Research Report

Influence of Properties and Composition of Diesel Fuels on Particulate Emissions
Part 2. Fuels for Single-Cylinder Engine Test in the Combustion Analysis for the WG of JCAP

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Abstract

To clarify the influence of the composition of aliphatic hydrocarbons and aromatic hydrocarbons on emissions, two series of fuels were prepared by the Combustion Analysis Working Group of the Japan Clean Air Program. The two series of fuels, which were named "Aliphatic fuels" and "Aromatic fuels", respectively from their compositions in this paper, were analyzed using precise analytical methods. In addition, the relationship between the fuel properties and particulate emissions from a single-cylinder engine was also regressively analyzed. As a result, the particulate emissions from "Aromatic fuels" were estimated by the backend fraction and the H/C of the fuels, whereas the particulate emissions from "Aliphatic fuels" could not be estimated by the two parameters. The particulate emissions from "Aliphatic fuels" were found to be influenced by the composition of structural isomers, which cannot be evaluated using the H/C. For the "Aliphatic fuels", the relationship between the fuel properties and particulate emissions were explained by precise analytical results for the fuels.

Keywords Diesel fuel, JCAP, Particulate matter (PM), Combustion analysis WG, Precise analyses, Multiple regression analysis

1. Introduction

From the point of view that improvement not only on vehicles, but also in fuel is necessary to reduce automobile emissions, a cooperative research study between automobile manufacturers and petroleum companies, named the Japan Clean Air Program (JCAP), was launched in Japan, following the European Programme on Emissions, Fuels and Engines technologies (EPEFE).[1, 2] In the JCAP, the relationship between fuel properties and diesel emissions were investigated by the Diesel Working Group (WG) and the Combustion Analysis WG.

In a previous paper: Part 1 of this report,[3] the relationship between fuel properties and the particulate matter (PM) emissions and soluble organic fraction (SOF) emissions obtained in the existing-step and the model-step were investigated. From the results, the PM emissions from the existing-step fuels and the model-step fuels could be explained by the backend fraction and the H/C of the fuels, and the relationship between the fuel properties and the SOF emissions were interpreted from the results of precise analyses. These results were accepted by the Combustion Analysis WG , in addition to the Diesel WG . As a result, precise analyses of the fuels tested with a single-cylinder engine were entrusted to Toyota Central R&D Laboratories, by the Combustion Analysis WG . Therefore, fuels were analyzed by precise analytical methods. We also analyzed the relationship between the fuel properties and either the PM emissions or the SOF emissions, regressively, and interpreted them using the results of the precise analyses.

2. Single-cylinder engine test

The main focus of the Combustion Analysis WG was to scientifically analyze the results obtained from the Diesel WG and to obtain information, useful for reducing emissions. In the fiscal year of 2001, the influence of the parameters concerning fuel properties and engine conditions, shown in **Table 1 and 2**, on emissions were investigated using a single-cylinder engine, with the specifications shown in **Table 3**.[4] The fuel properties and the analytical results of the fuels analyzed by conventional methods are shown in **Table 4**. As shown in Table 4, cetane numbers for these fuels, with the exception of fuels-T6, T7 and T12 (Table 4), were unified at the cetane number for fuel-T1S (Table 4).

3. Precise analyses of fuels

As shown in Table 4, the fuels for the single-cylinder engine test were prepared in an effort to clarify the influence of the structural isomerism of hydrocarbons on the emissions. For the purpose, these fuels were analyzed using some of the precise analytical methods,[5] including Field Ionization Mass Spectrometry (FIMS) and Carbon-13 Nuclear Magnetic Resonance Spectrometry (^{13}C-NMR). From FIMS, distributions along with double bond equivalence values (DBE) and carbon number distributions of the same DBE hydrocarbons, in other words, compositions along with molecular formulas, are obtained, as shown in **Fig. 1**. From

Table 1 Examined fuel parameters.

Fuel	Parameter	Unit
	Aliphatic Fuel	
T1, T9, T10, T12	T_{90}	
T1, T6, T7	n-Paraffin/ i-Paraffin	
T1, T5	Cycloparaffin	
	Aromatic Fuel	
T1S, T2, T3S, T4S	Number of Aromatic-ring	
T1S, T14, T15, T16, T17	Side-chain Structure of Mono-aromatic	

Note) T1, T1S : Base Fuel

Table 2 Examined engine parameters.

Intake System	Natural Aspiration, Turbo Charger	
Nozzle Hole Diameter	0.16, 0.18, 0.20, 0.25	mm
Excess Air Ratio (λ)	1.4, 4.0	
Injection Timing	-9, -6, -4, -2, 0.3	deg
Injection Pressure	30, 40, 50, 60, 100	MPa
Load	Heavy, Light	
Exhaust Gas Recirculation (EGR)	With (Hot), Without	

Table 3 Engine specifications.

Engine Type	Single-cylinder, Direct Injection	°C
Bore×Stroke	108φ×115	mm×mm
Displacement	1,053	mL
Compression Ratio	18.0	

^{13}C-NMR, concentrations of four kinds of carbons, that is, carbons in straight-chain, carbons at a branch (strictly speaking, carbons near branch), carbons in a double bond or triple bond and carbons in aromatic-rings were obtained.

In addition to FIMS and ^{13}C-NMR, these fuels were analyzed by Gas Chromatography (GC) in order to obtain the carbon number distributions of n-paraffins and i-paraffins, and analyzed by Gas Chromatography/ Mass Spectrometry (GC/MS) in order to identify the hydrocarbons added into the "Aromatic fuels".

4. Results of precise analyses of fuels

In this paper, an outline of the results of the precise analyses of fuels is described, since the details have already been published in the JCAP annual reports.[6)]

4. 1 Results of FIMS

From FIMS spectrum, which consists of molecular weights and the number of molecules, distributions along with DBE, so-called DBE distributions, and carbon number distributions of the same DBE hydrocarbons were obtained. **Figure 2** through **5** show the results. Interpretations of Figs. 2 and 3 are

Table 4 Properties and analytical results of fuels for single-cylinder engine test.

Group		Aliphatic-fuels							Aromatic-fuels							
Examined Influence		Base	T$_{90}$		i-P/n-P			Naph-thene	Base	Aromatic-ring			Side-chain/ Mono-arom.			
Test Item		T1	T9	T10	T6	T7	T12	T5	T1-S	T2	T3-S	T4-S	T14	T15	T16	T17
Density g/cm3		0.788	0.785	0.792	0.785	0.782	0.775	0.797	0.788	0.808	0.834	0.838	0.800	0.799	0.825	0.819
Distillation	IBP	213.5	213	211	218.5	222.5	235.5	211	218.5	190.5	224	221.5	181	223	214.5	230.5
JIS K2254	5vol%	228.5	229.5	229	231	234	247.5	223	228.5	207.5	231.5	231	192	232.5	221.5	239
vol. %	10vol%	229.5	230.5	233	232	234.5	249	225	230.5	210.5	234	235	196.5	235	224	241
	20vol%	234	234.5	237	237	240	254	227.5	235.5	222	237.5	240	209	239	229.5	244
	30vol%	239	240	242	241.5	244.5	261.5	231	240.5	233	241	244	225	245	236	248
	40vol%	244	243.5	248.5	247.5	250	269	236	244.5	246.5	245	249	241.5	250	244.5	251.5
	50vol%	249	247.5	254.5	253.5	256.5	276	243	250.5	257.5	250.5	255.5	253	256	254.5	255.5
	60vol%	254.5	251.5	264.5	261	267	284.5	251.5	257	265	258	265.5	260.5	263.5	264.5	261.5
	70vol%	265.5	256	283.5	273	282	293.5	264.5	267	272	272.5	281.5	268.5	273.5	273	270
	80vol%	283.5	263	335	293	300	303	281	284	281	297	301.5	281	287	282.5	284
	90vol%	307	275	387.5	311	313	313.5	304	308.5	299.5	314	313.5	301	301.5	302.5	305
	95vol%	318.5	286	395.5	320	321	319.5	326.5	320	324	324	*	324	310	333.5	325
	97vol%	324	290.5	396	326.5	327	322.5	331	327	330	331.5	*	340	315.5	340	334
	EP	326	295.5	396.5	327	327.5	324	335	329	335	332	*	340.5	318.5	340.5	334.5
	R290*1	17.0	3.0	29.0	21.0	25.0	34.0	16.0	18.0	15.0	23.0	26.0	15.5	18.0	16.0	17.0
Cetane Number*2	JIS K2280	48.8	48.6	48.5	60.4	70.7	97.8	49.2	50	48.7	50.2	50.1	50.8	51.6	51.8	51.1
Sulfur mass ppm	JIS K2541	0	0	0	0	0	0	0	0	0	8	173	0	0	0	0
H/C		2.118	2.101	2.101	2.085	2.085	2.184	2.068	2.201	2.019	1.889	1.873	2.019	2.085	1.937	1.986
Composi-	n-Paraffin	36	35	24	50	63	100	25	36	45	42	42	44	40	45	43
tion from	i-Paraffin	57	58	70	44	32	0	47	57	28	33	33	29	36	28	31
Preparation	Naphthene	7	7	6	6	5	0	28	7	7	5	5	7	4	7	6
vol. %	Mono-aromatics									20	0	0	20 (Short-R benzene)	20 (Long-R benzene)	20 (Tetraline)	20 (Phenyl cyclohexane)
	Di-aromatics									0	20	15				
	Tri-aromatics									0	0	5				

*1: Read from reconstructed distillation curve.

*2: No fuels include cetane improver.

described in columns-c, and d of **Table 5**, and the interpretations of Figs. 4 and 5 are described in column-f of Table 5. It is important to note, the carbon number distributions shown in Figs. 4 and 5 were classified by the pattern, and shown in column-e of Table 5. As seen in column-e, the n-paraffins in the fifteen fuels were found to be classified into 6 types: type-A, type-B, type-C, type-C', type-D, and type-E.

4. 2 Results of GC

It was found that even if ionized by field ionization (FI), i-paraffins do not produce molecular ions. Furthermore, five aliphatic fuels, excluding T5 and T12, consist of n-paraffins and i-paraffins, which amount to 93% to 95% in total, and include ≤ 7% of cycloparaffins. It was therefore thought that the carbon number distributions of i-paraffins in the fuels could be obtained using GC. The gas chromatograms of them were processed as follows. The peaks that appeared between the n-paraffin peak of carbon number n (Cn) and the n-paraffin peak of carbon number n+1 (Cn+1) were assigned to i-paraffins of carbon number n+1(Cn+1). Then, the peak areas of these i-paraffins were calculated. The peak areas were plotted against the carbon number. **Figure 6** shows the carbon number distribution of i-paraffins. From Fig. 6, the following results observations were made.

1) Though the carbon number distributions of i-paraffins in the five fuels are similar each other, they are classified into three types. The results of this classification are shown in column-g of Table 5.

2) The carbon number distributions of i-paraffins in the five fuels are located at a lower carbon number than the carbon number distributions of n-paraffins in the fuels. Namely, n-paraffins in these fuels correspond to high boiling point components and i-paraffins correspond to low boiling point components.

4. 3 Results of GC/MS

The number of molecular formulas of aromatic hydrocarbons in "Aromatic fuels" was found to be

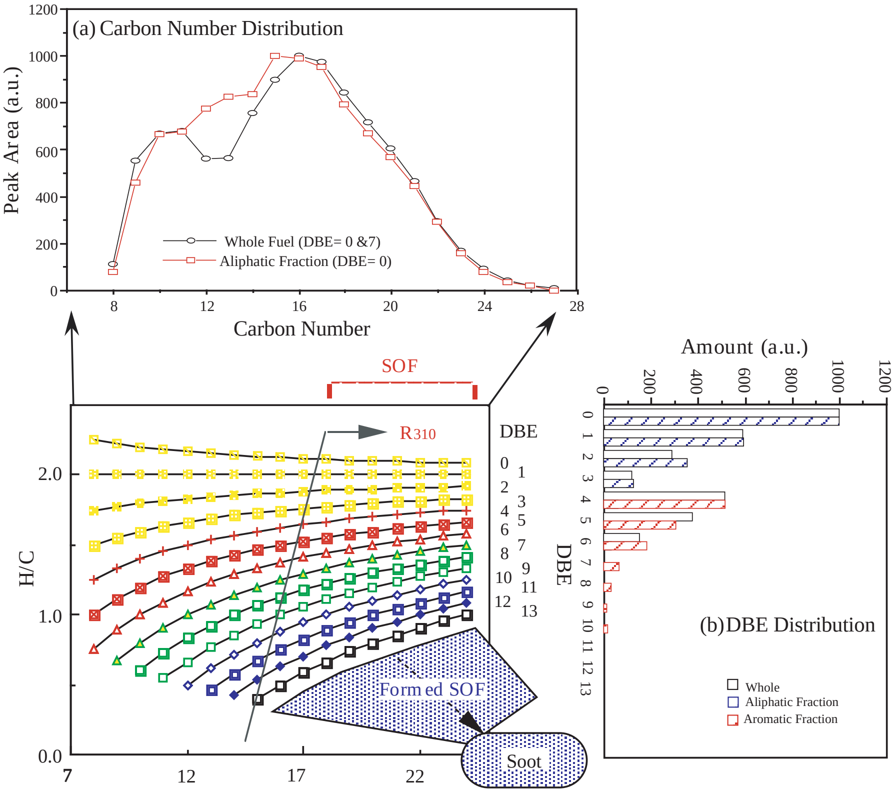


Fig. 1 Precise analytical results of diesel fuel and PM formation.

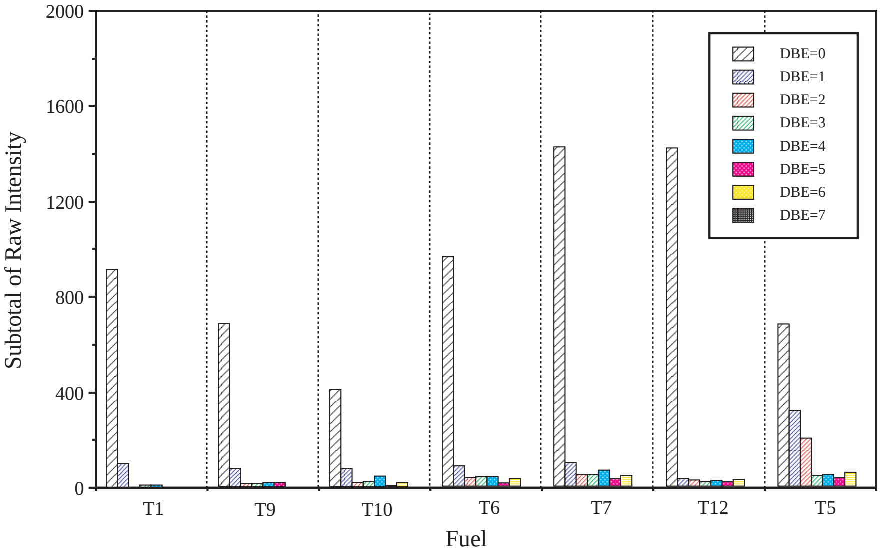


Fig. 2 DBE distributions of "Aliphatic Fuels".

less than ten, by FIMS. Therefore, these aromatic hydrocarbons were identified by GC/MS. Aliphatic fuel T10 was also analyzed by GC/MS, because T10 was observed to contain high boiling point hydrocarbons, by GC. Columns-j, k, l of Table 5 show the name, the H/C and the boiling points of identified hydrocarbons. **Figure 7** shows the relationship between the distillation temperature at which 90% of the fuel has been evaporated (T_{90}) for "Aromatic fuel" and the boiling point of the aromatic hydrocarbon in the "Aromatic fuel", where the T_{90} was used instead of the boiling point of whole fuel. **Figure 8** shows the relationship between the ratio of hydrogen to carbon (H/C) of "Aromatic fuel" and the H/C of aromatic hydrocarbons in the "Aromatic fuel". From Figs. 7 and 8, the either the boiling point or H/C of the added aromatic hydrocarbon, was reflected upon in either the the T_{90} or H/C of the whole fuel.

It is important to note, that differences were seen in many properties among the aromatic hydrocarbons added into the "Aromatic fuels". For example, there are differences in chain length, substituted number and chain structure, between i-butylbenzene in T14 and C18 alkylbenzene in T15. Accordingly, it was found that at least, two kinds of hydrocarbons (n-butylbenzene and n-dodecylbenzene) must be added into "Aromatic fuels" to clarify the influence of the structure of aromatic hydrocarbons on emissions.

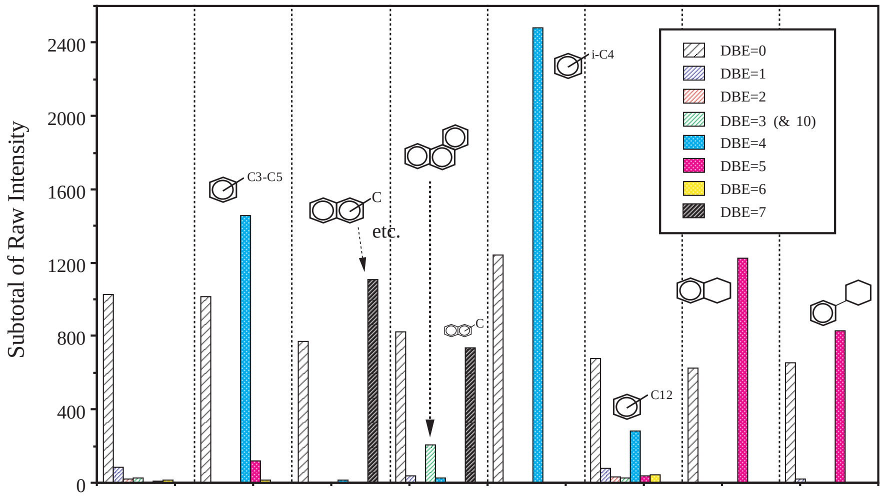


Fig. 3 DBE distributions of "Aromatic Fuels".

4. 4 Results of ^{13}C-NMR

The concentration of the carbon at branches in paraffins including i-paraffin and cycloparaffin was read from the ^{13}C-NMR spectra. The concentrations of the carbon at branches are shown in column-i of Table 5. The concentrations were plotted in **Fig. 9**, against the concentration of the i-paraffin in preparation. (Table 4).

From Fig. 9(a), it was found that the concentrations of carbon at branches showed a strong correlation with the concentration of the i-paraffin in preparation for the "Aliphatic fuels", with the exception of T5, in which the concentration of cycloparaffin was 28%. This indicates that the compositions of i-paraffin and other hydrocarbons, cycloparaffin in the case of "Aliphatic fuels", are about the same.

From Fig. 9(b), it was found that a linear relationship could not be seen between the concentration of carbon at the branch and the concentration of the i-paraffin, for the "Aromatic fuels". Thus, the added aromatic hydrocarbons, for instance, i-butylbenzene in T14 or phenylcyclohexane in T17, include the carbon at the branch in their alkyl-moiety.

5. Relationship between fuel properties or fuel compositions and PM emissions

Among the 52 sets of emission data obtained for the fuels shown in Table 1, and the engine conditions shown in Table 2, 14 sets of emission data were obtained by natural-aspiration-type engines without an exhaust gas recirculation (EGR) or a catalyzer.

The 14 sets emission data were classified by engine load and injection pressure, into four groups: (1) heavy load and high pressure, (2) heavy load and middle pressure, (3) light load and middle pressure, and (4) light load and low pressure.

Each group consisted of three to four sets of emission data: PM (SOF and soot) and nitrogen oxide (NOx), obtained for different fuel-injection timings. In this paper, data averaged from three to four sets of data were used to analyze the relationship. Of these averaged emissions, the average of SOF, soot and PM emissions are shown in Table 7 and **Figs. 10** and **11**. Where, Figs. 10 and 11 show the H/C, the R_{290} and the results of type-analyses (concentrations of n-paraffin, i-paraffin, and cycloparaffin) in addition to the SOF and soot emissions. From these figures, the information described in the next section was obtained.

5. 1 "Aliphatic fuels"

5. 1. 1 Influence of T_{90} and i-paraffin (T1, T9, T10)

The higher the T_{90} of the fuel was, the greater the SOF emission was under a light load, or the more the soot emission was under a heavy load. While i-paraffins in T9 consisted of low boiling point components, i-paraffins in T10 included a high boiling point component, squalane (i-$C_{30}H_{62}$).

Table 5 Summary of Results of FIMS, GC, ^{13}C-NMR and GC/MS.

Fuel	Design	FIMS				GC		^{13}C-NMR	GC/MS	H/C & b.p. of Aromatics	
a	b	c	d	e	f	g	h	i	j	k	l
		DBE of Aliphatics - Comparing with that of T1 -	DBE of Aromatics*	n-P	CND of n-Paraffin - Comparing with that of T1 -	i-P	CND of i-Paraffin - Comparing with that of T1 -	Branched Carbon	Additive	H/C	b.p.
T1	Basefuel	Concentration of paraffin in T1, T9 and T10 are 93-94%. Ion intensities of DBE=0 are not related to their paraffin concentration. It is thought that i-P/ n-P of T1, T9. T10 are different.		A		a		49.15			
T9	Lower T90			C	High MW HC and low MW HC are less.	b	In comparison with T1, high MW HC is less.	55.54			
T10	Higher T90			C	Low MW HC is less.	c	High b.p. HC is added.	39.56	Squalane (i-C30H62)		
T6	Less i-Paraffin	Paraffin (DBE=0) in T6, T7 are more than that in T1. T6, T7 include a little HC of DBE ≧4.		A	The same.	a	CND of i-Paraffin is the same as that of T1.	30.14			
T7	Lesser i-Paraffin			A	The same.	a	CND of i-Paraffin is the same as that of T1.	50.82			
T12	n-Paraffin only	Includes HC of DBE=1 - 6 (Contamination ?).		D	CND is wider than that of T1. High MW HC is more.	-		----			
T5	More cycloparaffin	Includes much cycloparaffin (DBE=1, 2).		B	High MW HC is less.	-		59.75	Cycloparaffins (C10-C14)		
T1-S	Basefuel			A	High MW HC is more.	a		49.16			
T2	Mono-aromatics		DBE=4, C9-C11	B	High MW HC is less.	-		36.30	Alkylbenzene (C9-C11)	1.4	<201
T3-S	Di-aromatics		DBE=7, C11	A	The same.	-	Composition of i-paraffin is different with that in T1S?	30.78	Methylnaphthalene	0.99	241-245
T4-S	Tri-aromatics		DBE=7, C11 DBE=10, C14	A	The same.	-	Composition of i-paraffin is different with that in T1S?	30.49	Methylnaphthalene & Phenanthlene	0.92**	268***
T14	Short-alkyl-benzene		DBE=4, C10	B	High MW HC is less.	-		40.88	i-Butylbenzene	1.4	173
T15	Long-alkyl-benzene		DBE=4, C18	A	The same.	-		40.52	Many isomers of C18	1.66	180/13
T16	Tetraline C10H12 (DBE=5) H/C=1.20		DBE=5, C10	B	High MW HC is less.	-		28.59	Tetraline	1.2	207
T17	Phenyl-cyclohexane C12H16 (DBE=5) H/C=1.33		DBE=5, C12	E	Low MW HC is a little.	-		40.36	Phenyl-cyclohexane	1.33	235

*: Discrimination of hydrocarbons with DBE = n and DBE = n+7 was done by GC/MS.
**: = 0.99×(15/20) + 0.71×(5/20)
***: = 241×(15/20) + 339×(5/20)

A: C12-C18 & C20
B: C12-C16
C: C14-C16
C': C14-C16 & C20
D: C12-C20
E: C13-C18 & C20

a: C11-C15 & C16-C18, C20
b: C11-C16
c: C11-C16 & C30

5. 1. 2 Influence of n-paraffin and high boiling point component (T1, T6, T7, T12)

1) Boiling points of n-paraffins are higher than those of i-paraffins, in T1, T6 and T7. This means that n-paraffins in T1, T6 and T7 are higher in flammability than i-paraffins, in T1, T6 and T7.

2) As n-paraffin increases, high boiling point components increase, in T1, T6, T7 and T12.

3) As n-paraffin increases, SOF emissions decrease, in the case of T1, T6, and T7.

The order of the concentrations of n-paraffin: T1 < T6 < T7. The order of the SOF emissions: T1 > T6 > T7

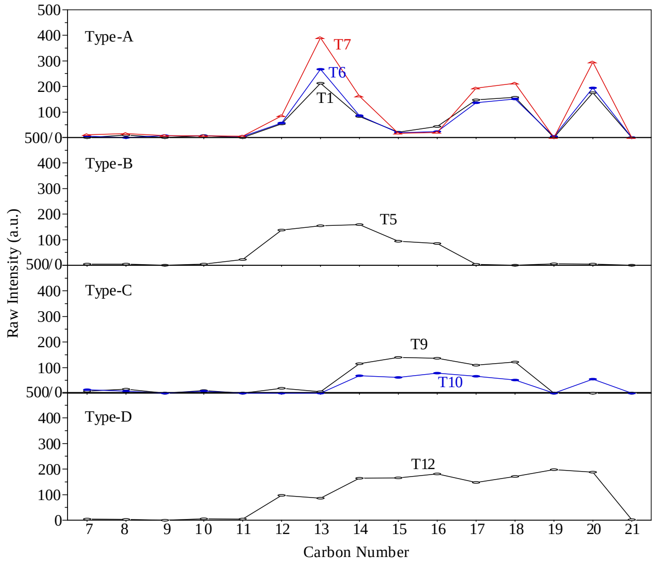


Fig. 4 Carbon number distributions of n-paraffins in "Aliphatic Fuels".

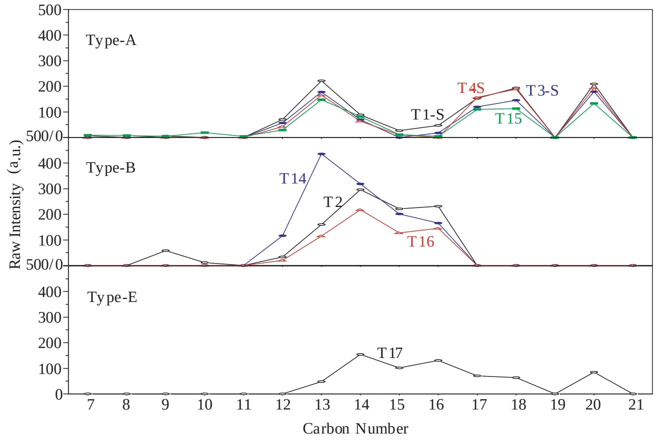


Fig. 5 Carbon number distributions of n-paraffins in "Aromatic Fuels".

This is thought to be caused by the decrease in HC emissions, because n-paraffins are the most flammable hydrocarbons.

4) Though T12 consists of only n-paraffins, it emits both SOF and soot in higher amounts, because the R_{290} of T12 is very high, that is, T12 includes many high boiling point n-paraffins.

High SOF emission under a light load was thought to be due to high boiling point components, which exist in T12 in large amounts.

High soot emission under a heavy load was thought to be due to the high flammability of T12, since the n-paraffins in T12 ignite before fully diffusing into a combustion chamber.

Development of an engine, which is suitable for flammable fuels, is thought to be required to further reduce the PM emissions.

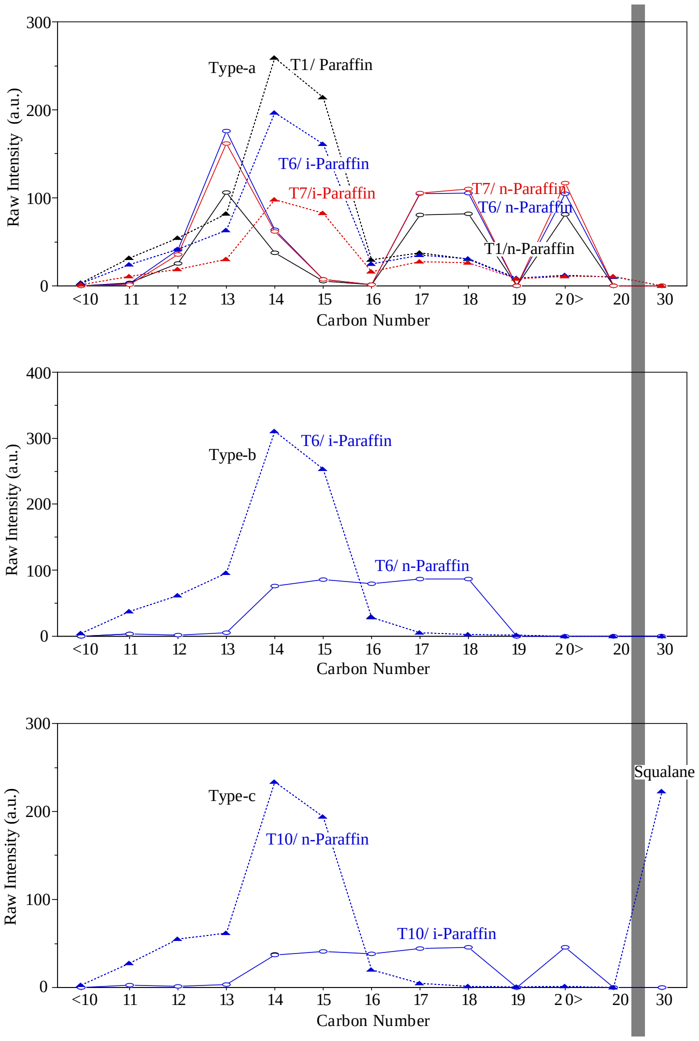


Fig. 6 Carbon number distributions of i-paraffins in "Aliphatic Fuels".

5. 1. 3. Influence of cycloparaffins and high boiling point components (T1 and T5)

As cycloparaffins increase, SOF and soot emissions increase under middle injection pressure. Though the boiling points of cycloparaffins in T5 are low, the soot emission under a heavy load was slightly high, because the thermal stability of cycloparaffins is high.

5. 2. "Aromatic fuels"

5. 2. 1. Influence of aromatic-ring and high boiling components (T1, T2, T3-S, T4-S)

1) The higher the number of aromatic-rings added to the aromatic hydrocarbon was, that is, the higher the boiling point of added aromatic hydrocarbon was, the more SOF and soot emissions there were.

2) An increase in the SOF and soot emissions was due to the high boiling point and high thermal stability of aromatic hydrocarbons (Figs. 7 and 11).

5. 2. 2 Influence of side-chain of aromatic hydrocarbon (T14, T15, T16, T17)

The higher the H/C of an aromatic hydrocarbon is, the lesser the SOF and soot emissions were, for T14,

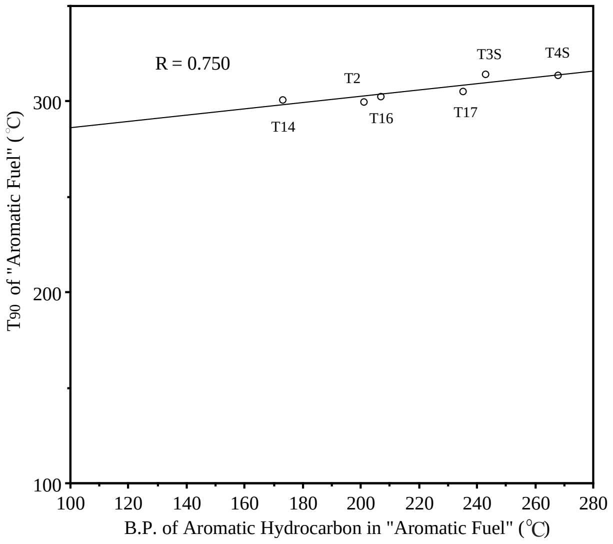


Fig. 7 Boiling point of aromatic hydrocarbon in "Aromatic Fuels" and T_{90} of "Aromatic Fuels".

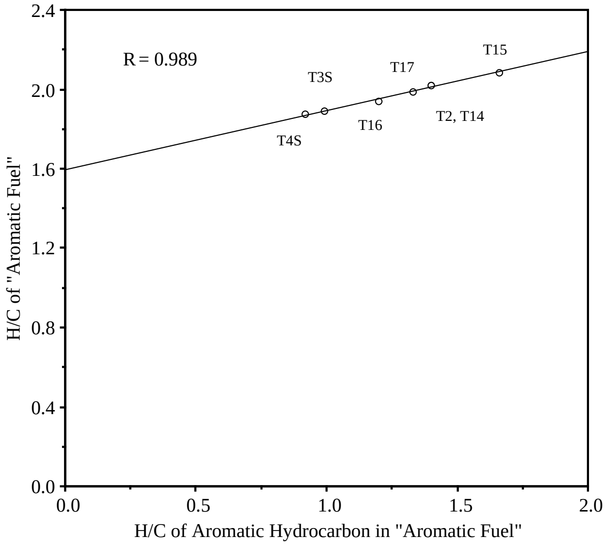


Fig. 8 H/C of aromatic hydrocarbon in "Aromatic Fuels" and H/C of "Aromatic Fuels".

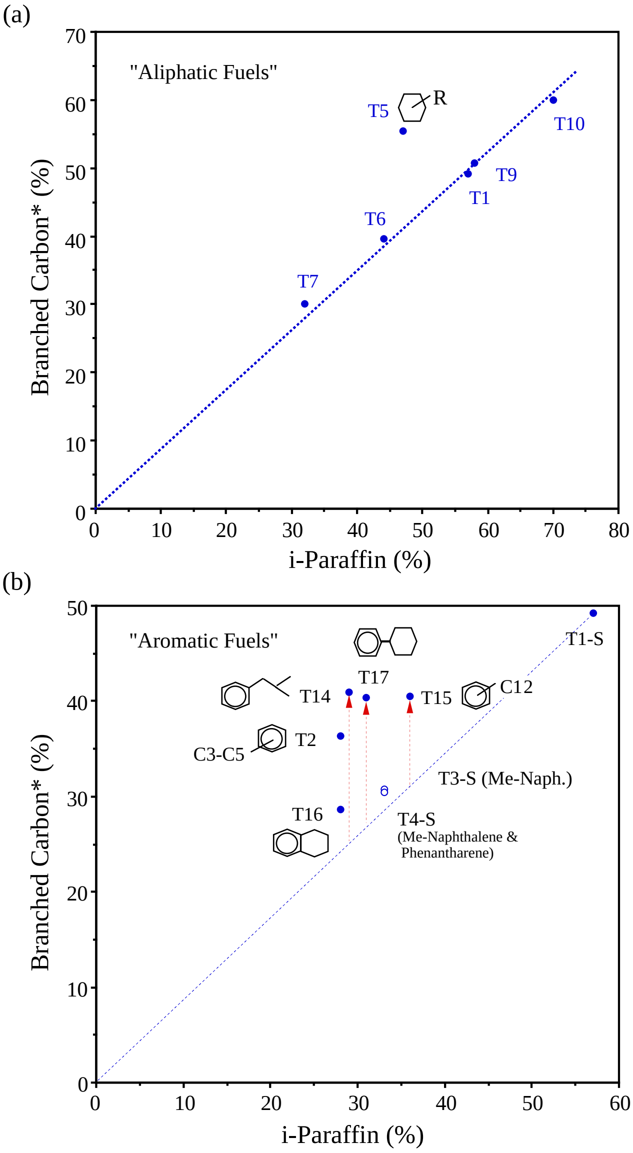


Fig. 9 Prescribed concentration of i-paraffin and amount of branched carbon* in "Aromatic Fuels" and "Aromatic Fuels" measured by ^{13}C-NMR
*: Branched carbon = Peak (0-60) - Peak (14) - Peak (22) - Peak (29) - Peak (32).
Where, the number in brackets show the chemical shift in ppm.

T15, T16 and T17 (Fig. 8 and 11).

6. Estimation of PM emission

The PM emissions shown in **Table 7**, were regressively analyzed by the backend fraction and the H/C shown in Table 4.

That is, PM emissions were analyzed using Eq. (1) established in a previous paper.[3)]

$$\mathrm{PM} = a \times R_{290} + b \times (H/C) + c \quad \cdots\cdots\cdots (1)$$

Where, the backend fraction at a distillation temperature of 290°C was used for calculations in this paper. Incidentally, Eq. (1) does not include a parameter concerning the sulfur content, because all of the fuels do not contain sulfur, with the exception of T4-S.

6. 1 Estimation of PM emission from "Aliphatic fuel"

As described thus far, "Aliphatic fuels": T1, T5, T6, T7, T9, T10 and T12 were the fuels in which the concentrations of n-paraffin and i-paraffin were varied or the isomeric compositions of n-paraffins and i-paraffins were varied.

On the other hand, the backend fraction and the H/C in Eq. (1) were not able to discriminate n-

Table 6 Properties of aromatic hydrocarbons in T14-T17 and n-butylbenzene.

Fuel	Type	DBE	C.No.	H/C	b.p. (°C)	Parameters which influence on PM*	Remarks
T14	i-Butylbenzene (Cumene)	4	10	1.4	153	vs. T15 C.N.*, Structure (b.p.) vs. T16 DBE, Structure (b.p.) vs. T17 DBE, C.N., Structure (b.p.)	By comparing with n-butylbenzene, the influence of branch will be clarified.
T15	Alkylbenzene of C18	4	18	1.7	288	vs. T16 DBE, C.N., Structure (b.p.) vs. T17 DBE, C.N., Structure (b.p.)	Main component is not long-chain alkylbenzene. C18-alkylbenzenes consist of many isomers: multi-substituted and/or with various alkyl-groups.
T16	Tetraline (Tetrahydronaphthalene)	5	10	1.2	207	vs. T17 C.N., Structure (b.p.)	Tetraline has 4 alicyclic-methylenes.
T17	Phenylcyclohexane	5	12	1.3	236		Phenylcyclohexane has a cyclohexyl-group.
Std.	n-Butylbenzene	4	10	1.4	183	vs. T14 Structure (b.p.)	Indispensable compound for clarifying influence of side-chain structure of mono-aromatics.

*: Cetane Number

Table 7 Averages of emissions at different engine conditions.

Run No.	Item	unit	T1	T5	T6	T7	T9	T10	T12	T2	T3-S	T4-S	T14	T15	T16	T17
			Load: Heavy, λ=1.4, Nozzle=0.18mm, Timing: -2 ~ 4°, Inj. Pressure=100MPa													
1 - 4	SOF	mg/kWh	6	7	9	7	4	6	11	6	7	11	6	6	8	8
	Soot	mg/kWh	86	88	90	96	82	97	113	118	121	159	108	106	123	119
	PM	mg/kWh	92	95	99	103	86	103	124	124	128	170	114	112	131	127
			Load: Heavy, λ=1.4, Nozzle=0.25mm, Timing: -6 ~ 0°, Inj. Pressure=60MPa													
15 - 18	SOF	mg/kWh	11	24	8	3	11	14	23	17	13	31	17	17	17	15
	Soot	mg/kWh	533	607	493	479	485	597	695	712	786	980	710	694	583	797
	PM	mg/kWh	544	631	501	482	496	611	718	729	799	1011	727	711	600	812
			Load: Light, λ =4, Nozzle=0.18mm, Timing: -6 ~ 0°, Inj. Pressure=50MPa													
33 - 35	SOF	mg/kWh	145	153	124	115	163	213	174	218	192	230	159	143	174	181
	Soot	mg/kWh	120	133	122	143	102	120	198	166	224	293	202	186	234	207
	PM	mg/kWh	265	286	246	258	265	333	372	384	416	523	361	329	408	388
			Load: Light, λ =4, Nozzle=0.25mm, Timing: -9 ~ -3°, Inj. Pressure=30MPa													
40 - 42	SOF	mg/kWh	181	233	246	170	139	320	292	256	290	362	233	208	271	248
	Soot	mg/kWh	696	677	885	939	697	748	857	826	1006	1279	901	794	995	815
	PM	mg/kWh	877	910	1131	1109	836	1068	1149	1082	1296	1641	1134	1002	1266	1063

paraffin and i-paraffin. Accordingly, the PM emission from "Aliphatic fuels" could not be estimated using Eq. (1), thus, it was needless to do analyses using Eq. (1).

As a reference, the results of regression analyses for the PM emission from "Aliphatic fuels" are shown in **Table 8(a)**. In addition, PM emissions observed and estimated by Eq. (1) shown in the right column and the central column of **Table 9(a)**, respectively, were plotted in **Fig. 12**. From Figure 12, it was found that these PM emissions were not estimated, with the exception of the PM emissions under a heavy load and a high injection pressure.

6. 2 Estimation of PM emission from "Aromatic fuel"

PM emissions from "Aromatic fuels" were analyzed using Eq. (1). Table 8(b) shows the results. In addition, PM emissions observed and estimated by Eq. (1), shown in the right column and the central column of Table 9(b), respectively, were plotted in **Fig. 13**. From Fig. 13, it was found that PM emissions under every engine condition were well estimated, except for the PM emissions from T3-S. Furthermore, while the determination coefficients for the fuels including the T3-S, range from 0. 694 to 0. 831, the determination coefficients for the fuels excluding T3-S, range from 0. 938 to 0. 975. Incidentally, the deviations from the regression line in Fig. 13 reflect the differences in thermal stability of the hydrocarbons.

7. Analyses of ultra-low aromatic fuel

Diesel fuels marketed before long-term exhaust gas regulation or marketed before desulfurization of diesel fuel, consisted of the hydrocarbons of a DBE of 0 to 13 and included about 130 kinds of molecular

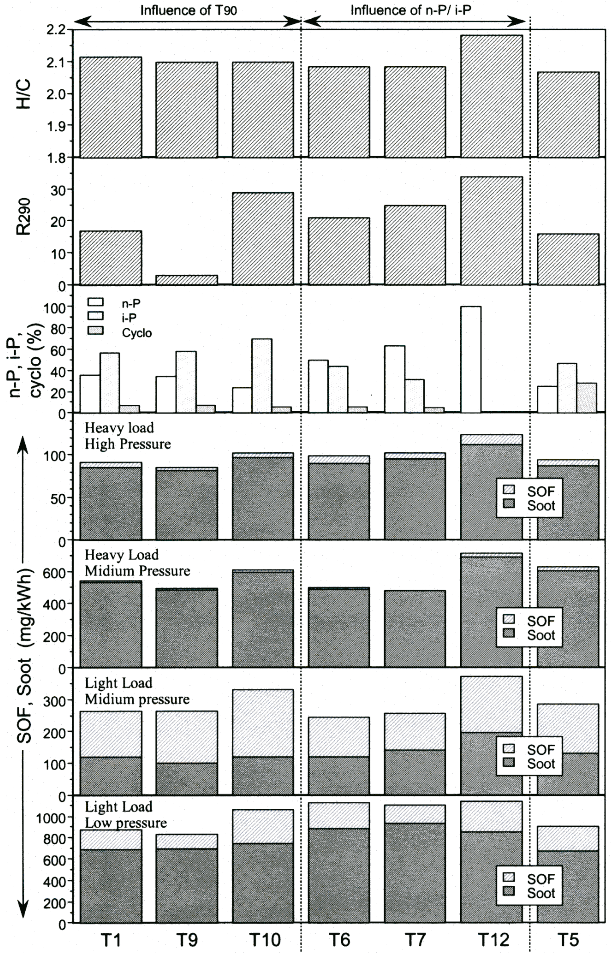


Fig. 10 Fuel properties and SOF and soot emissions from "Aliphatic Fuels".

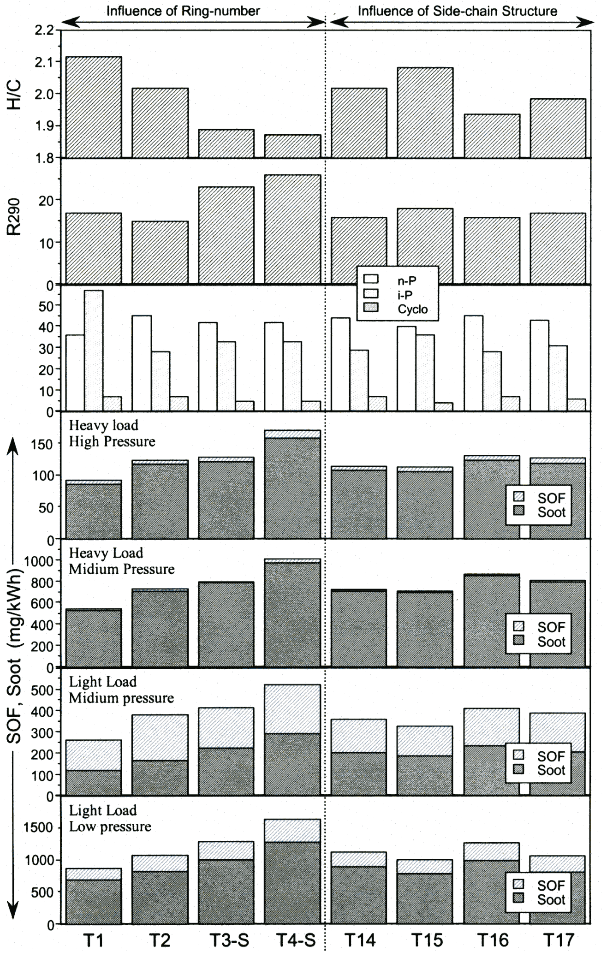


Fig. 11 Fuel properties and SOF and soot emissions from "Aromatic Fuels".

formulas of aromatic hydrocarbons as shown in **Fig. 14**(a).[5] However, as desulfurization of diesel fuels has proceeded, the amount and kinds of aromatic hydrocarbons, with a DBE of four or more, have decreased.

It is important to note that, both number of the molecular formula and amount of aromatic hydrocarbons in Swedish Class-1 fuels, which appeared on the market in the early 1990s as ultra-low aromatic fuels, were extremely small and consisted of hydrocarbons with a DBE of zero to six or seven, as shown in Fig. 14(b).[5] In addition, Gas to Liquid (GTL), which was announced as a fuel resulting in lesser PM emissions than Class-1, by the Department of Energy of the United States of America in 1998[7] consists of mainly hydrocarbons with a DBE of zero, that is, n-paraffins and i-paraffins, as shown in Fig. 14(c).[8]

In an evaluation of ultra-low aromatic fuels such as Class-1 or GTL, type-analysis along with aromatic ring number is almost meaningless. For these fuels, more detailed analyses, which discriminate or evaluate isomers of hydrocarbons, are necessary. However, the complete discrimination of the isomers in a diesel fuel is impossible, because the number of isomers in diesel fuel amounts to 10 thousands or more. Accordingly, development of a simple method, next to the complete isomer discrimination and identification will be a theme in the future.

Table 8 Results of regression analyses of PM emissions from single-cylinder engine.

Load	Injection	PM = a × R_{290} + b × (H/C) + c					
	Pressure	Multiple R	R^2	Std. Div.	a	b	c
(a) Aliphatic Fuel: T1- T12							
Heavy	High	0.953	0.908	4.512	0.849	121.766	-173.877
Heavy	Middle	0.692	0.479	77.499	3.014	1047.744	-1700.135
Light	Middle	0.811	0.658	33.069	1.772	668.183	-1154.609
Light	Low	0.862	0.743	81.978	12.098	-538.550	1895.018
(b) Aromatic Fuel: T2- T17							
Heavy	High	0.829	0.687	12.863	1.871	-116.917	325.050
Heavy	Middle	0.833	0.694	71.742	5.658	-909.135	2495.876
Light	Middle	0.896	0.802	33.274	4.260	-529.386	1365.955
Light	Low	0.912	0.831	109.490	20.965	-1641.558	4057.886

Table 9 PM emissions observed and estimated by R_{290} and H/C.

Fuel	R_{290}	H/C	Observed PM (mg/kWh)				Estimated PM* (mg/kWh)			
			HL, HP	HL, MP	LL, MP	LL, LP	HL, HP	HL, MP	LL, MP	LL, LP
(a) Aliphatic Fuel: T1 - T12										
T1	17	2.118	92	544	264	878	98	570	291	960
T9	3	2.101	86	496	266	836	84	510	255	800
T10	29	2.101	103	611	333	1068	107	589	301	1114
T6	21	2.085	98	501	246	1131	98	548	276	1026
T7	25	2.085	103	481	258	1109	101	560	283	1075
T12	34	2.184	124	718	372	1148	121	691	365	1130
T5	16	2.068	95	631	286	910	92	515	256	975

PM=0.848 × RT+121.7× (H/C)-173.9 Where, RT means R_{290}.
PM=3.01× RT + 1047.7× (H/C)-1700.1
PM=1.771× RT + 668.18× (H/C)-1154
PM=12.098 ×RT -538.5× (H/C) + 1895

Fuel	R_{290}	H/C	Observed PM (mg/kWh)				Estimated PM* (mg/kWh)			
			HL, HP	HL, MP	LL, MP	LL, LP	HL, HP	HL, MP	LL, MP	LL, LP
(b) Aromatic Fuel: T2 - T17										
T2	15	2.019	124	729	385	1081	117	745	361	1058
T3-S	23	1.889	128	799	416	1296	147	909	464	1439
T4-S	26	1.873	169	1011	523	1642	155	940	485	1528
T14	16	2.019	114	727	360	1134	118	748	363	1069
T15	18	2.085	113	711	329	1002	115	702	339	1013
T16	16	1.937	131	870	409	1266	129	825	409	1214
T17	17	1.986	127	812	388	1064	125	787	387	1154

HL: Heavy Load PM=1.871× RT -116.9 ×(H/C) +325.1 Where, RT means R_{290}.
LL: Light Load PM=5.658 × RT -909.1 × (H/C) + 2495.9
HP: High Pressure PM=4.26 ×RT -529.4 ×(H/C) +1366
LP: Low Pressure PM=20.965× RT -1641.6× (H/C) + 4057.9
MP: Middle Pressure

8. Conclusion

The relationship between fuel properties and PM emissions were analyzed using the backend fraction and the H/C of the fuels tested using a single-cylinder engine for the Combustion Analysis WG of the JCAP, which were named "Aliphatic fuels" and "Aromatic fuels" in this paper. In addition, for "Aliphatic fuels", which were not explained using the backend fraction and the H/C, the relationship between the fuel properties and the PM emissions were interpreted using the results of precise analyses. As a result, the following was found.

Estimation of PM emissions from "Aliphatic fuels"

1) PM emission obtained under the conditions of heavy load and high injection pressure could be estimated by the backend fraction and the H/C.

2) The PM emissions obtained under the other conditions could not be estimated by the backend fraction and the H/C. However, they could be interpreted with the precise analytical results, that is, the compositions of n-paraffins, i- paraffins and cycloparaffins.

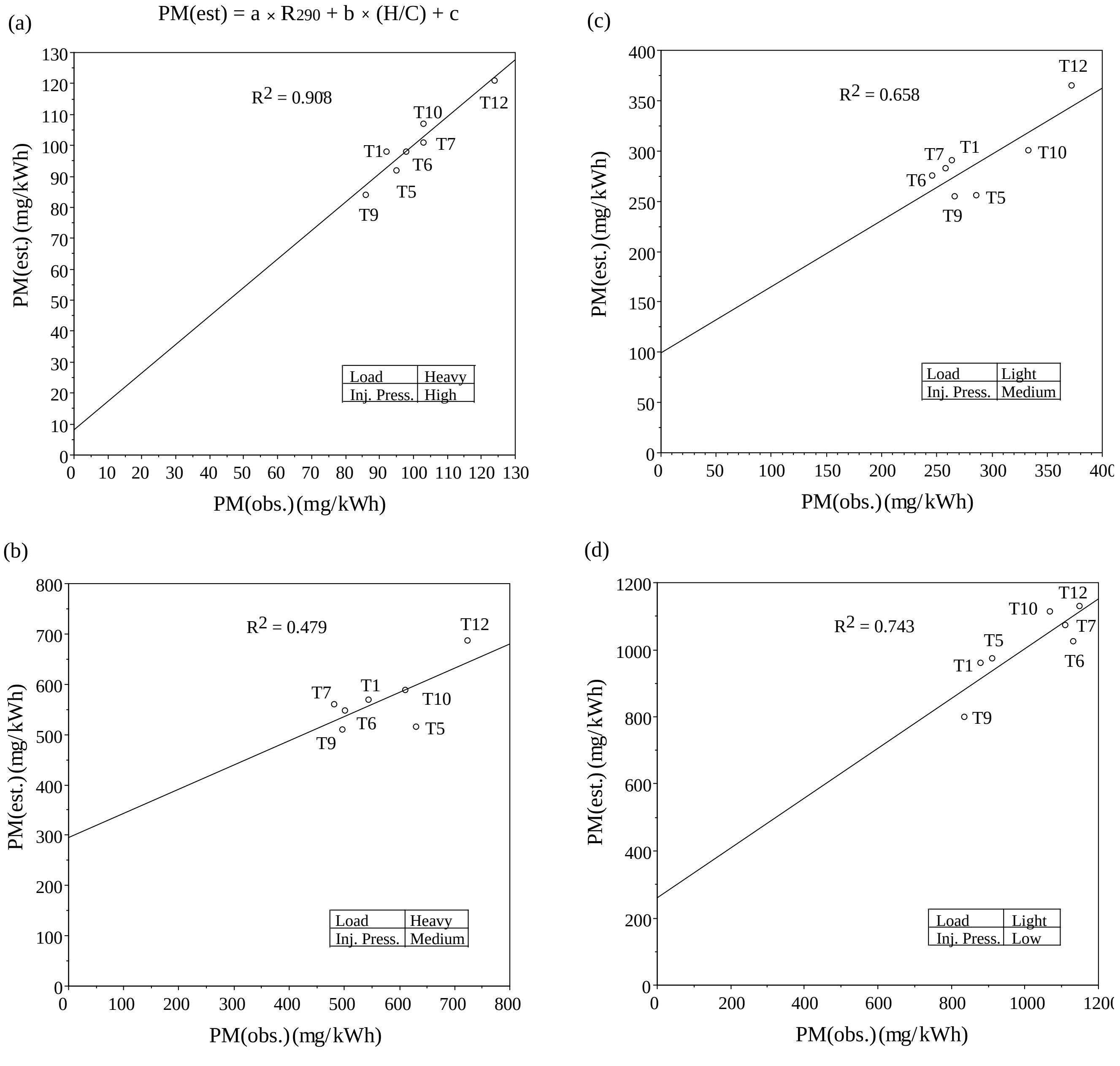


Fig. 12 PM emissions observed and estimated from "Aliphatic Fuels".

Estimation of PM emissions from "Aromatic fuels"

1) PM emissions from all of "Aromatic fuels" could be estimated by the backend fraction and the H/C of the fuels.

2) H/C of added aromatic hydrocarbon was found to be related to the H/C of the whole fuel and boiling point of added aromatic hydrocarbon was found to be related to the T_{90}s of the whole fuel.

In summary, it was found that the PM emissions from a series of fuels whose compositions were different at the level of molecular formula could be estimated by the backend fraction and the H/C of fuel, on the other hand, PM emissions from the fuels, which are different in the compositions of structural isomers, could not be estimated by these parameters. For these fuels, evaluation concerning structural isomers must be conducted.

Acknowledgement

The authors are sincerely grateful to Dr. Minoru Yamamoto and Dr. Yoshiharu Hirose for many helpful suggestions during the course of this work.

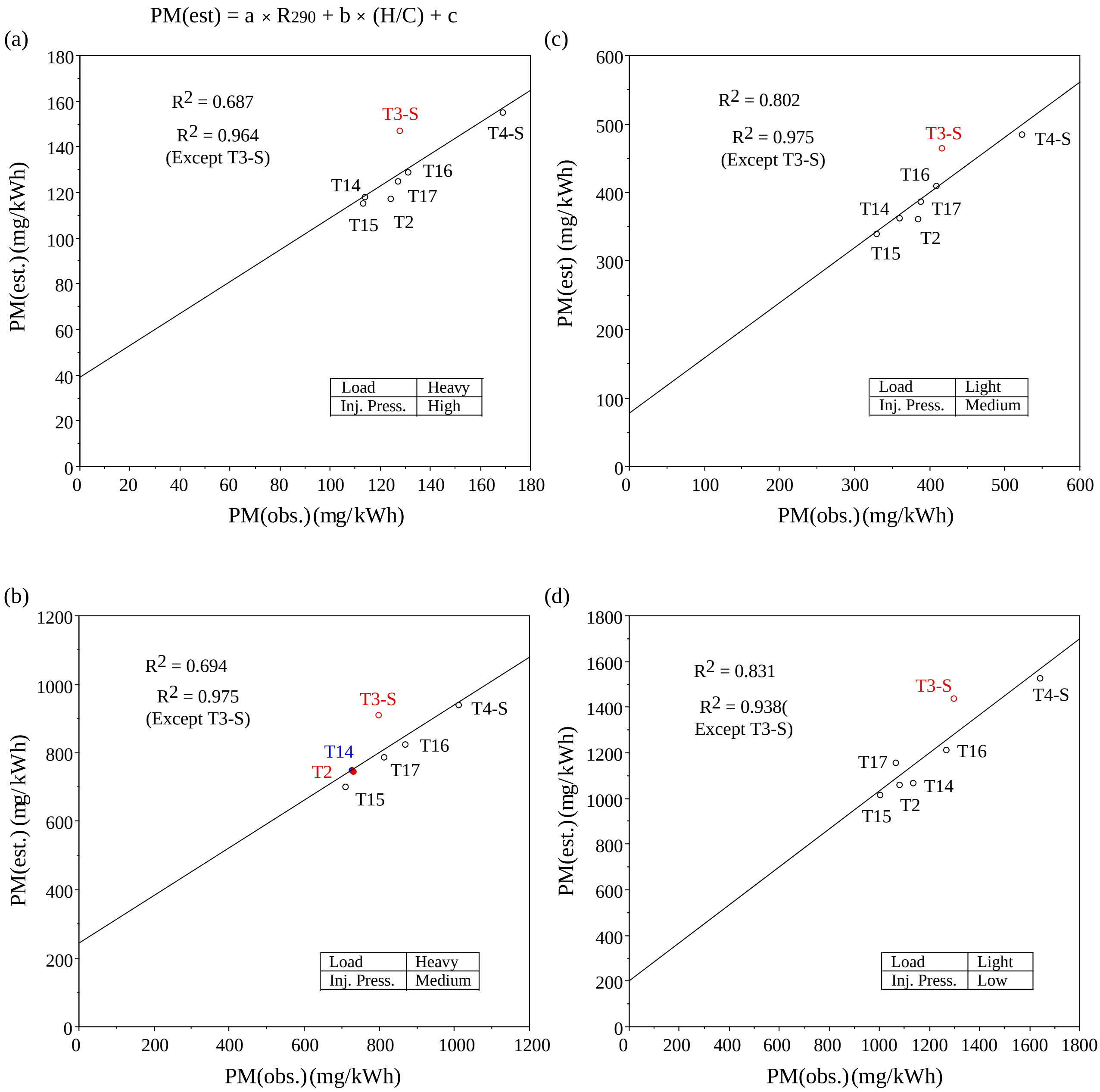
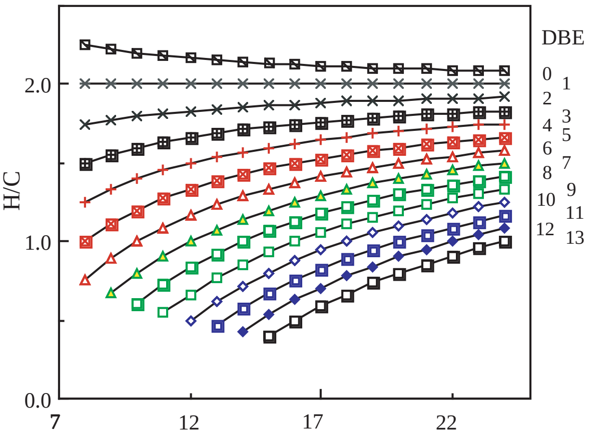
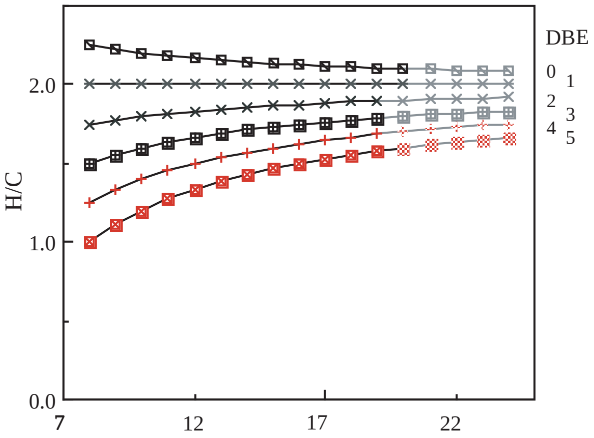


Fig. 13 PM Emissions Observed and Estimated from "Aromatic Fuels".

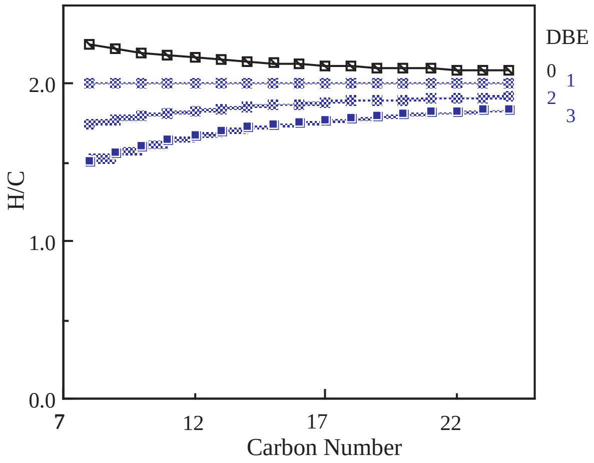
The authors are also thankful to Ms. Keiko Fukumoto for ^{13}C-NMR analysis and Mr. Masami Yamamoto and Ms. Ayako Ohgawara for GC analysis.



(a) Conventional Fuel



(b) Swedish Class-1



(c) GTL

Fig. 14 Compositions of conventional fuel, swedish Class-1 and GTL.

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(Report received on Nov. 14, 2003)

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