Chemical Kinetic Investigations of Ignition and Combustion Phenomena in a DI Diesel Engine Fueled with Methanol*

(Ignition Characteristics of Methanol Mixture)

Jin KUSAKA**, Yasuhiro DAISHO**
and Takeshi SAITO**

A methanol-fueled direct-injection diesel engine with a glow-assisted ignition system tends to suffer from poor ignitability under low load conditions. Chemical delay phenomena associated with methanol mixture ignition were investigated to improve ignitability. The effects of the vaporization heat of liquid methanol, the surface temperature of the glow-plug, the heat created by the glow-plug and the O_2 excess ratio of methanol-air mixtures on the ignition characteristics were examined. Our numerical model considers these parameters, and a detailed chemical kinetic scheme, including 39 chemical species and 157 elementary reactions, was used to predict the delay in methanol mixture ignition.

Key Words: Chemical Reaction, Alternative Energy, Ignition, Diesel Engine, Methanol

1. Introduction

When methanol, which is considered to be a clean alternative fuel, is used for diesel engines, an assisted ignition system is required due to its low cetane number and poor ignitability. There are some disadvantages including in using a glow-plug for ignition assistance, poor ignitability and slow flame propagation under low load conditions, which cause low thermal efficiency and high unburned methanol and formaldehyde emissions. This is because the glow-plug surface temperature decreases markedly with decrease in gas temperature and the methanol mixture concentration becomes so low that ignitability deteriorates under low load conditions.

In this work, first, pressure data was obtained from engine tests using a 3.6-liter direct-injection diesel engine with a compression ratio of 17.5 : 1

which had been modified for methanol fuel. Then, for the specific purpose of determining design concepts for reliable ignition, the effects of the methanol mixture concentration and the glow-plug surface temperature on the ignition characteristics of the mixture were investigated by a numerical simulation model based on the pressure diagram obtained from experiments in which detailed chemical schemes⁽¹⁾ were taken into account.

2. Analytical Procedure

2.1 Modeling of evaporation and ignition processes

Figure 1 shows the combustion pressure and fuel injection rate obtained from the engine experiment, and the calculated mass burned fraction, burning rate and mean gas temperature estimated from the gas state equation in the cylinder. Here, the mass burned fraction and burning rate were calculated based on the energy conservation equation including heat loss through the combustion chamber wall. The engine test was carried out with a 41 mg/cyc·cyl fueling, which was equivalent to a 1/4 load, where the engine speed was kept at 1 000 rpm. In the experiments, the

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** Department of Mechanical Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169, Japan

Table 1 Engine test conditions

Engine speed	rpm	1,000
Fuel injection timing	deg BTDC	18
Fuel injection duration	deg CA	13
Ignition timing	deg BTDC	7
Ignition lag	deg CA	11
	msec	1.8
Cylinder pressure at the start of the fuel injection	MPa	1.95
Mean gas temperature at the start of the fuel injection	K	737

Fig. 1 Cylinder pressure, fuel injection rate, burning rate, mass burned fraction and mean gas temperature (Engine speed: 1 000 rpm, Fueling: 41 mg/cyc)

ignition delay was defined as the period between the start of fuel injection into the cylinder and the commencement of the burning rate.

As shown in Fig. 1, 11° CA was required to ignite the methanol injected into the cylinder at 18° BTDC. At the start of injection, the cylinder pressure was 1.95 MPa and the mean gas temperature was 737 K. These conditions are listed in Table 1. Methanol injected into the cylinder mixes with the cylinder air to form a methanol-air mixture. In the mixture, it was assumed that there was a small mixture element which was ignited earlier than any other mixture because it was heated on the surface of the glow-plug. Then, the flame developed from the ignited element. In the calculation, the ignition process was analyzed numerically by application of the chemical kinetics and dynamics for the phenomena occurring in the element which was ignited first. In the calculation, taking 39 chemical species and 157 elementary reactions into consideration, the following assumptions were made to simplify the model and determine the ignition characteristics.

(i) Liquid methanol injected into the cylinder is

Fig. 2 Model of case 1

Fig. 3 Model of case 2

atomized into small droplets. The representative droplet diameter is 30 μm based on the measurement described in a previous work⁽²⁾.

(ii) The oxygen excess ratio of the methanol-air mixture to be ignited, λ , ranges from 0.4 to 1.6 since the mixture concentration is heterogeneous. The value of λ is kept constant during the ignition delay since the delay is sufficiently short and for simplicity.

(iii) Liquid methanol injected into the cylinder is evaporated instantaneously. In other words, the evaporation time is zero.

(iv) In the mixture element under consideration, no mixing or heat transfer with the surrounding gas occurs.

(v) As for the heat energy supplied to the mixture element from the glow-plug, two cases were assumed. For case 1 as shown in Fig. 2, the mixture collides with the surface of the glow-plug and the mixture temperature becomes equal to the glow-plug surface temperature because the glow plug tip has a much larger heat capacity than the element. On the other hand, in case 2, heat energy is supplied to the element from the surface of the glow-plug due to forced convective heat transfer as illustrated in Fig. 3. In this case, radiative heat transfer is not taken into account due to its negligible effect. Elementary reactions concerned with methanol decomposition are listed in Table 2. In the calculation, O_2 , N_2 , CO_2 and H_2O are used for initial species because the radicals which may be included in the residual gas are few.

Table 2 Elementary reactions concerned with $\text{CH}_3\text{OH}^{(1)}$

No.	Reactions	$k = A \cdot T^n \cdot \exp(-E/RT)$		
		A	n	E
22.	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_2\text{OH} + \text{CH}_4$	2.0×10^{11}	0.0	40719.
23.	$\text{CH}_3\text{OH} + \text{O}_2 = \text{CH}_2\text{OH} + \text{HO}_2$	4.0×10^{13}	0.0	211489.5
24.	$\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$	6.3×10^{12}	0.0	80607.2
25.	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$	3.2×10^{13}	0.0	29084.9
26.	$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$	1.0×10^{13}	0.0	19561.6
27.	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$	1.0×10^{13}	0.0	7046.8
28.	$\text{CH}_3\text{OH} + \text{M} = \text{CH}_3 + \text{OH} + \text{M}$	3.2×10^{18}	0.0	332400.1
29.	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_3 + \text{H}_2\text{O}$	2.5×10^{13}	0.0	22021.3

2.2 Calculation procedure

Some of the methanol injected into the cylinder is assumed to mix with the compressed air at a given oxygen excess ratio, λ , to form a methanol-air mixture of which the temperature is represented as T_{gas} . The enthalpy of the fuel and the air before and after mixing are written as H_1 and H_2 respectively, where

$$H_1 = (N_i \cdot h_i(T_a)) + N_f \cdot h_{lf}(T_{lf}) \quad (1)$$

and

$$H_2 = (N_i \cdot h_i(T_{\text{gas}})) + N_f \cdot h_{gf}(T_{\text{gas}}) \quad (2)$$

where N : Mole of species, H : Enthalpy, h : specific enthalpy, and T : temperature, and subscripts i : N_2 , O_2 , CO_2 , H_2O , a : air, f : fuel, l : liquid, and g : gas. The value of each N can be determined by the given value of λ . The temperature of injected liquid methanol, T_{lf} , is assumed to be 353 K (80°C.) Thus, its specific enthalpy is:

$$h_{gf} = h_{lf} + r_f \quad (3)$$

where r_f : is the evaporation heat of methanol. By assuming that the evaporation and mixing occur at a constant pressure according to assumption (iii), the enthalpy before mixing is conserved after mixing.

Therefore,

$$H_1 = H_2 \quad (4)$$

The value of T_{gas} is obtained from Eqs. (1), (2), (3) and (4) using an iterative procedure. The oxidation process is assumed to occur when the temperature of the mixture increases to T_{ign} as a result of heating by the glow-plug. Here, it is noted that T_{ign} , which is the initial value of the kinetic calculation, is independent of λ in case 1 because T_{ign} is assumed to be equal to the surface temperature, T_{glow} , although the value of T_{gas} is dependent on the oxygen excess ratio, λ . On the other hand, in case 2, the heat, Q , transferred between the mixture and the glow-plug was estimated as follows according to assumption (v).

$$Q = A \cdot \alpha \cdot \Delta t \cdot (T_{\text{glow}} - T_{\text{gas}}) \quad (5)$$

where symbol A denotes the surface area of the mixture, α the heat transfer coefficient between the mixture and the glow-plug and Δt the duration of heat transfer, respectively. The surface area, A , is obtained by assuming that the mixture which consists

Fig. 4 Definition of the distance between the center of the cavity and the glow-plug, r

Fig. 5 A model of the element passing the half side of the glow-plug

of a methanol droplet whose diameter is $30 \mu\text{m}$ and the air quantified by a given λ has a globular form. Therefore, the sum of mole numbers in the element and its volume increases in proportion to the oxygen excess ratio, λ . Furthermore, the diameter of the element is proportional to the cubic root of λ , and the area is proportional to the cubic root of λ squared. Values of α and Δt can be estimated as follows.

The air in the cylinder was assumed to rotate as a solid body at angular velocity, ω rad/s, or engine speed, N_e rpm, around the center of the vortex. As illustrated in Fig. 4, the mean velocity at the glow-plug, u , is given from swirl ratio, R_s , and distance, r , between the center of the vortex which was assumed to be the same as that of the cavity and the glow-plug.

$$u = r \cdot \omega \cdot R_s \quad (6)$$

This element passes half of the glow-plug surface whose diameter is d_0 as illustrated in Fig. 5. Thus, heat is supplied to the element during the time Δt expressed as:

$$\Delta t = 0.5 \pi d_0 / u = 0.5 \pi d_0 / (r \cdot \omega \cdot R_s) \quad (7)$$

Woschni's formula⁽³⁾ can be applied for estimation of the heat transfer coefficient between the element and the glow-plug surface at as high a pressure and temperature as in the combustion chamber of the diesel engine. Thus, the heat transfer coefficient is:

$$\alpha = 12.3 \cdot d_0^{-0.214} \cdot (C_m \cdot P)^{0.786} \cdot T_{gas}^{-0.525} \\ = 12.3 \cdot d_0^{-0.214} \cdot \{(2 \cdot S \cdot N_e / 60) \cdot P\}^{0.786} \cdot T_{gas}^{-0.525} \quad (8)$$

where C_m : mean velocity of the piston m/s, S : Stroke m, P : cylinder pressure kPa.

The temperature T_{ign} is defined as the mixture temperature after the heating it.

Thus,

$$H_3 = (N_i \cdot h_i(T_{ign})) + N_f \cdot h_{gf}(T_{ign}) \quad (9)$$

and

$$H_2 + Q = H_3 \quad (10)$$

As indicated in Eq. (7), when the engine is operated at 1 000 rpm, Δt is equal to 6.4 deg CA. For this duration, α and the element temperature change as a function of crank angle. Thus, in the heating process, T_{ign} , which is the element temperature after the heating process, is calculated step by step by taking both the effect of the convective heat transfer based on Eq. (10) and that of the increment of the temperature due to the raised cylinder pressure into consideration.

The kinetic calculation in the element is started after the heating process. CHEMKIN II⁽⁴⁾ and SENKIN⁽⁵⁾ were applied in the kinetic calculation. These codes have been developed by Sandia National Laboratories as general-purpose programs for analysis of gas phase chemical kinetics. CHEMKIN consists of two major software components: an Interpreter and a Gas-Phase Subroutine Library. SENKIN computes the time evolution of a homogeneous reacting gas mixture in a closed system. The model accounts for finite-rate elementary chemical reactions, and also performs kinetics sensitive analysis with respect to the reaction rates. SENKIN runs in conjunction with the CHEMKIN package. The time step was chosen automatically to minimize the CPU time by means of the Gear method⁽⁶⁾. The time step at the start of methanol oxidation is equal to about 0.2 μ s in the present calculation. The computer used was a HP 735 and the typical CPU time was about 150 sec per condition.

3. Results and Discussion

3.1 Effects of O_2 excess ratio on the mixture temperature

Figure 6 shows the influence of the O_2 excess ratio on the methanol mixture temperature compared to the diesel fuel mixture (JIS second class). Evidently, the temperature of the methanol mixture formed after

Table 3 Comparison of properties for each fuel

	Methanol	Diesel
Lower heat energy H_u kJ/mol	675.6	9387.
Heat of evaporation r_f kJ/mol	37.5	58.9
r_f / H_u	0.0555	0.00627

Fig. 6 Element temperature after mixing fuel droplets and air

Fig. 7 History of each chemical species and temperature profile during the oxidation process ($\lambda=1.0$, $T_{glow}=1123$ K)

evaporation is more than 100 K lower than that of the diesel fuel mixture. The temperature difference between methanol and diesel fuel mixtures tends to increase with the decrease in O_2 excess ratio. This can be explained by the fact that the value of evaporation heat is greater than that of diesel fuel as shown in Table 3. This tendency suggests that the cylinder temperature should be higher in methanol engines than in conventional diesel engines. Increasing the compression ratio is useful for this purpose.

3.2 Effects of initial temperature on ignition delay phenomena (Case 1)

Figure 7 shows the history of each chemical species and temperature profile during the oxidation process in the case of $T_{glow}=1173$ K and $\lambda=1.0$. From this figure, in this calculation, the ignition timing is defined as that when the mixture temperature becomes 400 K higher than the initial temperature for the following reasons.

(1) The methanol oxidation process is completed during a very short period of time, that is a few μ sec as illustrated in Fig. 7.

(2) The increase in temperature of any unburned mixtures compressed adiabatically by the cylinder pressure after ignition does not exceed 400 K.

Figure 8 indicates the influence of the O_2 excess ratio and glow-plug temperature on ignition delay for case 1. It is clear from this figure that at a constant initial temperature for each λ , the ignition delay tends to be reduced with a decrease in O_2 excess ratio. In the case of real methanol spray combustion, however, the initial mixture temperature changes due to O_2 excess ratio. Here, it is understood as a basic characteristic of methanol mixtures that the ignition delay is reduced with a decreased oxygen excess ratio, λ , at a constant initial temperature.

3.3 Effects of O_2 excess ratio and glow temperature on ignition delay phenomena (Case 2)

The effects of the evaporation heat of methanol and the convective heat transfer from the glow-plug on ignition delay were investigated. Figure 9 shows the calculated mixture temperatures as a function of O_2 excess ratio at glow-plug temperatures ranging from 873 K to 1123 K. Element temperature profiles

during the heating process on the surface of the glow-plug are also indicated in Fig. 10. From this figure, the rate of increase in element temperature at the early stage of the heating process tends to increase with decreasing oxygen excess ratio, λ , because the temperature difference between the element and the surface of the glow-plug increases with the decrease in λ . After that, however, the rate of increase in element temperature later in the heating process tends to decrease because the temperature difference between the element and the surface of the glow-plug decreases due to the increased element temperature. As a result, T_{ign} is as shown in Fig. 9. Figure. 11 shows the effect of glow-plug temperature and oxygen excess ratio on the ignition delay. Ignition cannot occur at less than 1073 K. This result suggests that the ignition misfires thus decreasing the glow-plug surface temperature to below 1073 K. As indicated in Fig. 8, at a constant initial temperature, ignition delay was reduced with the decrease in O_2 excess ratio. However, taking the effect of the heat of the evaporation and the convective heat transfer into account, the

Fig. 8 Comparison of chemical ignition delay for each glow-plug surface temperature in case 1

Fig. 9 Effects of the glow-plug surface temperature after the heating

Fig. 10 Element temperature profile during the heating process on the surface of the glow-plug

Fig. 11 Comparison of chemical ignition delay for each glow-plug surface temperature in case 2

oxygen excess ratios at which ignition delay has the minimum value ranges from 0.6 to 0.8. With richer mixtures whose λ is less than 0.6, the basic characteristic of the increased reaction rate as shown in Fig. 8 is cancelled and the ignition delay tends to be longer due to the decreased element temperature, which is attributed to the heat of evaporation. With a mixture whose λ is more than 0.8, ignition delay also becomes longer with increased λ because of the lean mixture, although the mixture temperature tends to increase slightly with increased λ . Considering the effect of the surface temperature of the glow-plug on ignition delay, it is known that the glow-plug temperature increases, the effect of the oxygen excess ratio on the ignition delay becomes minor and the ignition delay becomes shorter.

3.4 Comparison of ignition delay for the calculated and measured

The following calculation was conducted to add physical delay to the chemical one calculated in the previous section because the ignition delay in actual engines was the sum of the physical and chemical processes. The duration required for injected methanol to reach the glow-plug can be calculated by Hiroyasu's formula⁽⁷⁾:

$$t = r / 0.39(2\Delta p / \rho_0) - 0.5 = 3.29 \times 10^{-4} \text{ s} \\ = 2.97 \text{ deg} \cdot \text{CA} \quad (11)$$

Here, $r = 0.026 \text{ m}$, $\rho_0 = 787 \text{ kg/m}^3$, $\Delta p = 16.5 \text{ MPa}$ (Needle opening pressure: 18.5 MPa)

As defined in Eq.(2), Δt , which is the duration required for the element to pass half of the glow-plug surface as illustrated in Fig. 5, can be written by:

$$\Delta t = 1.068 \times 10^{-3} \text{ s} = 6.4 \text{ deg} \cdot \text{CA} \quad (12)$$

As the physical delay can be considered as the sum of Eqs. (11) and (12), the ignition delay is calculated by adding the chemical delay calculated in the previous section to these physical delays. In our engine experiments, the glow-plug temperature was adjusted to 1 173, 1 223 and 1 273 K and fuel injection rate and the time taken by injection were kept constant. For each glow-plug temperature, the ignition lag was estimated as the period between the start of ignition and that of the burning rate. Thereby, the ignition lag in experiments can be considered to be dependent only on the chemical process because the physical processes were the same for each glow-plug temperature. The results of ignition lag in the experiments are listed in Table 4. Figure 12 shows a comparison between the calculated and measured ignition delay. In this figure, the horizontal and vertical axes denote the reciprocal temperature and logarithmic ignition delay, respectively, based on Arrhenius form. Here, it is noted that the compression ratio and scavenging volume of the glow-assisted DI engine used in this experiment differs

slightly from the engine discussed in the previous section. In the experiment, the surface temperature were considered to be lower than the inner temperature which was measured by the thermocouple installed in the glow-tip. Thus, the surface temperatures of engine tests in Fig. 12 were plotted to be 100 K lower than the measured inner ones, because in a previous work⁽⁸⁾, which described the heat transfer calculation of the glow-plug tip at atmospheric pressure, the surface temperature was about 100 K lower than the inner one. As shown in Fig. 12, there are differences between the results of $\lambda = 0.4, 1.4$ and those of 0.8, 1.0, because oxygen excess ratios of 0.4/1.4 were so rich/lean that chemical ignition delay became longer as shown in Fig. 11. The measured ignition delay is shorter than the calculated one because the real fuel droplet diameter may be smaller than the assumed diameter which is equal to 30 μm . As shown in Fig. 13, however, the calculated activated energy of the overall reaction obtained from the

Table 4 Measured ignition delay

Glow-plug inner temperature K	Ignition delay deg CA (ms)
1273	7 (1.17)
1223	8 (1.33)
1173	9 (1.50)

Fig. 12 Comparison between the calculated and measured ignition delay

Fig. 13 Comparison of activated energy for overall reaction between the calculated and measured value

gradient in the figure agreed well with the measured one. Moreover, it is suggested that such a mixture, as its oxygen excess ratio is about 0.8, can be ignited easily because the activated energy is minimum at that oxygen excess ratio.

Conclusions

A chemical kinetics model has been developed in order to use detailed elementary reactions for improvement of ignitability in a DI methanol engine with glow-plug ignition assistance. Conclusions are drawn from the results as follows:

(1) The temperature of the compressed air in the cylinder of methanol engines remains higher than that in normal diesel engines because the methanol mixture temperature is 100 K lower than that of diesel.

(2) If the initial temperature is the same for each oxygen excess ratio, the ignition delay becomes shorter for a richer mixture.

(3) Ignition can be improved by forming slightly rich mixtures around the glow-plug, because ignition time is minimum at $\lambda=0.85$, taking convective heat transfer into account.

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