third cycle is well scavenged due to the fact that the prior cycle is the nonflamed skip cycle. Since the normal scavenging efficiency of the engine is roughly 80% as they described, the second cycle contains 80% fresh charge and 20% recycled products of combustion. It starts out with a high initial diluent concentration that rouses no autoignition. The third cycle, well scavenged containing 96% fresh charge and 4% recycled products of combustion, is easily led to a hot ignition by a piston compression, even though the compression temperature may be much lower than the second cycle.

The results obtained in these two papers seem to indicate that the residual products of hot combustion carried over from the previous cycle and mixed with the fresh incoming fuel-air

charge have the possibility to shorten the ignition delay, but scarcely show remarkable accelerating effects on the chemistry preceding the autoignition under the real engine operating conditions. EGR systems would give a retarding effect rather than accelerating one.

## CONCLUDING REMARKS

In relation to the engine knock in spark ignition engines in which EGR system is armed, the effects of initial-charge dilution and chemical preconditioning of the recycled residual products of combustion on the autoignition process were examined.

As the temperature and pressure of the charge will be raised when hot recycled products are introduced into the fresh charge, the ignition delay becomes usually shorter according to the temperature and pressure dependence for the ignition reactions.

When mixture is diluted by an inert gas, such as argon or nitrogen, the cool-flame delay  $\tau_1$  is not changing, and only the blue-flame onset retards; i. e. the  $\tau_2$  is elongated, almost due to the increase of mixture heat capacity per unit mass of fuel caused by inert gas enhancement.

Carbon dioxide or water vapor dilution makes cool-flame delay  $\tau_1$  slightly longer, and the addition of water vapor results in an extreme retardation of blue flame appearance in the high temperature side of the negative temperature-coefficient regime. Carbon dioxide and water vapor show effects of the chain-branching reaction nature as well as the thermal one.

Residual products carried over by an EGR and mixed with the fresh charge give a possibility chemically-active species could be recycled and dispense with initiation reaction for autoignitions, but scarcely show effects on the chemistry preceding the autoignition under the real engine conditions.

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