Spray Process and Fuel Pyrolysis in the Initial Stage of Diesel Combustion

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To elucidate the spray processes in a diesel engine, with special regard to the gasification and thermal decomposition of the injected fuel at an elevated air temperature, a study was carried out on a simulated two-cycle engine using a fast gas-sampling technique. The results obtained suggest that already in the period before an appreciable pressure rise in the cylinder is observed, in other words, even during the so-called ignition delay period, the injected fuel quickly gasifies and decomposes, forming a large quantity of split hydrocarbons. This phenomenon may be partly attributed to the fact that the hot burnt gas formed in the vicinity of the spray jet is sucked into the spray core, thus promoting the gasification and thermal decomposition. It is also suggested that a quantity of decomposed products which undergo turbulent mixing will accumulate in the downstream of the fuel jet.

Key Words: Internal Combustion Engine, Diesel Combustion, Spray, Ignition Delay, Pyrolysis, Hydrocarbons, Mixtures Formation, Gas Sampling.

1. Introduction

Atomization, evaporation, and mixing of fuel injected into the cylinder play an important role in the diesel combustion process as well as in the formation of air-pollutants. The properties of fuel spray have accordingly been the subject of much research(1)-(2). However, behavior of the spray at high temperatures close to those in actual operating engines has not been made clear in detail, because most experimental studies have been carried out at a relatively low temperature.

In the previous paper(5), the present authors obtained the following results from the study carried out experimentally using the fast gas-sampling method: (1) thermal decomposition of spray fuel depends on air temperature, (2) the soluble organic fraction (SOF) in the exhaust particulates is formed during impingement of raw fuel on the chamber walls at low temperature, and (3) solid carbon in particulates is produced at high temperatures. In the present paper, behavior of the the fuel spray at an elevated temperature is studied in detail by means of a similar sampling method, paying special attention to thermal cracking of the fuel during ignition delay and just after the start of combustion.

2. Experimental

To sample a gas in a developing spray in a combustion chamber with a fast gas-sampling valve, a loop-scavenged two-cycle engine having a bore of 80 mm, a stroke of 90 mm, and a compression ratio of 14.7:1 is employed. As is shown in Fig. 1, the combustion space is grooved on the piston head. Inside the cylinder head is a demountable cover which allows the gas sampling valve to be installed at different positions. This model engine simulates the combustion process of any of eight sprays in a quiescent shallow-dished chamber of an engine having a 160 mm bore and allows observation of the behavior of a single spray. A specially distilled fuel consisting of 23% dodecane, 54% tridecane, and 23% tetradecane in mole fraction is used to make raw fuel and cracked products discernible during the chemical analysis of the sample. Injection is per-
formed by a single-hole nozzle with a 0.25 mm diameter at a preset opening pressure of 23.5 MPa, using an ordinary Bosch PB18908 jerk pump with a damping retraction valve to ensure normal injection. The injection timing is set at 15° BTDC and detected by an eddy-current displacement sensor. All tests are made at a fixed engine speed of 1,000 rpm at a constant fuel delivery of 13.5 mg (overall equivalence ratio being 0.60). In order to attain a high purity of air charge in the cylinder, double-scavenging is employed, i.e., scavenging is performed twice for each firing. Scavenging air temperature is kept at 80° C by a preheater in the inlet port, to establish the normal ignition delay encountered in an actual engine.

3. Development of Spray before Ignition

Prior to the gas sampling study, high-speed photographs of the spray injected into air, which was under high pressure and temperature were taken using a HITACHI 16 HM camera at a rate of 5,000 frames per second. To see the effect of air temperature on the spray, the spray

under the above condition, Case A, is first compared with sprays under two other sets of conditions. In one, the spray was injected into nitrogen gas as charge in place of normal air, Case B, and the in another, the spray injected into a very cold nitrogen to keep the temperature as low as 400 K at the compression end which was realised by using a liquid nitrogen, Case C.

Figure 2 compares the appearance of these three sprays at 7.5° BTDC, 1.25 ms after the beginning of injection. The injection timing is 15° BTDC and the timing of the pictures corresponds to the onset of pressure rise (see 1 in Figure 3) in the case of spray A. It should be noted that the visible spray length is dependent on the presence of oxygen.

Figure 3 shows the changes of visible spray length L with time t and crank angle 0 after the start of injection obtained from the photographs. Figure 3 also indicates pressure diagrams obtained in Cases A and B. As the graph shows, pressure being to rise at 7.8° BTDC in Case A (see 1 in the figure), that is, 1.2 ms after the beginning of injection. A luminous flame begins at 5.4° BTDC (see 2 in the figure), 1.6 ms after the onset of injection, indicating that there is a considerable delay between real pressure rise and the occurrence of luminous flame. The graph also shows that the distance of the spray tip from the nozzle in the case of A is much shorter and the width of the spray is smaller in Case A than in Cases B and C. The visible spray length L does not exceed 39 mm, indicating that most fuel is converted into vapor at this position. On the contrary, in Case B, when air is

Fig. 1 Experimental cylinder head and position

Fig. 2 Comparisons of sprays in different gases

Fig. 3 Comparison of visible tip length of spray in different gases
replaced by nitrogen, the spray width is thicker and the visible length is larger than in Case A, even though the levels of temperature and pressure are nearly the same. This suggests that in Case A the disappearance of fuel droplets around the spray is promoted by the presence of oxygen. Possibly, the droplets inside the spray make contact with hot sucked gases and are quickly heated, since exothermic oxidation reactions in the vicinity of the spray proceed even during the ignition delay period. Furthermore, the shorter spray in the case of A seems to result from the fact that the droplets of the spray core are heated by the hot gases entrained into the spray, and converted to vapor more quickly than those in Case B. In Case C, when the scavange gas temperature is lowered to $-130^\circ$ C, the spray length agrees closely with that predicted by Nakuri's momentum theory until the spray impinges on the combustion chamber wall. This is because no chemical reaction takes place at a compression temperature as low as 350 K which is much lower than 855 K in Cases A and B. In other words, the difference between sprays B and C clearly reflects the difference in temperature level.

The above observations may lead to the following suggestions:
(1) To simplify experimental conditions, Solvent No. 0 is used as a fuel. The critical pressure and temperature of tri-decane, the main ingredients of this fuel, are 3.68 MPa and 676 K, respectively, while cylinder pressure and temperature at the compression end are 3.47 MPa and 855 K, respectively, both appreciably higher than the critical pressure and temperature. Thus the droplet temperature may readily be elevated to the critical level. As soon as liquid fuel contacts the hot gas and is heated, the fuel droplets may exceed the critical temperature to be broken up immediately forming a dense gas.
(2) Even during the ignition delay period, it is likely that a combustible mixture is found and exothermic reactions proceed owing to a high temperature and a high oxygen concentration in the vicinity of the spray. Therefore, the droplets heated early in the vicinity may exceed the critical temperature, causing the spray to become thin due to gasification. Moreover, it is likely that the droplets in the spray core are quickly heated on account of hot gases entrained into the spray and reach the critical condition. Accordingly at a certain distance the spray becomes invisible.
(3) As suggested in (2), an amount of heat is released even during the ignition delay period. This obscures the definition of ignition. As long as ignition start is equated with pressure rise as is usually done, we must assume that such a heat release before ignition is counterbalanced by heat absorption due to endothermic reactions, such as heat consumed in raising the droplet temperature. Therefore the whole process may go on adiabatically during the ignition delay. Furthermore, thermal decomposition of the fuel is also endothermic, and this may be one of the factors which cancel heat release, as will be explained later.

Among these inferences, the possibility of fuel droplets reaching a critical condition has been pointed out by Hirobayas et al. It has also been pointed out that the ignition delay of perfectly mixed fuel vapor and air is shorter than that of a heterogeneous diesel spray at high temperatures. Possibly, this supports the item (3) stating the possibility of oxidation reactions during the ignition delay.

In this study, a specially-distilled fuel containing a high percentage of tri-decane is used. Nevertheless a similar result is expected in the case of ordinary diesel fuels.

4. Thermal Decomposition of Fuel and Combustion

4.1 Method of gas sampling and analysis
To further clarify reactions taking place in the spray during the ignition delay, a fast gas-sampling method developed in the previous study is applied. Particular attention is paid to confirming the occurrence of thermal decomposition and local heat release. Since the method of gas-sampling and analysis is essentially the same as that described elsewhere, only the main points and differences from the previous study will be described here. The sampling valve employed is an electromagnetic needle type (Tsuchia Sokken Co.). The sampling position is represented by the distance from the nozzle tip X (mm), the angle from the spray centerline o, and the depth from the head surface Z (mm), as may be seen from Fig. 4. A volume of 3 ml in atmosphere is sampled per fired cycle. The effective sampling duration is invariably 5 degrees in crank angle throughout.

The sampled gas is analyzed for inorganic gases such as O$_2$, CO$_2$, CO, H$_2$ and NO, for lower hydrocarbons having carbon numbers of one through five, and for middle and higher hydrocarbons of carbon numbers greater than five. To prevent condensing of the substances having carbon numbers greater than five, a stainless-steel pipe from the sampling valve to the gaschromatograph is electrically heated to 250$^\circ$ C. Fractions of these substances are analyzed with a flame
ionisation detector (FID) using a programmed heater (Yanagimoto, HSO-1).

In diesel combustion, products of activated species such as aldehydes and of other heavier hydrocarbons including carbonaceous matter are normal. Hence all hydrocarbons up to fuel components are grossly measured using the heated FID with a glass bead column at 250°C equal to the boiling point of the fuel. Moreover all hydrocarbons higher than the fuel are estimated from comparison of data obtained with and without after-oxidation, using an additional by-pass circuit heated directly by electricity. Similarly, the local fuel-air equivalence ratio is determined from the same data.

4.2 Behavior of Fuel during Ignition Delay

The behavior of the injected fuel and the process of thermal decomposition during ignition delay period are first investigated, and then the possibility of exothermic reactions is estimated from the obtained data. The initial pressure rise by ignition occurs at around 7.6° BTD as described earlier. To extract the sample well before ignition, sampling is made at 10° BTD on the centerline of the spray considering the fact that the effective sampling duration is 5 degrees CA. In Fig. 5, some examples of gas chromatograms obtained at x=19 mm, 39 mm and 53 mm are reproduced. The left side of each chromatogram shows the result of the activated alumina-squalene column, and the right side the result of a 3% Silicone OV-101 on the Celite 545 column. The sensitivity of the latter is set at ten times the former. For hydrocarbons having carbon numbers higher than five, only the positions of saturated normal chain hydrocarbons are indicated.

At x=19 mm, the position at which many fuel droplets can be found as shown in Fig. 3, a lot of raw fuel C_{12}H_{26}, C_{13}H_{28} and C_{14}H_{30} may be seen. In addition, not only a bit of hydrocarbons of middle boiling point ranging from C_{2} to C_{5}, but also an amount of lower hydrocarbons exist in this position. Probably this indicates that pyrolysis of fuel begins in the position near the nozzle. It may be surmised that cracking mainly takes place in the hot region in the vicinity of the spray. At x=59 mm, liquid fuel no longer exists, but a lot of raw fuel is seen. The concentrations of middle hydrocarbons are low at this position, which suggests that such hydrocarbons are converted into fractions of lower boiling point of carbon numbers less than five. From this result, it may be known that pyrolysis of the fuel leading to gasification proceeds quite quickly. At the position x=53 mm near the wall which the gas jet may hit, raw fuel almost completely disappears, being converted into either low hydrocarbons or inorganic substances.

Figure 6 shows mass fractions of components estimated from the heated FID results with a glass bead column, the result of quantitative analysis of high
boiling point hydrocarbons using a by-pass circuit for after-oxidation (7), and those of an inorganic analysis, under the same condition in Fig. 5. The abscissa is so taken such that constituents closer to the fuel may be on the right side while inorganic components such as N₂, O₂ and CO₂ may be near the left side. From this figure, it is noted that at X=19 mm raw fuel exists and thermal decomposed hydrocarbons more than C₅ are simultaneously created. On the contrary, at X=39 mm there are hydrocarbons having lower boiling points are greater in quantity due to thermal cracking. At this position there are more unsaturated hydrocarbons than saturated ones. Judging from the fact that oxidized products such as CO and CO₂ exist at the same time, and that the C₅H₂ concentration is high, we can guess that heat is released locally leading to high local temperatures. Furthermore, in the downstream of the spray at X=53 mm, the amount of raw fuel is greatly decreased and the concentrations of CO, CO₂ and H₂O are high, possibly because reactions to combustion products progress. However, the ratio of N₂ to O₂ remains about the same as in normal air, showing that little oxygen is consumed. It appears from these results that regular exothermic reactions do not yet occur and that local oxidation and thermal decomposition proceed at a rate determined by turbulence mixing.

The presence of C₂H₂ at X=19 mm near the nozzle suggests that the heat release is taking place in the vicinity of the spray, as shown earlier. To further clarify this, the concentrations of some species are measured at X=25 mm. Figure 7 shows the result. The abscissa and ordinate denote, respectively the angle from the spray centerline and the dry-base mole fractions of species excluding hydrocarbons of carbon numbers more than C₅. This measurement of dry-base concentrations are not very accurate, but it may at least be suggested that CO₂ concentration is high in the sheath of the spray and a high CO concentration exists inside the CO₂ zone. This region may be at a high temperature because C₂H₂ coexists with CO₂ at a high concentration. Uyeshara (8) who predicted equilibrium product concentrations of propane-air mixture indicates that C₂H₂ is produced only above 1,000 K and quickly increases with temperature. From this result, it may be guessed that the temperature of the region under consideration is not lower than 1,000 K even though the influence of pressure, concentration of oxygen, and constituents of the fuel are taken into account. Accordingly, heat release is likely to take place around the spray, as mentioned in the previous chapter.

It is thus suggested that fuel droplets are heated quickly, changed into the gas phase, and thermally decomposed into split hydrocarbons around the spray, forming a gas jet that contains a lot of unsaturated hydrocarbons. Furthermore, as a result of thermal decomposition and other reactions, various components are produced and accumulated in the region beyond the point where the fuel droplets disappear due to local oxidation in the outer layer of the spray. The hot gases produced by heat release are entrained into the spray, thereby accelerating heating, evaporating, and cracking. Probably because the heat release is not very large during the ignition delay period and counterbalances the latent heat and the decomposition heat, overall heat liberation is not appreciable. This requires further examination, and this matter is important when considering ignition of a spray.

4.3 Transition to main combustion

Changes in the composition of the spray until the start of combustion were investigated. Under the present test conditions, the cylinder pressure starts to rise due to combustion at 7.8° BTDC and a luminous flame nucleus occurs at 5.4° BTDC, as was mentioned above. High-speed photographs and pressure records show that the luminous flame then spreads over the spray and the pressure rises quickly to reach a peak at 5° BTDC.

Figure 8 shows gaseous components including hydrocarbons having carbon numbers less than C₆ in mole fraction on a dry basis at each position on the centerline of the spray during combustion. As shown in the figure, at the position near the wall, X=53 mm, components such as C₂H₆ and C₃H₆ disappear unlike those in the upper stream, and inorganic fractions such
as CO and H₂ accumulate in their place. This is because a lot of fuel has been gasified and pyrolysis has already begun during ignition delay. That both heat release and pyrolysis proceed rapidly can be suggested from the result of mass fraction in Fig. 8. Thereafter, CO₂ is quickly consumed soon after ignition, while concentrations of CO, CO₂, C₂H₂ and CH₄ become higher. The concentrations of cracked products reach their peaks around top dead center. Concentrations of C₂H₂ and CH₄ are both high at the same time, suggesting that fuel-rich parts and high temperature parts coexist in this stage. According to chemical equilibrium calculations, C₂H₂ is almost independent of the fuel concentration and increases with temperature, so that C₂H₂ concentration is an appropriate indicator of temperature. At this position, the peak concentration of C₂H₂ is 1.8 % and hence local temperature might be higher than 2500 K. On the other hand, CH₄ increases with a decrease in temperature and with equivalence ratio φ. For instance, at φ=2.2, CH₄ reaches its maximum of 2 % at 800 K. Indeed chemical equilibrium cannot be expected even locally, but we can still infer that rich fuel zones and high temperature zones coexist in a heterogeneous state. The fuel containing eddies and the hot eddies containing fresh air are stirred up by strong turbulence due to a shear layer of the spray. Thus a high temperature is produced at the interface between these eddies. For this reason, oxygen may be detected although it is as low as 0.5 %. NO may be formed at the same position. Furthermore, it may be estimated that solid carbon is formed because the fuel is exposed to local high temperatures.

In Fig. 9, mole fractions of main components are mapped on the distance X and the position angle ϑ plane for several crank angle degrees. The position angle drawn in each map is twice the actual one. It is seen from the figure that at 10° BTDC, contours of C₂H₂, CH₄, and CO concentrations taper off at the tip of the spray, while that of C₂H₂ widens toward the spray tip and, at 5° BTDC, spreads out along the wall of the combustion chamber.

Figure 10 shows the measured results of local fuel-air equivalence ratio against angle ϑ, for two different positions of X=25 mm and 53 mm. At X=25 mm, ϑ first increases with crank angle, reaches a peak on the spray axis, and then decreases quickly with ϑ. This quick decrease may be because of air entrainment into the spray core after injection. At X=53 mm, ϑ is high at a larger ϑ because the fuel jet is deflected to flow along the wall. The peak equivalence ratio amounts to 2.2, which is followed by a gradual decrease, partly because of air entrainment into the fuel jet and partly because of turbulent mixing engulfing fresh surrounding air. Figure 11 is a map of oxygen mole fraction near the chamber wall on the ϑ versus X plane, showing the occurrence of periodic fluctuations of O₂ concentration in the ϑ direction at later crank angles. The period is between 4° and 6° in ϑ that might be the same order with the fuel jet.
width. This may lead to a state that eddies having sizes almost equal to the jet width are distributed near the wall, and promote engulfment of fresh air from the outside of the wall jet. This may be believed to be one of the factors causing gradually decreasing of $\phi$ with crank angle in the main burning period.

5. Conclusions

Experimental studies focusing on thermal decomposition and oxidations in the earlier stages of diesel combustion are made with simulated quiescent direct-injection diesel engine, using high-speed photography and a fast in-cylinder gas-sampling technique. The obtained results might be summarized as follows:

(1) Fuel injected as a spray in sufficiently hot compressed air undergoes rapid evaporation, thermal decomposition, and exothermic reaction, due to the contact with the hot surrounding air near the injection nozzle. In the spray core, a large quantity of cracked intermediates having carbon numbers greater than five can be formed.

(2) During the ignition delay period, many unsaturated split hydrocarbons are produced, some of which are converted into carbon monoxide and hydrocarbons due to oxidation. Local heat release due to oxidation is counterbalanced by endothermic reactions such as gasification of fuel and thermal decomposition, and hence no appreciable pressure rise takes place during the ignition delay.

(3) In the outer region of the spray, heat release can take place even before any detectable pressure rise. The hot gas thus formed is entrained in the spray and promotes gasification and thermal decomposition of fuel in the spray core region. At a certain length, the spray becomes close to a gaseous jet containing a lot of fuel vapor and unsaturated hydrocarbons.

(4) A fuel-rich mixture formed in the upper stream is conveyed together with the entrained air to the side wall of the chamber, where a zone of non-uniform concentration is formed and turbulent mixing proceeds.

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