

Realization of Dual Phase High Temperature Heat Release Combustion of Base Gasoline Blends from Oil Refineries and a Study of HCCI Combustion Processes

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ABSTRACT

It was reported that n-heptane and toluene blended fuels (NTL series fuels) showed the dual phase high temperature heat release (**DP-HTHR**) combustion in a previous SAE paper [1]. DP-HTHR has the potential to enlarge the engine operational range to high load conditions and lower the engine combustion noise. Further research has been reported in this paper. Initial interests were in the combustion characteristics of a second “bump” in the high temperature heat release (**2nd HTHR**) in DP-HTHR, since this kind of two-stage combustion appears, when CO oxidation radically occurs over the 1450K temperature range. To prove this 2nd HTHR of DP-HTHR was not caused by a rapid CO oxidation process, and indeed by the decomposition and oxidation of the benzene ring in toluene (benzyl radicals and aromatics), exhaust emissions (THC, NO_x, CO, CO₂) and in-cylinder pressure data were measured at the same HTHR CA50 (the crank angle of 50% burn of high temperature heat release) and IMEP condition with the DP-HTHR fuel (NTL75) and non-DP-HTHR fuels (PRF90, NDB90 and NMP85). The CO emissions were evaluated by vol% scale and emitted quantity to correct the differences of fuel density, the H/C ratio and injected fuel quantity between the fuels. These data analyses supported that the decomposition and oxidation of the benzene ring at hot flame temperature was the starting trigger of the 2nd HTHR in DP-HTHR combustion. The second interest was the possibility of DP-HTHR combustion with the blends of the refinery-based gasoline. NTL fuels are the surrogate fuels consisting of n-heptane and toluene.

To apply this DP-HTHR technique to the refinery blended fuels, three base gasoline blends of Nippon Oil refinery were chosen. Three different gasoline prototypes (GAS2, GAS3 and GAS4) were made, and the combustion of each fuel was evaluated by a 4 cylinder HCCI engine. The engine test results showed that DP-HTHR combustion could be achieved with GAS4 fuel. Furthermore, a uniform low temperature heat release (LTHR) was also reported, which is a special characteristic of DP-HTHR. In DP-HTHR combustion, the magnitude of LTHR and LTHR CA50 do not change even if the load changes. This is a unique combustion characteristic of DP-HTHR and gives a better idea of HCCI combustion processes, since DP-HTHR is a simple combustion model. The fundamentals of HCCI combustion processes are further investigated and discussed in this paper.

INTRODUCTION

Though the HCCI engine has the potential for low NO_x emission combined with diesel-like engine efficiency, the engine operational speed-torque ranges change depending on fuel composition. Octane and cetane numbers are not a sufficient fuel index for HCCI engine control. This is one of the technical barriers that block HCCI engine development in automotive companies. Kalghatgi experimentally developed an “octane index”, as shown in equation (1) [2-6], and showed that the combustion characteristics of fuels changed depending on the engines and HCCI operational conditions.

$OI = (1-K) RON + K MON$ (1)
 OI: Octane index
 K: Factor, varies by engine and operating conditions
 RON: Research octane number
 MON: Motor octane number

Nissan and Nippon Oil have also researched the effect of fuel compositions on HCCI engine operation [1, 7-13] since 2002. HCCI combustion typically occurs in two stages [14]. A low temperature heat release (**LTHR**) occurs first, followed by a high temperature heat release (**HTHR**). These combustion phases do not occur independently. For instance, **HTHR CA50** (the crank angle at 50 % burn of HTHR) can be described as a function of LTHR CA50 and LTHR heating value [8], as shown in equation (2).

$$HTHR\ CA50 = G(LTHR\ CA50, LTHR\ heating\ value) \quad (2)$$

Equation (3) and (4) are the experimental formulas of our test engine under two different operational conditions, based on equation (2).

$$\begin{aligned}
 <900rpm\ IMEP\ 470kPa> \quad (R^2 = 0.955) \\
 HTHR\ CA50 &= 2.48 \times (LTHR\ CA50) \\
 &\quad - 0.178 \times (LTHR\ QJ) + 39.39 \quad (3)
 \end{aligned}$$

$$\begin{aligned}
 <1000rpm\ IMEP\ 530kPa> \quad (R^2 = 0.967) \\
 HTHR\ CA50 &= 2.12 \times (LTHR\ CA50) \\
 &\quad - 0.366 \times (LTHR\ QJ) + 39.82 \quad (4)
 \end{aligned}$$

HTHR CA50: Statistically calculated HTHR CA50
 LTHR CA50: LTHR CA50 (engine data)
 LTHR QJ: LTHR heating value (engine data)

The LTHR oxidation process is shown schematically in Figure 1 [15-19]. The oxidation and chain-branching reactions, mainly caused by n-paraffins and iso-paraffins, occur at 750-850 K. H_2O_2 is produced from two sets of HO_2 and accumulates in the range of 850-900K. H_2O_2 decomposition into OH radicals occurs above 900K and this is the start of HTHR [9]. The equation (b) in Figure 1 is a reversible reaction, and as the temperature goes up, the reaction moves to the left side and the LTHR stops. This can be observed as the negative temperature coefficient (**NTC**) area in Arrhenius plot. There are two types of LTHR inhibitor effects and those can be explained by this LTHR reaction diagram. The first example of LTHR inhibitor effect can be observed for toluene and m-xylene. For these hydrocarbons, R radicals in equation (a) are stable and the following reactions shown in equation (b)-(j) do not occur. The second example of LTHR inhibitor effect can be observed for olefins [8] and oxygenates [20-23]. Hydrogen radicals produced by the dehydration reactions or aldehyde radicals produced by the oxidation of oxygenates react with OH radicals, that play an active and important role of LTHR start reaction in equation (a), and the LTHR is inhibited.

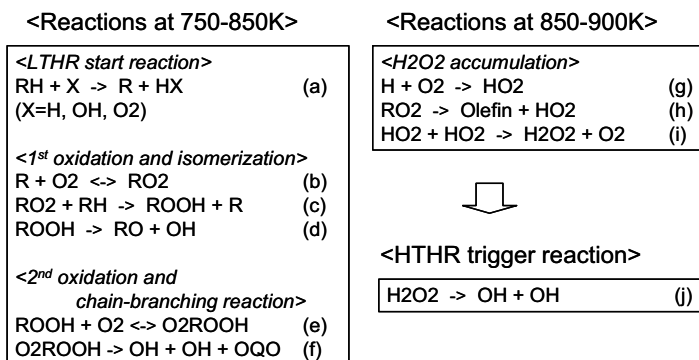


Figure 1 LTHR reactions and HTHR start reaction

The H_2O_2 decomposition into OH radicals occurs under a certain temperature-pressure conditions shown in Figure 2 [9]. With the higher concentration of H_2O_2 during the LTHR period, HTHR starts at a low temperature and high pressure condition, while with the lower concentration of H_2O_2 during LTHR, HTHR starts at a high temperature and low pressure condition.

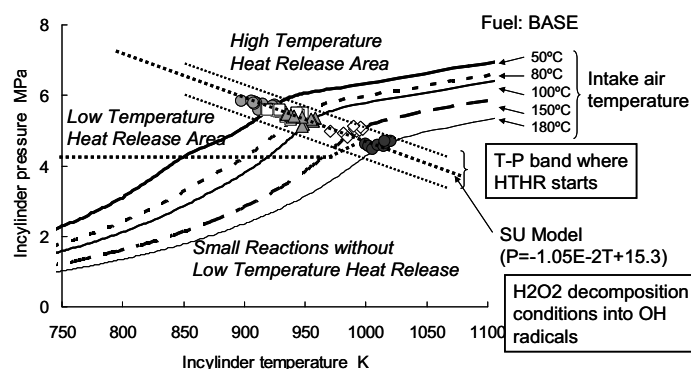


Figure 2 Temperature-pressure map before and after auto-ignition

The characteristics of HTHR itself have not been thoroughly discussed. In a previous paper [10], it was reported that there existed a HTHR case without LTHR, as shown in Figure 3. At high intake air temperature, LTHR and LTHR inhibitor effect do not exist but there are still the HTHR differences between fuels. Therefore it was obvious that equation (2) was not a sufficient formula to predict the HTHR CA50.

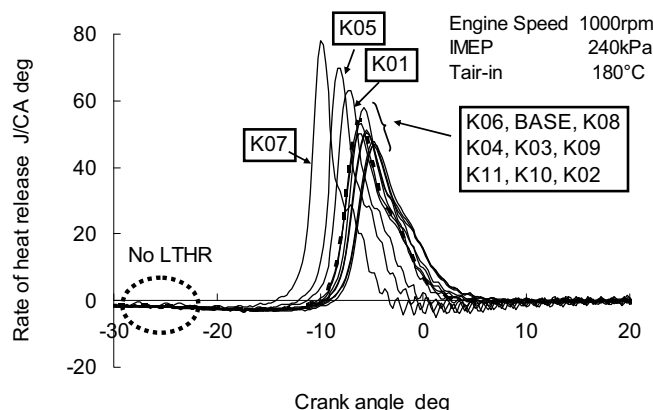


Figure 3 Difference of HTHR without LTHR case [10]

Throughout the HCCI fuel research, it was found that the following 5 parameters determined the HTHR CA50.

<Parameters that determine HCCI auto-ignition>

- (1) LTHR potential (plus heating value)
- (2) LTHR timing
- (3) LTHR inhibitor effect potential (minus heating value)
- (4) LTHR inhibitor effect timing
- (5) HTHR characteristic under no LTHR condition

Based on these parameters, an absolute HCCI auto-ignition fuel index was developed, as shown in equation (5) [10]. Each coefficient of parameter is characterized depending on the in-cylinder temperature range at 15bar during the compression stroke, as shown in Table 1. The difference between equations (1) and (5) is a relative and absolute HCCI auto-ignition fuel index respectively, but basically both equations have the same meaning, as a result [10].

$$\text{HCCI Index (abs)} = r\text{RON} + a'(n\text{-P}) + b'(\text{i-P}) + c'(\text{O}) + d'(\text{A}) + e'(\text{OX}) + Y' \quad (5)$$

(RON: Research octane number, n-P: n-Paraffins vol%, i-P: iso-Paraffins vol%, O: Olefins vol%, A: Aromatics vol%, OX: Oxygenates vol%)

Table 1 Coefficients of parameters against temperature at 15bar (1.5MPa) in-cylinder pressure

Temp. @15bar (1.5MPa)		- 670K	670-700K	700-730K	730-790K	790-820K	820K -
RON	r	0.848	0.858	0.831	0.523	0.207	0.161
n-Paraffin	a'	-0.203	-0.256	-0.320	-0.244	-0.103	-0.050
iso-Paraffin	b'	-0.198	-0.267	-0.336	-0.187	-0.012	0.014
Olefin	c'	-0.134	-0.193	-0.259	-0.176	-0.064	-0.043
Aromatic	d'	0.006	-0.087	-0.186	-0.109	-0.009	0.008
ETBE	e'	-0.032	-0.072	-0.132	-0.088	-0.003	0.018
Et-OH	e'	0.172	0.089	-0.036	-0.054	-0.026	-0.020
MTBE	e'	0.025	0.023	0.004	-0.004	0.018	0.031
y-intercept	Y'	-60.028	-56.041	-48.828	-32.109	-18.947	-19.276

For ideal high performance HCCI engine development, both the optimization of the engine and fuel developments are required. Since gasoline and diesel fuels on the market are not appropriate for full range HCCI operation, the development of combustion control has been required. For gasoline HCCI, HCCI operation is restricted to low engine speed and torque operation surrounded by noise (HCCI knocking) and misfire limits. As gasoline is well vaporized and mixed with air, the mixture auto-ignites at the same time. This leads to heavy HCCI engine noise (HCCI knocking). To avoid this rapid in-cylinder combustion and enlarge the HCCI operation into high load condition, the stratification of air-fuel mixture, exhaust gas recirculation (EGR) or thermal stratification has been researched by many researchers [24-28]. HCCI combustion is determined by the chemical kinetics of the mixture and much effort has been performed to optimize CA50 (the crank angle of 50% burn) in heat releases. The fuel injection timing effects [29], initial boost pressure-temperature effects [14, 30] and turbulence effects [31-32] on the HCCI combustion period were investigated. From the engine development side, spark assist HCCI [33-35], split fuel injection [36], air assist injection [37] and dual fuel strategies [20, 38, 39] have also been reported. Since the chemical hydrocarbon contents in the fuel affect the auto-ignition process, HCCI combustion has been deeply researched on the chemical reaction side [40-43]. Primary reference fuel (PRF) and DME were well researched [16, 19, 22, 23, 44-46] to make simple reaction computation models.

In our fuel research, the binary hydrocarbon blended fuels of n-heptane and toluene (**NTL series fuels**) had the potential to enlarge the engine operation range to higher load [1]. The fundamentals of the combustion of NTL series fuels are shown in Figure 4. The combustion of NTL series fuels are consisted of one low temperature heat release and two high temperature heat releases. Some of n-heptane molecules of the NTL fuel start to break down during the cool flame period (750-900K) and the reactivity radicals, such as OH and CHO radicals, are produced. When the in-cylinder temperature reaches 900K, the rest of the n-heptane molecules react with these radicals. This is the blue flame period. A few toluene molecules react and change to benzyl radicals and aromatics, but mostly they stay as toluene molecules. Those benzyl radicals and aromatics are very stable during blue flame period (900-1100K) because of the strong structure of the benzene ring. Once the temperature reaches at hot flame temperature (1100K>), the aromatics and benzyl radicals start to break down. Therefore the high temperature heat release is consisted from two heat releases caused by n-heptane and toluene (benzyl radicals and aromatics) independently, as shown in Figure 4. A "step" (inflection point) between the heat releases could be found. This combustion phenomenon was named "dual phase high temperature heat release" combustion and abbreviated as "DP-HTHR". The 1st HTHR of DP-HTHR is caused by the decomposition and oxidation of n-heptane started from blue flame temperature, and the 2nd HTHR of DP-HTHR occurs by the decomposition and oxidation of benzene ring in toluene (benzyl radicals and aromatics) started from hot flame temperature. The key point of the DP-HTHR combustion is the blending of the two different auto ignitability hydrocarbons: one hydrocarbon has a high auto ignitability and the other hydrocarbon has a low auto ignitability.

The effects of DP-HTHR on engine performance were investigated. The maximum pressure rise rate at the same HTHR CA50 (1.5deg CA ATDC) and IMEP (500kPa) condition were measured over 400 cycles, as shown in Figure 5 [1].

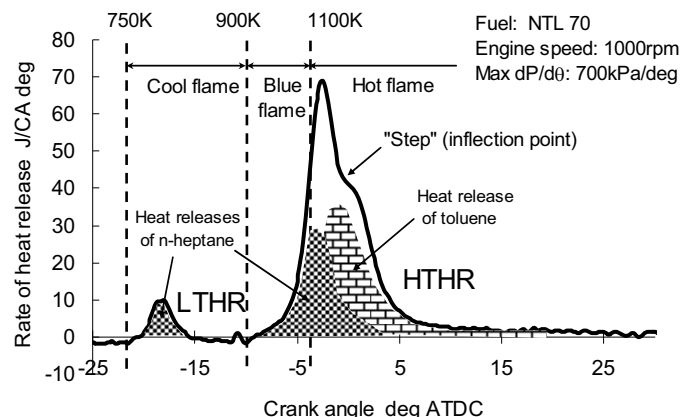


Figure 4 The mechanism of dual phase high temperature heat release combustion

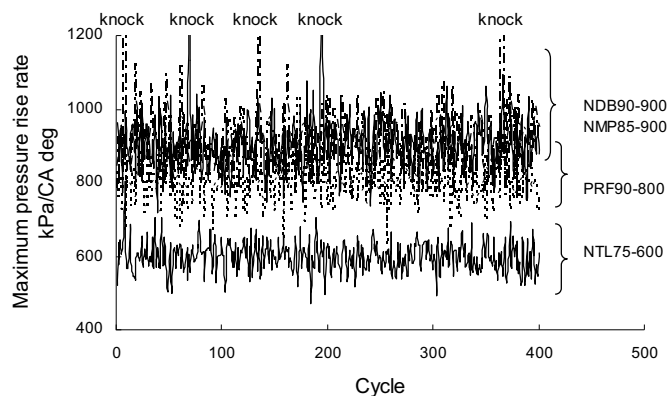


Figure 5 Maximum pressure rise rate over 400 cycles at the same HTHR CA50 and IMEP condition

In this figure NTL75-600 has DP-HTHR combustion and the other fuels have the single phase high temperature heat release (**SP-HTHR**) combustion. The maximum pressure rise rate of NTL75-600 was completely independent from those of the other fuels and less engine combustion noise was detected. This test result also suggested that the NTL series fuels had the potential of the HCCI engine operation at higher load.

The combustion characteristics of the same research octane number fuels, that were PRF75, NDB75, NMP75, NTL75, and NCP75, were compared in Figure 6 and 7 [1]. These data were taken at a maximum pressure rise rate of 800kPa/deg. Figure 6 shows the pressure histories of these five fuels. The maximum pressure of NTL75 was the highest of the five fuels, but the maximum pressure rise rates were all the same. This is because the NTL75 fuel had DP-HTHR combustion. This DP-HTHR allowed increased fuel injection to achieve the highest engine torque operation. Therefore the IMEP of NTL75 was 30% higher than those of the other fuels, and the coefficient of variation (COV) of NTL75 was the lowest of the five fuels. From these results, DP-HTHR combustion of NTL series fuels is effective for low engine combustion noise and high IMEP engine operation.

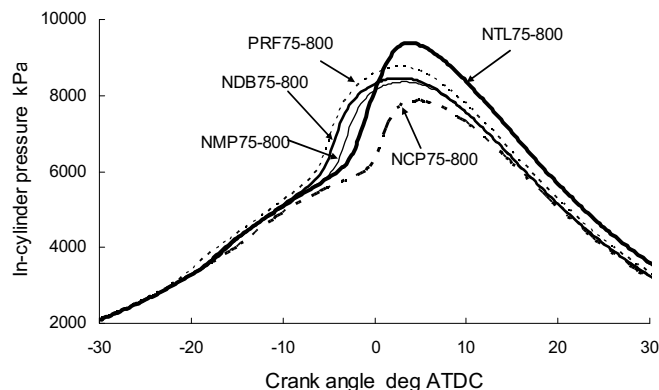


Figure 6 Pressure histories of RON75 fuels

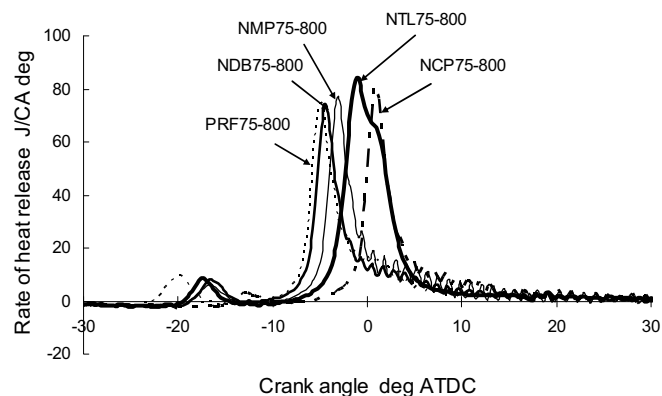


Figure 7 Heat release data of RON75 fuels

Except for the DP-HTHR combustion cases, two-stage high temperature heat release combustion can also be found when CO oxidation occurs radically over the 1450K temperature range. Two types of heat release data are compared in Figure 8. The engine was operated at the same engine speed (1000rpm) and IMEP (270kPa) for Fuel A (K07) and Fuel B (K02) [10]. Fuel A has 40vol% n-paraffin in the fuel and the HTHR occurs rapidly. When the in-cylinder temperature exceeds 1450K, the 2nd HTHR (dashed area) appears. This heat release is caused by the rapid CO oxidation process. In the case of Fuel B (K02), less n-paraffin is contained in the fuel (22.9vol%) and its HTHR proceeds slower. The in-cylinder temperature does not reach 1450K and a rapid CO oxidation process can not be found in its heat release history. Therefore, CO and hydrocarbon emissions of Fuel A were less than half of those of Fuel B, respectively. Much HCCI emission research has been reported from the point of fuel compositions and engine operating conditions [47-51], but DP-HTHR (which is caused not by CO oxidation) has only been recently documented [1].

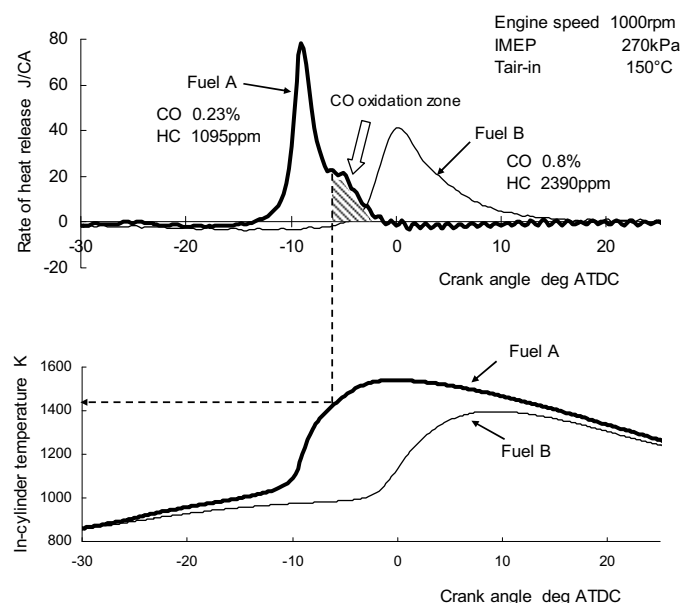


Figure 8 Two step heat release combustion by CO oxidation (Fuel A; K07 fuel, Fuel B; K02 fuel)

From these backgrounds, it is important to investigate the combustion characteristics of the 2nd HTHR of NTL series fuels. It is especially important to scientifically analyze that

the 2nd HTHR of DP-HTHR is not caused by a rapid CO oxidation process, but by the decomposition and oxidation of a benzene ring in toluene (benzyl radicals and aromatics). The exhaust emissions (THC, NO_x, CO, CO₂) and in-cylinder pressure histories were measured at a same HTHR CA50 (the crank angle of 50% burn of high temperature heat release) and IMEP condition with NTL fuel and non-DP-HTHR fuels, including the combustion characteristics of the 2nd HTHR of NTL series fuels.

The second interest was the possibility of DP-HTHR combustion with blends of the refinery based gasoline fuels. NTL fuels consist of the binary-blended pure hydrocarbons of n-heptane and toluene. NTL fuels work well for research laboratory fuels, but not realistic as HCCI market fuels. To apply these DP-HTHR techniques to the refinery blended fuels, light naphtha (**LSR**), heavy naphtha (**HSR**) and catalytic reformattd gasoline (**FMT**) were chosen from a Nippon Oil refinery and blended. Three different fuels were made, and the combustion of each fuel was evaluated by the 4 cylinder HCCI engine. The concepts of the fuel blends were mentioned, and HCCI engine test results of DP-HTHR combustion with refinery blended fuels were evaluated.

Uniformity of low temperature heat release magnitude and LTHR CA50, even with changes in load, is a special characteristic of DP-HTHR combustion that is being reported. This is a unique combustion characteristic of DP-HTHR and gives us a better idea of HCCI combustion since DP-HTHR is a relatively simple combustion model. The fundamentals of HCCI combustion processes are further investigated and discussed in this paper.

EXPERIMENTAL DESCRIPTION

ENGINE BENCH SETUP

The engine was operated in an environmentally controlled chamber where the temperature, relative humidity and atmospheric pressure were maintained at 20 °C, 60% and 101 kPa abs, respectively, to ensure constant intake air conditions. A schematic of the research engine bench is shown in Figure 9. The engine employed in the experiment was a supercharged 4-cylinder engine with high compression pistons (compression ratio=15:1), 4 valves per cylinder, and centrally located spark plugs. The intake manifold was equipped with separate electric heaters for each cylinder (200 V, total 6 kW) allowing independent control of intake air temperature up to 200 °C at 1500 rpm. The engine was equipped with a pressure transducer for each cylinder. Pressure data was transmitted to a PC at 200 cycles of crank angle resolved pressure data for each test condition. Each injector fuel quantity was independently controlled to yield the same IMEP for each cylinder. The specifications of the HCCI engine are given in Table 2. For all test conditions in this paper, the water jacket temperature and engine oil temperature were kept at 80 °C.

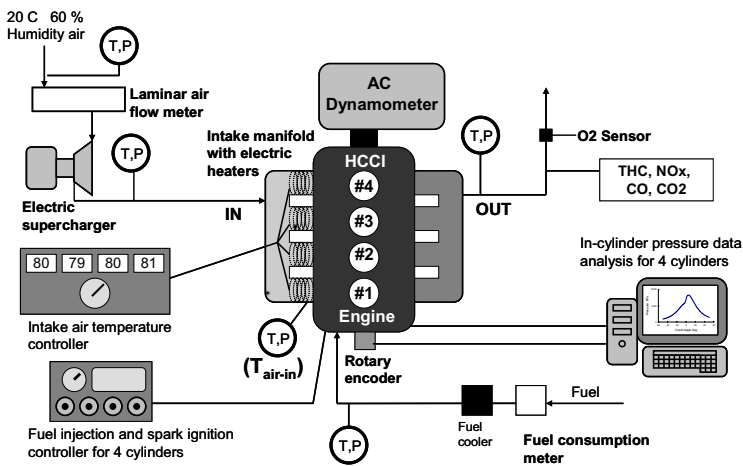


Figure 9 Experimental engine set-up

Engine type	4 cylinder MPI
Compression ratio	15:1
Bore	86mm
Stroke	86mm
Displacement	1998cc
Exhaust valve open	53°CA BBDC
Exhaust valve close	7°CA ATDC
Intake valve open	1°CA ATDC
Intake valve close	19°CA ABDC

Two different HCCI engine tests were mainly performed in this paper. Test 1 data was mainly used to investigate the 2nd HTHR of DP-HTHR of NTL series fuels. Test 2 was performed to realize DP-HTHR combustion with base gasoline blends from oil refineries. Sometimes data from Test 2 was used to help explain combustion results from Test1, and vice versa. The HCCI engine was operated at 1000 rpm. Intake air was supercharged to 155 kPa abs and its temperature was kept at 58 °C.

TEST 1: CHEMICAL AND PHYSICAL INVESTIGATION OF THE 2nd HTHR IN DP-HTHR COMBUSTION

First investigation was the possibility of rapid CO oxidation in the 2nd HTHR of DP-HTHR combustion. In our previous paper [1], 18 kinds of different binary hydrocarbon blended fuels under various maximum pressure rise rate conditions were tested. The IMEP-HTHR CA50 operational range of each fuel is shown in Figure 10.

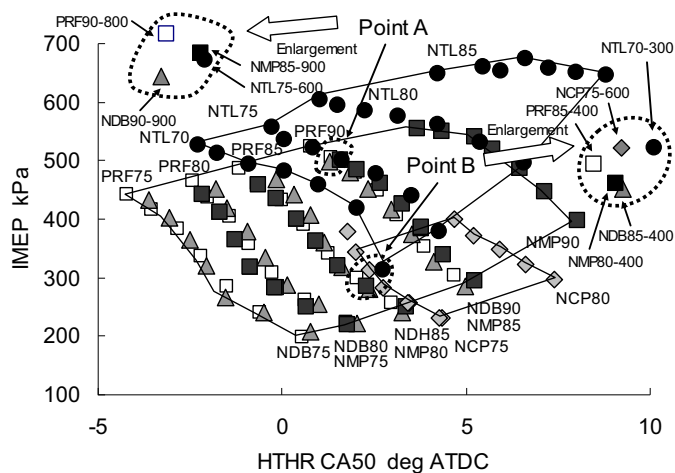


Figure 10 Engine operation maps of the PRF, NDB, NMP, NTL and NCP series fuels

All test fuels were blended from two hydrocarbons: one was n-heptane and the other varied between fuel types. The fuel blends' counterpart hydrocarbons were iso-octane for PRF series fuels, diisobutylene for NDB series fuels, 4-methyl-1-pentene for NMP series fuels, toluene for NTL series fuels, and cyclopentane for NCP series fuels. For example, a NTL75 fuel means the binary blend of n-heptane and toluene with a research octane number of 75. Point A in Figure 10 is the position where the HCCI engine can be run at the same HTHR CA50 and IMEP condition with 4 different fuels, which are PRF90, NDB90, NMP85 and NTL75, as shown in Table 3 (NTL75-600 means the NTL75 fuel tested at 600kPa/deg maximum pressure rise rate). The fuel properties of PRF90, NDB90, NMP85 and NTL75 are shown in Table 4.

Table 3 Engine performance at Point A for four fuels

	Max dP/dθ		IMEP	HTHR CA50	DP-HTHR
	kPa/deg	deg ATDC	kPa	deg ATDC	
PRF90-800	799.7	-0.20	504.5	1.34	No
NDB90-900	902.7	-0.02	498.0	1.30	No
NMP85-900	903.1	0.28	501.6	1.60	No
NTL75-600	599.9	-0.19	500.4	1.63	Yes

Table 4 Description of test fuel properties for Test 1

Fuel type		PRF90	NDB90	NMP85	NTL75
Research octane number		90.0	89.3	85.0	74.5
Density	g/cm3 @15°C	0.6938	0.7076	0.6723	0.7986
Hydrocarbons	n-Heptane	10.0	38.1	19.7	40.5
	iso-Octane	90.0			
vol%	Di-isobutylene		61.9		
	4Methyl-1-pentene			80.3	
	Toluene				50.5
Stoic. A/F		15.12	14.92	14.85	14.07
H/C		2.27	2.12	2.07	1.53
CH wt %	C	84.09	84.99	85.28	88.68
	H	15.91	15.01	14.72	11.32
Heating value kJ/kg		44367	44249	44249	41937
Remarks		CO emission measurement @ Pint A (Test 1)			

The HCCI engine was re-operated at Point A in Figure 10 by PRF90, NDB90, NMP85 and NTL75 fuels. Basic engine performance, exhaust emissions (THC, NO_x, CO, CO₂) and pressure data were recorded. CO emissions were

measured in volume percent, with a Best Sokki NBY-401 emissions analyzer, and in mass as well. This is because of the differences of H/C ratios and injected fuel quantities at the same load between the fuels. Rate of heat release and in-cylinder temperature data were calculated from in-cylinder pressure data.

Emission data was taken at Point B in Figure 10, but the IMEP range of Point B was 280-330kPa, which was wider than Point A. Therefore detailed emissions comparisons were only analyzed in a main body of the paper at Point A, while Point B engine performance and emissions data was listed in Table AP-1 of Appendix (1).

TEST 2: REALIZATION OF DP-HTHR COMBUSTION OF BASE GASOLINE BLENDS FROM OIL REFINERIES

To achieve DP-HTHR combustion with refinery fuels, high and low ignitability base gasoline fuels were prepared. Though diesel fuel is a high ignitability fuel, its vaporization characteristics are inferior to gasoline, and therefore was not used in this test. A base gasoline which has high ignitability is naphtha. In Nippon Oil, there are two types of naphtha: one is light naphtha (**LSR**) and the other is heavy naphtha (**HSR**). A base gasoline which has low ignitability and rich aromatic content is catalytically reformed gasoline (**FMT**). The fuel properties of those base gasoline fuels are listed in Table 5.

Table 5 Description of base gasoline properties

BASE gasolines		LSR	HSR	FMT
Octane numbers	RON	72.7	48.1	105.6
	MON	77-79	48.5	95.1
Density	g/cm ³ @15°C	0.6434	0.7305	0.8481
RVP	kPa	120.0	13.5	6.5
Distillation	IBP	24.0	80.0	105.5
	10%	33.0	95.0	108.0
	30%	38.5	101.0	108.5
	50%	43.5	109.0	109.0
	70%	50.5	118.0	110.0
	90%	61.5	130.0	113.0
	EP	70.0	152.0	126.5
Fuel composition vol%	n-Paraffins	55.19	33.72	5.57
	iso-Paraffins	38.99	35.80	4.92
	Olefins	0.01	0.47	2.91
	Naphthenes	4.84	19.06	2.63
	Aromatics	0.97	10.87	83.89
	C4-C6 n-Paraffins	55.14	8.02	0.03
	C7-C9 n-Paraffins	0.05	25.69	5.54
	Toluene	0.01	3.93	76.98

LSR is mainly consisted from C4-C6 paraffins and 55vol% of LSR is n-paraffin molecules. FMT is 84vol% aromatics and 77vol% of toluene is included in FMT. HSR is used as a "cushioning base gasoline" not to change the fuel properties too much, especially distillation and vapor pressure when the blending ratio of LSR and FMT is changed to make HCCI fuels.

In our previous paper [1], NTL70, NTL75, NTL80 and NTL85 showed DP-HTHR combustion. The characteristics of the series fuels can be described as the following.