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Ignition of Premixed *n*-heptane within Air by a Low Speed Motoring Compression*

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In this paper correlations of the ignition starting gas law temperature and molecular concentration instead of a critical compression ratio were obtained under the conditions; premixed *n*-heptane and air, equivalence ratio (*S*): 0.5~3, mean piston speed: 1 m/sec, without residuals, lubricant: molybdenum-disulphide. The pressure was so high that the reaction was automatically led to a hot flame after τ_1 regime. Thrice stoichiometric charge also actively burnt consuming oxygen as well as at a stoichiometry, nevertheless pressure rise rate was less than that. Cool flame starting temperatures, ignition triggers, were in a narrow range of 400~430°C over *S*=0.5~3. Shapes of indicator diagram are two-stage ignition at *S*=0.5, single stage ignition at *S*=2, 3. At *S*=1, two-stage ignition obviously at the molecular concentration of 0.21 kmol/m³, and at 0.43 kmol/m³ two-stage but similar to single stage ignition.

1. Introduction

Concerning the influence of a mixture ratio on the ignition of hydrocarbons, for example, the research of Anagnostou⁽¹⁾ or Salooja⁽²⁾ strongly stresses the good ignitability of rich mixtures, but in their experiments pressures are low. In the fundamental studies^{(3)~(8)} for the internal combustion engine, the ranges of mixture strength are narrow, namely few experiments for rich side mixture beyond twice stoichiometry have been realized. And also the critical compression ratio as a scale of ignitability was used. In the practical use this representation is effective, nevertheless from the standpoint of combustion phenomenon the temperature and pressure are more direct expressions, moreover the increase in compression ratio in order to elevate temperature must be accompanied by the increase of pressure without fail so that the single effect of either of both temperature and pressure can not be examined separately.

In this paper the effects of instantaneous pressure on the temperature at both which the ignition initiated were studied, with fuels weaker to rich in mixture, by use of the pressure-time traces taken during the compression stroke. The mean piston speed was so slow, 1 msec⁻¹, that the charge could be ignitable over a wide range of fuel-air ratios.

The hot flames were made to occur at T.D.C. and its neighborhoods. The temperature for ignition, in this paper, is the gas law temperature calculated by use of the instantaneous values of pressure and volume from the pressure traces and number of molecules in the air-tight cylinder. According to the hot flame, the rate of pressure rise was determined and the exhaust gas analysis was made. For the purpose of changing the pressure-time trace, but not doing the temperature history, a throttling apparatus was set up in the intake flow line between cylinder and mixing chamber. In this experiment the ignition starting pressure was taken between 10 and 20 at, and the equivalence ratio (*S*) was between 0.5 and 3.

Experiments were made considering the following three points. (1) Excluding the effect upon the ignition of the exhaust gas, we took photographs of pressure trace that were at the first perfect compression stroke after uncompressible motoring. (2) Using the noncompression motoring of engine, the fuel air mixture was made to go and return between the combustion chamber and mixing chamber for homogeneity of the charge, at the same time the mixture was stirred by the fan within the mixing chamber. (3) For the lubrication inside a cylinder molybdenum-disulphide was used instead of a usual oil.

2. Parameters

A pre-flame reaction must be governed by temperature as well as a concentration of chemical

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species, and those distributions may be determined by a cylinder size and a piston speed, but so far as a premixed charge is used only the distribution of a concentration can be disregarded. Then the parameters in this experiment are a cylinder shape and size, initial temperature and pressure, number of molecules, mixture strength, coolant temperature, rotating speed, compression ratio, and crank angle. In addition to that, the history of these parameters up to ignition determines the state quantities at a start of ignition.

There has been a theoretical proposition⁽⁹⁾ for this history, nevertheless in this paper the state quantities at the start of ignition are used to the co-ordinates, because only a short period before the ignition is necessary as mentioned next. It has been shown by Gluckstein⁽¹⁰⁾ that in a full compression stroke only a short period proceeding to ignition is important, in the same way the identical relation is suggested by Fig. 1, namely the period of about 15 degrees before the ignition may be effective. In this figure there are two curves, one of them shows a polytropic change that index is 1.31 in accordance with the experiment, another does the relation between ignition lag, and ignition temperature from Rögner's empirical formula⁽¹¹⁾, under the assumptions that the ignition occurs at T.D.C., and the ignition temperature and pressure are 450°C and 9.2 ata, and the rotating speed is 300 rpm, all of which are experimental values.

In this work, once the τ_1 regime reaction had

Fig. 1 Ignition lag on rapid compression machine and motoring compression temperature

finished at T.D.C. or its neighborhoods, the reaction never failed to go on the hot flame, the reason of which seems to be that the pressure is high.

3. Experimental apparatus and operating conditions

3.1 Engine

An appearance of the apparatus and a scheme of the combustion chamber are shown in Fig. 2 and Fig. 3. Yanma NT 85; bore $\times$ stroke: 85 $\times$ 100 mm, displacement volume: 568 cc, the length of connecting rod vs. crank radius ratio: 4, was used. A new cylinder head was designed on purpose to have a single combustion chamber with an intake valve alone, removing an exhaust valve. The cylinder and the mixing chamber (B) are connected through the intake valve. On the head two seats are set up on which a pressure transducer (C) and a quartz window (D) are installed. The combustion chamber consists of two parts: the disk type space between the cylinder head and the piston surface, and two hollows of the seats for a pressure pick up and a quartz window. The values of specific surface are shown Fig. 4.

Beforehand, a premixed charge on the desired temperature and pressure was prepared in the mixing

B: Mixing chamber, C: Quartz window
D: Pressure transducer, E: Autocalibration rotary switch
F: Throttling apparatus

Fig. 2

Fig. 3 Scheme of the hollows on the cylinder head

chamber (B), 3 l, with a heater and a mixing fan. The intake valve had been held up by the stopper (provisional name) so that the charge could not be compressed. The engine was motor-driven at engine speed of 150 rpm during 1.5 minutes (225 strokes). By use of this non-compression motoring, the charge was made to go and return between combustion chamber and mixing chamber, at the same time the mixture was stirred by a fan, so that a homogeneousness could be expected. After 1.5 minutes, the engine was stopped, and the leakage of mixture was checked. The engine again was run at 300 rpm, in 15 seconds, the turn-buckle connected to the stopper was loosened. Whenever the turnbuckle was loosed, the stopper mentioned above was allowed to become free during the suction stroke firstly. And so, the first perfect compression stroke and accordingly the ignition followed in the absence of residual gas, when an indicator diagram was taken. At the same time the valve linkage was made loose so that the combustion gas was enclosed in the cylinder. Instead of measuring the number of molecules within a cylinder directly, the decrease in number of molecules in the mixing chamber was calculated by use of the gas law. In order to be airtight, O-rings were used around the moving parts such as a piston and a valve stem. An O-ring was set up between two piston rings which were useful as back up rings, too (Fig. 5).

The boiling water was forced to pass through the cylinder jacket and both temperatures of the mixing chamber and the intake flow passage were made equal to 100°C, because a temperature gradient through the charge in the cylinder must be small.

3.2 Fuel and lubricant

The *n*-heptane, standard reference fuel, was used. As a lubricant for inside of a cylinder liner, molybdenum-disulphide (MoS_2) based on a silicone grease was painted in order to remove the effect on ignition phenomena of a usual lubricant oil, as far

as possible. Nevertheless for a main bearing and a wrist pin molybdenum-disulphide could not be painted so that a very small amount of usual oil was dropped. For cleaning the mixing chamber in every experiment, the blower was used, instead of a reciprocating compressor, because in discharge of the latter some oil droplets might be contained. A fresh air was blown into the mixing chamber, at the same time the engine was run during 600 strokes on purpose to clean the combustion chamber by passing the air through the intake valve. Especially in the experiment of a rich mixture the quartz window was removed at every time, from which the residuals were exhausted, not returning to the mixing chamber, and through which the wall of chamber was cleaned.

3.3 Throttling

For the purpose of separating the temperature effect on ignition from the pressure effect, the initial pressure was varied with the initial temperature held constant i.e. a throttling of the intake flow was tried (the Point F in Fig. 2). The heat transfer surface was provided after the orifice, to prevent the stream temperature after throttling from going down to the dew point of fuel vapor, and from condensing. Size of the heat transfer passage was: 2×18 mm section, 300 mm length; two such slit-like passages were cut on the aluminium block. At the end plate of the block, the reed like nonreturn valve the same as a vibrator of harmonica was

Table 1

Name	Rocol MX 44 (Molybdenum disulphide based on silicone grease)
Flash point	315°C
Solidification point	minus 40°C
Penetration at 25°C	250

Fig. 4 Surface volume ratio

Fig. 5 O-ring setting

used, on which a small hole was drilled. Under a strong throttling, it was afraid that the cylinder might be isolated from the mixing chamber and a disagreement might arise in both mixture compositions between cylinder and mixing chamber. Nevertheless, by gas analysis, it was ascertained that there was no such likelihood when the noncompression motoring had been operated for 90 seconds at 150 rpm, where the gas analysis was done by use of carbon dioxide instead of *n*-heptane vapor.

3.4 Indicator diagrams

In photographing the pressure time trace the series as follows was used: the strain gage type pressure transducer and the bridge with calibrator, both made by Kyowa Co., and the synchroscope with D.C. amplifier, National PV 541 A. A few points dotted in Fig. 6~9 were traced by the alternating current amplifier (Kyowa Dengyo PM10N). On the Braun tube surface the electron beam has been chopped between both levels of the charge pressure and the atmosphere. The rotary switch for mechanical chopping is indicated in Fig. 2 by the point E. Assuming the series of square pulses to be a model of the periodic, chopping phenomenon, the upper frequency limit of A.C. amplifier, 20 kc/sec, is sufficiently higher than the basic frequency, 75 c/sec, but pulse width vs. pulse period ratio: 1/6. The deviation from that by D.C. amplifier was within the measuring errors.

3.5 Gas analysis

Carbondioxide, gas phase heavy hydrocarbons, and oxygen were analyzed by Orsat apparatus. Nitrogen, hydrogen, carbonmonoxide, and methane were analyzed by the gaschromatograph, Yanagimoto GCG 220. The column was copper; dia.: 6 mm, length: 4 m, temperature: 40°C. The fixing phases were molecular sieve 13 X. The carrier gases were argon for the analysis of hydrogen with flow rate of 30 cc/min; and helium for that of carbonmonoxide and methane with that of 60 cc/min.

4. Results and discussions

4.1 Ignition starting pressure and temperature

There are indicator diagrams in Figs. 12 and 13. The start of ignition mentioned now is a point beginning to leave from a compression pressure trace, the end of τ_1 regime, so that in the two-stage ignition it is the point of cool flame initiation. The influences of a molecular concentration on the pressure, both at the start of ignition, are shown in

Fig. 7

Fig. 8

Fig. 6

Fig. 9

Figs. 6~9 in which all the ignitions occurred between zero and eight degrees in crank angle before top dead center. The dotted points exist on a straight line to the zeroth approximation, so that it is suggested that the dependence of τ_1 regime reaction on the molecular concentration (pressure) is poor.

It can be expected that by throttling the intake flow a temperature-time history will hardly be influenced, on the other hand a pressure-time history will be much affected. If an exothermic release during τ_1 regime was negligible, the history of temperature up to ignition would hardly be changed by throttling, provided that the compression ratio, rotating speed, equivalence ratio, and coolant temperature are all constant, and so the initial temperature and ignition time are invariable. These experimental results (Figs. 6~9) show that the above discussion is nearly correct, namely the dependence of τ_1 regime reaction on temperature is strong, but that upon pressure is weak. When the pressure is high, it was reported by Livengood⁽⁹⁾ or Scheuermeyer⁽¹²⁾ that the dependence of the ignition lag on the pressure became poor with a rapid compression machine, and by other papers by use of a motoring method⁽³⁾, and a bomb method⁽¹³⁾. The present test results have agreed with other author's data, and moreover indicated that these properties have been observed even in rich, such as thrice stoichiometric, mixture which had never been examined in these experiments.

In this work the cool flames of a stoichiometric mixture initiated at the instantaneous temperature of 420~430°C at 0.21 kmol/m³ concentration which could be comparable to the value of 770°F (410°C) read from the graph given by Corzilius et al.⁽³⁾, but a few data on one stoichiometry and few data on other stoichiometry were available. As the throttling apparatus has been used, temperatures on every mixture strength became comparable at the same concentration. This result has given an approximate constancy of ignition temperature over the range $S=0.5\sim3$, wider than those of the former works.

The old papers in which the charge less than twice stoichiometry was examined pointed out that the richer a fuel concentration was, the higher the ignitable compression ratio was, i.e., the poorer the ignitability was. Nevertheless the richer the fuel concentration is, the smaller the value of C_p/C_v is, hence compression temperatures instead of the critical compression ratios should be, in other way, approximately invariable. In Tables 2(a) and (b), there are critical compression ratios as to cool flames of iso-octane proposed by Downs⁽¹⁴⁾ and for *n*-heptane by Carzilius⁽³⁾. The approximately constant compression temperatures have been transformed from

these compression ratios by use of polytropic indices which are nearly equal to those in the present paper and make the heat losses with regard to polytropic changes to be uniform at every mixture ratio [Table 2(a) and (b)]. However it is noted that the variation in the compression pressure by the change of mixture ratio is so large that the comparison of ignition temperature with respect to the fuel air ratio is not correct, precisely.

There must be a little disagreement among the histories of temperature in this experiment, because there is a difference between the compression ratios followed by changing of the mixture strength. To make a rough estimate of the disagreement, two groups of polytropic change are shown in Fig. 10, one of them has next quantities: a stoichiometry, compression ratio of 8, polytropic index of 1.31, and another: thrice stoichiometry, compression ratios of 13 and 14, polytropic index of 1.27, respectively, where, the values of the compression ratio and the polytropic index are same as those of the experiment, and both ends of the polytropic changes are

Table 2
Examination of the data of cool flame critical compression ratio

(a) iso-octane (Downs et al. ⁽¹⁴⁾)					
<i>S</i>	Compression ratio ϵ	Polytropic index n	Specific heat ratio κ^*	Temperature ratio T/T_0	Pressure ratio P/P_0
1	11.5	1.30	1.37	2.10	24
2	17.5	1.27	1.34	2.15	37
2.5	21.8	1.25	1.32	2.15	47

(b) <i>n</i> -heptane (Corzilius et al. ⁽³⁾)					
<i>S</i>	ϵ	n	κ^*	T/T_0	P/P_0
1	6	1.30	1.37	1.72	10.2
2	8.3	1.27	1.34	1.75	14.3

* Calculated as a perfect gas mixture, where using κ of *n* hexane in 1.08⁽¹⁶⁾ instead of *n*-heptane

Fig. 10 Temperature history vs. mixture ratio

same respectively. At the same mixture ratio the difference between curves by the change in compression ratio from 13 to 14 is negligible in the last part of the polytropic change, but the difference by the equivalence ratio change between 1 and 3 is not negligible, being about 1.5% in temperature disagreement at 15° BTDC. Then in this experiment the disagreement of the temperature history may be ignored approximately in discussing the ignition temperatures.

4.2 Effect of soot on the wall

In the thrice stoichiometric mixture a large amount of soot was formed by combustion. There are a datum⁽¹⁷⁾ on acetylene indicating that a large difference in ignition lag is observed between with or without a deposit on the wall. Then this effect was examined. The reference⁽¹⁵⁾ to cleaning of a wall using hydrochloric acid was made, hence, without chemical treatment the examination may not be perfect. For the purpose of studying under the condition of practical use, only the mechanical cleaning of the wall has been made. And so

examinations have been done only as to the deposit effect in the absence of residual gases. However no appreciable difference has been observed, for example in the ignition starting pressures and in piston positions.

4.3 Shapes of indicator diagram

The typical indicator diagrams for explosion at T.D.C. or its neighborhoods are shown in Figs. 12

Fig. 11 Cool flame and blue flame, S: Equivalence ratio, DC: Direct current amplifier (the following are same)

(a) S: 0.5, C: 0.21, DC

(b) S: 1, C: 0.21, DC

(c) S: 2, C: 0.21, DC

(d) S: 3, C: 0.22, DC

Fig. 12 C: Ignition starting molecular concentration kmol/m³, time marks; eleven points, interval of 10°, 50° BTDC ~ 50° ATDC, middle point: TDC, pressure reference interval: all 20 at

and 13, one group of them and another having a molecular concentration of about either 0.21 or 0.43 kmol m^{-3} , except Fig. 13(b). The indicator diagrams in Fig. 13 measured by use of a usual alternating current amplifier are not correct quantitatively but may be useful for comparison of shapes [Fig. 12(b), by use of DC amplifier, and Fig. 13(b) are same in both fuel air ratio and molecular concentration. There is not a distinction between two shapes of curve after ignition start]. The shapes of indicator diagrams show those of two-stage ignition at half stoichiometry and single (normal) ignition at twice and thrice stoichiometry. Jost⁽⁸⁾ and Gaubatz's⁽⁷⁾ photographs had shown the same results, nevertheless their ranges of fuel air ratio were narrower than in this experiment. The form of two-stage ignition at a stoichiometry is obviously observed at the concentration of 0.21 kmol m^{-3} [Fig. 12(b), 13(b)], but becomes less obviously at 0.43 kmol m^{-3} [Fig. 13(c)]. It may be thought that the τ_2 period may become short with an increase

in pressure, as mentioned by Jost⁽⁸⁾.

A clear blue flame has been always observed in 0.3 times stoichiometric charge (Fig. 11), and several times also at half stoichiometry. At other mixture ratios a yellow flame was observed, the

(a) S: 0.5, C: 4.3 AC (alternating current amplifier)

(b) S: 1, C: 0.22, AC

(c) S: 1, C: 0.43, AC

(d) S: 2, C: 0.43, AC

(e) S: 3, C: 0.43, AC

Fig. 13

brightness of which was maximum at a stoichiometry and went down to both lean and rich side. To the naked eyes the flame colours with either a usual lubricant oil or molybdenum-disulphide have not been distinguished.

Even in fuel excess exhaust gases, about 1% of oxygen the same as at a stoichiometry has remained (Fig. 14) so that it is suggested that a rich mixture of such as $S=3$ also can consume oxygen as much as at $S=1$.

The relation of the pressure rise rate, $dp/d\theta$ vs. the mixture ratio is shown in Fig. 15. The $dp/d\theta$ at $S=3$ is not so small as that at $S=0.5$, but obviously is less than that at $S=1$. After all, it is understood that by use of the low speed motoring at 1 msec^{-1} , the rich mixture such as thrice stoichiometry is sufficiently ignitable and actively explodes by consuming much oxygen, nevertheless $dp/d\theta$ of the hot flame is less than that at a stoichiometry.

Fig. 14 Exhaust gas composition

Fig. 15 Hot flame pressure rise rate vs. mixture ratio

5. Conclusions

The ignition of *n*-heptane premixed in the air was made to occur at T.D.C. and its neighborhood by use of the engine, cylinder size of which was $85 \times 100 \text{ mm}$ and the length of connecting rod vs. crank radius ratio was 4; with the piston speed of 1 msec^{-1} in the absence of residual gas and a usual lubricant oil. The range of equivalence ratio was made wider than usual. The experiments were made at above the molecular concentration shown in Table 3, i.e., the pressure was so high that the τ_1 regime was automatically followed by the hot flame reaction. Defining the start of ignition to be the point of beginning to leave from the compression pressure trace, the conclusions are as follows:

(1) The dependence of the τ_1 regime reaction upon temperature is strong, but that on molecular concentration (pressure) is weak. This is also observed at the rich fuel concentration such as thrice stoichiometry.

(2) The ignition starting temperature is between about $400 \sim 430^\circ\text{C}$, over the mixture ratio range of 0.5~3 times stoichiometry under the same molecular concentration of 0.21 mol m^{-3} .

(3) The thrice stoichiometric charge can consume oxygen as much as the correct mixture and actively explodes, nevertheless the rate of pressure rise in the hot flame is not so poor as at half stoichiometry, but less than at a stoichiometry.

(4) The shapes of the indicator diagram are that of the two-stage ignition at half stoichiometry, and that of single ignition at twice and thrice stoichiometry. The correct mixture makes two-stage ignition at 0.21 kmol m^{-3} of the ignition starting concentration, and at 0.43 kmol m^{-3} it does single stage ignition or two-stage, but nearly equal to single stage, ignition.

(5) The flame colour at an equivalence ratio of 0.3 is blue, that is, a mild explosion; at the other mixture ratio the flames are yellow whose intensity is changed by the mixture strength.

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Table 3

Equivalence ratio	0.5	1	2	3
Molecular concentration kmol/m^3	0.13	0.13	0.18	0.20
Pressure ata (approximate)	8	8	10	11

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Errata (Vol. 12, No. 53, October, 1969)

Author	Page	Column	Line	For	Read
T. HANABUSA et al.	934	left	18	X-rayelastic	X-ray elastic
	937	Fig. 14 (the axis of abscissa)		No explanation	"Macroscopic residual strain %"
M. SHIBAHARA et al.	979	right	9	in the inne circle	in the inner circle
M. MIYAGAWA	999	Table 2		10 ⁻⁶ mm	10 ⁻⁶
et al.	1 002	Table 3	1	... with G (kg/mm)	(kg/mm ²)
T. KAZAMAKI	1 011	right	10	$2r$	2γ
S. IWANAMI et al.	1 042		29	... of ... = $-h_2'$	... of ... = $-h_2'$.
			31	$=(h_1/2\pi)[(1+v_1)^2 \log_e \dots]$	$=(h_1/2\pi)[(1+v_1^2) \log_e \dots]$
	1 044	right	14	occures	occurs
	1 050	Fig. 19		ζ_{w12} (the value of ordinate)	ζ_{12}
	1 058	left	20	$\textcircled{B} \rightarrow \textcircled{D}$	$\textcircled{B} \rightarrow \textcircled{C}$
T. KASAI et al.	1 090	right	Ref. (3)	27	287
K. KASAI	1 094		Eq. (27)	... $-2\sigma\omega(1+\mu_u)$	... $-2\sigma\omega(1+\mu_u)$
				$\times \sinh \frac{\tau_d}{2} \sigma \cos \frac{\tau_d}{2} \omega$	$\times \sinh \frac{\tau_d}{2} \sigma \sin \frac{\tau_d}{2} \omega$
K. ICHIRYU	1 110	left	20	rool	role
	1 116	right	7	$+K_{e1}\dot{x}_{n1}=\dots$	$+K_{e1}x_{n1}=\dots$
T. SAWADA et al.	1 146	left	10	$(G_1\sqrt{T_1}/P_1)$	$[G_1\sqrt{T_1}/P_1]$
		right	8	inlet $(G_3\sqrt{T_3}/P_3)$	inlet cmf $[G_3\sqrt{T_3}/P_3]$
			19	... Point 7' in and VII-plane, and ...	... point 7' and ...
	1 148	right	4 from the bottom	... acuracy.	... accuracy.