

Molecular Structure of Hydrocarbons and Auto-Ignition Characteristics of HCCI Engines

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ABSTRACT

The chemical composition of marketed gasoline varies depending on the crude oil, refinery processes of oil refineries, and season. The combustion characteristics of HCCI engines are very sensitive to the fuel composition, and a fuel standard for HCCI is needed for HCCI vehicles to be commercially viable. In this paper, the effects of the structure of the fuel components on auto-ignition characteristics and HCCI engine performance were investigated. The engine employed in the experiments is a research, single cylinder HCCI engine with a compression ratio of 14.7. The intake manifold was equipped with a heater attachment allowing control of the intake air temperature up to 150 °C at 2000 rpm. Thirteen kinds of hydrocarbons, 4 kinds of paraffins, 3 kinds of naphthenes, and 6 kinds of aromatics, were chosen for the investigation, and 20 vol% of each of the pure hydrocarbons was blended with the 80 vol% of PFR50 fuel. The HCCI engine was operated with the thirteen kinds of fuels under the same equivalence ratio, and the relative ignitability (the HI index: the hydrocarbon ignitability index, defined in this paper) of each hydrocarbon was calculated from the HTHR CA10 and evaluated. The parameters of the HCCI engine operations were the intake air temperature, engine speed, and intake oxygen content controlled by EGR. The test results show that the relative ignitability of the paraffins does not change with intake air temperature, engine speed, and intake oxygen content, but with naphthenes and aromatics there are changes by the intake air temperature and engine speed. As the intake air temperature increases, the relative ignitability of naphthenes deteriorates, while that of aromatics improves. With increasing engine speed, the relative ignitability of the naphthenes and aromatics deteriorates. To understand the ignitability of hydrocarbons, the relation between the hydrocarbon structure and research octane number was investigated. It is clearly shown that the ignitability differences of the hydrocarbons were mainly caused by the straight chain length of alkanes and side chains, the ring size of naphthenes, and the benzene ring in aromatics. Based on these findings, the HCCI engine test results were also statistically analyzed with the chemical structure parameters, and are discussed here. Further, the ignition timing of the HCCI combustion was estimated by the Livengood-Wu integral and compared with the engine test data.

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INTRODUCTION

Cetane and octane numbers have been used for the conventional diesel and gasoline engines as fuel ignitability indices. These indices are measured by the cooperative fuel research (CFR) engine, equipped with a low pressure injection system for diesel or a carburetor for gasoline measurements. After the electric fuel injection system by common rail was introduced around 1997, high pressure and multi fuel injection can be achieved in diesel engines, and direct gasoline injection has become common in gasoline engines. These technologies have contributed to reductions in emissions and improvements in engine performance, but the combustion characteristics can not be predicted by the conventional indices (cetane number or octane number), because of the wide variety in combustion conditions.

The HCCI engine is especially sensitive to fuel compositions. The heat release data of regular gasoline and PRF90.5 is shown in [Figure 1](#). Both of these fuels have the same research octane number of 90.5, however the heat release phasings are completely different.

The octane index, shown in [Equation \(1\)](#), was developed by Kalghatgi and it is very helpful in this area [1, 2, 3, 4].

$$OI = (1-K) RON + K MON \quad (1)$$

OI: Octane index

K: Factor which varies by engine and operating conditions

RON: Research octane number

MON: Motor octane number

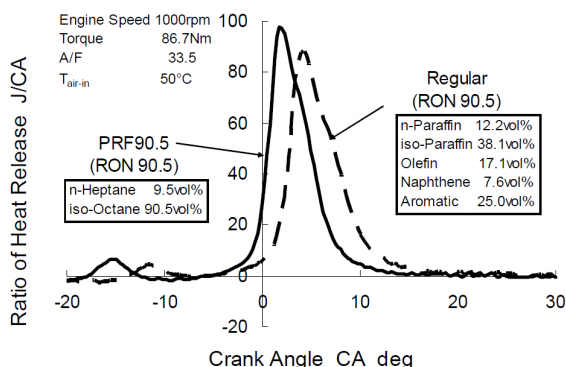


Figure 1. Heat release data of PRF90.5 and regular gasoline

Shibata and Urushihara have investigated the fuel ignitability characteristics with surrogate fuels [5, 6, 7, 8, 9, 10]. The heating value and the radicals generated in the low temperature heat release (LTHR) strongly affect the start and the development of the high temperature heat release (HTHR), and the engine performance changes due to the LTHR characteristics.

The conventional auto ignition characteristics, RON and MON, were generally accepted for pure hydrocarbons by the CFR engine, and it is an example of a method to obtain the relation between the chemical structure and ignitability. In this paper, the chemical parameters that determine the fuel ignitability were statistically extracted from the RON data. The HCCI engine was operated with the thirteen kinds of fuels under the same equivalence ratio and the chemical parameters were applied to HCCI engine test data to determine how the coefficient changes by the intake air temperature, engine speed and intake oxygen content. Further, the ignition timing of the HCCI combustion was estimated by the Livengood-Wu integral.

EXPERIMENTAL DESCRIPTION

Calculated Research Octane Number

The relation between hydrocarbon structure and ignitability was statistically investigated from the research octane numbers of pure hydrocarbons. Figure 2 shows the structure of paraffins, aromatics, olefins, and naphthenes. Focused on the carbon-carbon bond structure in the molecule, 9 parameters, C_1 , C_2 , C_3 , C_4 , C_o , C_n , C_b , C_{2n} , and C_d , were used: C_1 , C_2 , C_3 , and C_4 stand for the number of primary carbon atoms, secondary carbon atoms, tertiary carbon atoms and quaternary carbon atoms respectively; C_o , C_n , and C_b are for the number of olefin carbon atoms, naphthene ring carbon atoms, and benzene ring carbon atoms respectively; C_{2n} is for the number of the secondary carbon atoms in the side chains of the naphthene ring, and a dummy variable C_d was also used. Both C_{2n} and C_2 are the number of secondary carbon atoms, and these two parameters were distinguished because the ignitability changes of C_{2n} and C_2 were different in the engine test experiments. For the n-paraffins, the ignitability of hydrocarbon changes dramatically when the carbon number is higher than six. If the carbon number of the straight chain is higher than six, it is set to $C_d=1$, and if there are fewer than or just six, it is

set to $C_d=0$. The research octane number and the nine parameters (C_1 , C_2 , C_3 , C_4 , C_o , C_n , C_b , C_{2n} , and C_d) of 58 pure hydrocarbons, 17 paraffins, 17 olefins, 13 naphthenes, and 11 aromatics, are listed in Table 1, and the research octane number, statistically calculated from these 9 explanatory variables, was defined as RON_{calc} , and evaluated. (These parameters were initially expressed by number of molecules combusted with oxygen equivalents, however the correlation between the octane numbers and these parameters for the 58 hydrocarbon was very low. With trial and error, a better correlation could be achieved by the nine parameters detailed immediately above.)

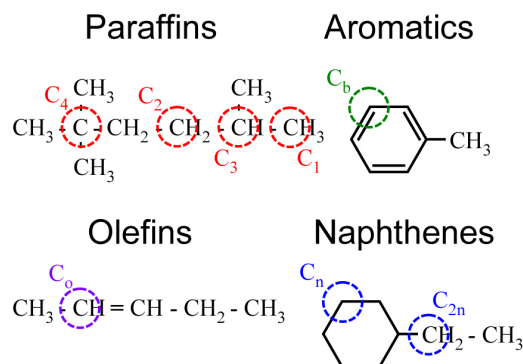


Figure 2. Hydrocarbon structures and carbon-carbon bond parameters

Engine Bench Set Up

A schematic outline of the research engine bench is shown in Figure 3. The HCCI engine employed in the experiments was a single cylinder four cycle engine, with the specifications given in Table 2. The fuels were supplied from 800 mm upstream of the intake port and a homogeneous gas charge was formed at the intake port. The intake manifold was equipped with an electric heater allowing the control of the intake air temperature up to 150 °C at 2000 rpm. The engine was equipped with a pressure transducer (Kistler 6125A) and pressure data was transmitted to a PC at 45 cycles of crank angle resolved pressure data. For all test conditions in this paper, the water jacket and engine oil temperatures were maintained at 80 °C.

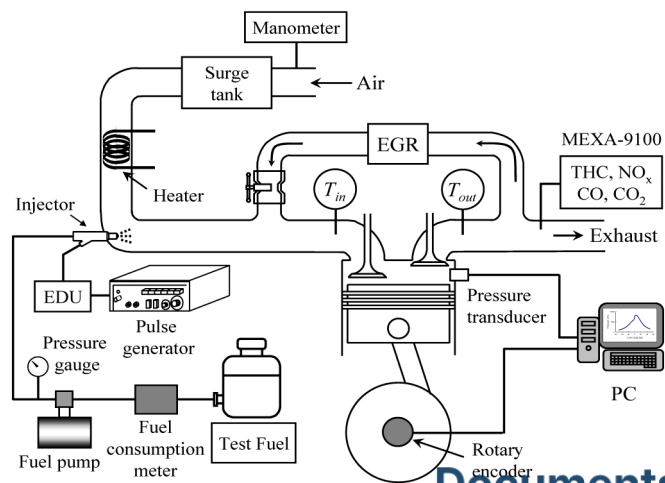


Figure 3. Outline of the engine bench

Table 1. Research octane number and structure parameters of pure hydrocarbons

Type	No.	Hydrocarbons	RON	C1	C2	C3	C4	Co	Cn	Cb	C2n	Cd	PON
Paraffin	1	n-Pentane	61.7	2	3	0	0	0	0	0	0	0	79.81
	2	n-Hexane	25	2	4	0	0	0	0	0	0	1	24.66
	3	n-Heptane	0	2	5	0	0	0	0	0	0	1	15.54
	4	iso-Pentane	92.3	3	1	1	0	0	0	0	0	0	98.07
	5	2,2-Dimethyl-Butane	91.8	4	1	0	1	0	0	0	0	0	98.07
	6	2,3-Dimethyl-Butane	103.5	4	0	2	0	0	0	0	0	0	107.2
	7	iso-Hexane	73.4	3	2	1	0	0	0	0	0	0	88.94
	8	2,2-Dimethyl-Pentane	92.8	4	2	0	1	0	0	0	0	0	88.94
	9	2,3-Dimethyl-Pentane	91.1	4	1	2	0	0	0	0	0	0	98.07
	10	2,2,3-Trimethyl-Butane	112.1	5	0	1	1	0	0	0	0	0	107.2
	11	3-Ethyl-Pentane	65	3	3	1	0	0	0	0	0	0	79.81
	12	4-Methyl-Heptane	26.7	3	4	1	0	0	0	0	0	1	24.66
	13	iso-Octane	100	5	1	1	1	0	0	0	0	0	98.07
	14	2,3,4-Trimethyl-Pentane	102.5	5	0	3	0	0	0	0	0	0	107.2
	15	2,2-Dimethyl-3-ethyl-	112.1	5	2	1	1	0	0	0	0	0	88.94
	16	2,4-Dimethyl-3-ethyl-	105.3	5	1	3	0	0	0	0	0	0	98.07
	17	2,2,3,3-Tetramethyl-	116.8	6	1	0	2	0	0	0	0	0	98.07
Olefin	18	1-Pentene	90.9	1	2	0	0	2	0	0	0	0	88.94
	19	2-Methyl-1-Butene	102.5	2	1	0	0	2	0	0	0	0	98.07
	20	1-Hexene	76.4	1	3	0	0	2	0	0	0	0	79.81
	21	2-Methyl-2-Pentene	97.8	3	1	0	0	2	0	0	0	0	98.07
	22	2,3-Dimethyl-1-Butene	101.3	3	0	1	0	2	0	0	0	0	107.2
	23	2-Ethyl-1-Butene	98.3	2	2	0	0	2	0	0	0	0	88.94
	24	2-Methyl-2-Hexene	91.6	3	2	0	0	2	0	0	0	0	88.94
	25	3,3-Dimethyl-1-Pentene	103.5	3	1	0	1	2	0	0	0	0	98.07
	26	2,3-Dimethyl-2-Pentene	97.5	4	1	0	0	2	0	0	0	0	98.07
	27	2,3,3-Trimethyl-1-Butene	105.3	4	0	0	1	2	0	0	0	0	107.2
	28	1-Octene	28.7	1	5	0	0	2	0	0	0	1	15.54
	29	2-Octene	56.3	2	4	0	0	2	0	0	0	0	70.68
	30	trans-3-Octene	72.5	2	4	0	0	2	0	0	0	0	70.68
	31	2-Methyl-2-Heptene	79.8	3	3	0	0	2	0	0	0	0	79.81
	32	2,3-Dimethyl-1-Hexene	96.3	3	2	1	0	2	0	0	0	0	88.94
	33	Diisobutylene	106	4	1	0	1	2	0	0	0	0	98.07
	34	2,4,4-Trimethyl-2-Pentene	103.5	5	0	0	1	2	0	0	0	0	107.2
Naphthen	35	Cyclopentane	101.3	0	0	0	0	0	5	0	0	0	84.04
	36	Cyclohexane	83	0	0	0	0	0	6	0	0	0	79.41
	37	Methyl-Cyclopentane	91.3	1	0	0	0	0	5	0	0	0	84.04
	38	Methyl-Cyclohexane	74.8	1	0	0	0	0	6	0	0	0	79.41
	39	1,3-Dimethyl-Cyclopentane	79.2	2	0	0	0	0	5	0	0	0	84.04
	40	Ethyl-Cyclopentane	67.2	1	0	0	0	0	5	0	1	0	56.08
	41	cis-1,2-Dimethyl-	80.9	2	0	0	0	0	6	0	0	0	79.41
	42	Ethyl-Cyclohexane	45.6	1	0	0	0	0	6	0	1	0	51.45
	43	n-Propyl-Cyclopentane	31.2	1	0	0	0	0	5	0	2	0	28.13
	44	iso-Propyl-Cyclopentane	81.1	2	0	1	0	0	5	0	0	0	84.04
	45	1,1,3-Trimethyl-	81.3	3	0	0	0	0	6	0	0	0	79.41
	46	n- Propyl -Cyclohexane	17.8	1	0	0	0	0	6	0	2	0	23.5
	47	iso- Propyl -Cyclohexane	62.8	2	0	1	0	0	6	0	0	0	79.41
Aromatics	48	Benzene	125	0	0	0	0	0	0	6	0	0	121
	49	Toluene	120.1	1	0	0	0	0	0	6	0	0	121
	50	p-Xylene	109.6	2	0	0	0	0	0	6	0	0	121
	51	Ethyl-Benzene	107.4	1	1	0	0	0	0	6	0	0	111.9
	52	1,3,5-Trimethyl-Benzene	120.3	3	0	0	0	0	0	6	0	0	121
	53	1-Methyl-3-Ethyl-Benzene	112.1	2	1	0	0	0	0	6	0	0	111.9
	54	n-Propyl-Benzene	111	1	2	0	0	0	0	6	0	0	102.8
	55	iso-Propyl-Benzene	113.1	2	0	1	0	0	0	6	0	0	121
	56	1,3-Diethyl-Benzene	115.5	2	2	0	0	0	0	6	0	0	102.8
	57	1-Methyl-4-iso-Propyl-	110.5	3	0	1	0	0	0	6	0	0	121
	58	n-Butyl-Benzene	104.4	1	3	0	0	0	0	6	0	0	93.63

Table 2. Test engine specifications

Engine type	Nissan SC-77
Number of cylinders	Single cylinder
Bore x stroke	φ 85mm x 88mm
Displacement	499 cm ³
Compression ratio	14.7

Test Fuels

The test fuels are shown in Table 3. The Base fuel is PRF 50, a mixture of equal parts of n-heptane and iso-octane. Each of the A-M fuels was a blend of 80% Base fuel and 20% of one of the 13 pure hydrocarbons. The reasons for using these hydrocarbons are the following:

1. Paraffin hydrocarbons for Fuels A-D

The n-heptane, n-hexane, n-pentane, and iso-octane were selected to investigate the effect of the length of the straight chain on the ignitability.

2. Naphthene hydrocarbons for Fuels E-G

The ethyl-cyclohexane, methyl-cyclohexane, and cyclohexane were selected to investigate the effect of the length of the side chains in naphthenes on the ignitability

3. Aromatic hydrocarbons for Fuels H-M

The toluene, o-xylene, m-xylene, ethyl-benzene, n-propylbenzene, and n-butyl-benzene were selected to investigate the effects of the number, location, and length of the side chains in these aromatics on the ignitability.

The chemical structures of these thirteen hydrocarbons (Fuels AM) are shown in Figure 4. The fuels were pressurized to 350 kPa by a fuel pump and injected from the injector controlled by the TTL (transistor and transistor logic) signal of the pulse generator synchronized with the engine cycle.

Table 3. Test fuel properties

No.	Fuel name	Base fuel 80 vol%	Added hydrocarbon 20 vol%
1	Fuel A	PRF 50 (n-Heptane 50 vol% + iso-Octane 50 vol%)	n-Heptane
2	Fuel B		n-Hexane
3	Fuel C		n-Pentane
4	Fuel D		iso-Octane
5	Fuel E		Ethyl-cyclohexane
6	Fuel F		Methyl-cyclohexane
7	Fuel G		Cyclohexane
8	Fuel H		Toluene
9	Fuel I		m-Xylene
10	Fuel J		o-Xylene
11	Fuel K		Ethyl-benzene
12	Fuel L		n-Propyl-benzene
13	Fuel M		n-Butyl-benzene

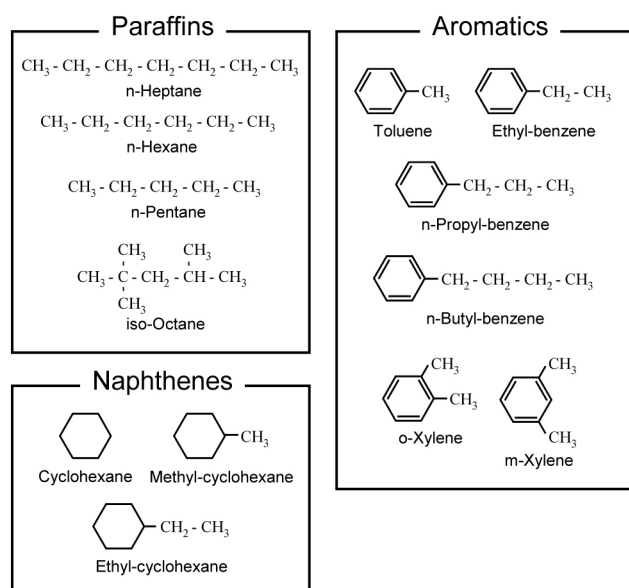


Figure 4. Chemical structure of the 13 kinds of added pure hydrocarbons

Engine Test Conditions

Three different engine tests were conducted, and the detailed test conditions are shown in Table 4.

Test 1: The Effects of Intake Air Temperature on Hydrocarbon Ignitability

The HCCI engine operated at 1400 rpm, 0.34 equivalence ratio, and 21% intake oxygen, and the effects of the intake air temperature, 50, 100, and 150 °C, on the ignitability of the HTHR investigated.

Test 2: The Effects of Engine Speed on Hydrocarbon Ignitability

The HCCI engine operated at 21% intake oxygen content, 0.34 equivalence ratio, and 150 °C intake air temperature, and the effects of the engine speed, 1000, 1400, and 1800 rpm, on the ignitability of the HTHR investigated.

Test 3: The Effects of Intake Oxygen Content by EGR on Hydrocarbon Ignitability

The HCCI engine operated at 1400 rpm and 150 °C intake air temperature, and the effects of the intake oxygen concentration, varied by EGR, 21, 19, and 17%, on the ignitability of the HTHR investigated.

Table 4. Engine test conditions

	Engine speed [rpm]	Test fuel equivalence ratio	T_{in} [°C]	$O_{2\ in}$ [%]
Test1	1400	0.34	50	21
			100	
			150	
Test2	1000	0.34	150	21
	1400			
	1800			
Test3	1400	0.34	150	21
		0.37		19
		0.44		17

Definition of Heat Release Data

Figure 5 shows the heat release data of the HCCI engine test and the two heat releases of the LTHR and HTHR are clearly distinguishable. All the heat release data and in-cylinder temperatures in this paper were calculated from an average of 45 cycles of cylinder pressure data. The heating values of the LTHR and HTHR are calculated independently and the HTHR CA10 is the crank angle timing when 10% of the HTHR combustion is complete and defined as the start of the HCCI combustion. The crank angle resolution is 0.2 CA degrees.