

# Influence of Properties and Composition of Diesel Fuels on Particulate Emissions

## Part 1. The Step-I Fuels of the Diesel WG of JCAP

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### 粒子状物質に及ぼす軽油の性状と組成の影響 (第1報) JCAPディーゼル車WGのStep-I 軽油

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#### Abstract

In a previous paper, a number of diesel fuels, exhaust gasses and the soluble organic fractions (SOFs) in the particulate matter (PM) were analyzed. The results revealed that SOF was primarily associated with the high boiling point components in the fuel and the soot in PM was primarily associated with the ratio of hydrogen to carbon (H/C) of the fuel. In addition, a regression equation which consists of the backend fraction at 310°C ( $R_{310}$ ) and H/C of fuel:  $PM = a \times R_{310} + b \times (H/C) + c$ , proved useful for estimating PM emissions.

In this paper, the regression equation was applied to existing-step research and model-step research conducted by the Diesel Working Group (WG) of the Japan Clean Air Program (JCAP). Consequently, PM emissions from the existing-step research were well estimated using the  $R_{310}$  and the H/C and most of the PM emissions from the model-step research were also well estimated using the  $R_{290}$  and the H/C.

#### Keywords

Diesel fuel, JCAP, Particulate matter (PM), Diesel WG, H/C, Backend fraction, Multiple regression analysis

#### 要 旨

我々は以前の研究において、軽油と排気そしてPM中のSOFを分析し、その結果から、PM中の煤には軽油のH/Cが、一方、SOFには軽油中の高沸点分が主に関わっていることを明らかにした。そして、軽油の残油率とH/Cから成るPM量予測式を見い出した。本報では、この予測式をJapan Clean Air Program (JCAP) のディーゼル車WGで研

究された既存ステップとモデルステップの軽油に適用した。その結果、既存ステップで得られたPM量の全てが、軽油の310°Cでの残油率( $R_{310}$ )とH/Cで説明できることが判った。また、モデルステップで得られたPM量の大部分が軽油の $R_{290}$ とH/Cで説明できることが判った。

#### キーワード

軽油, JCAP, 粒子状物質(PM), ディーゼル車WG, H/C, 残油率, 重回帰分析

## 1. Introduction

From the view point 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 Air Quality Improvement Research Program (AQIRP), was launched in 1989 in the United States of America. This program focused on investigating emissions from gasoline engines.<sup>1)</sup>

On the other hand, in a cooperative research study launched in Europe in 1993, named European Programme on Emissions, Fuels and Engines technologies (EPEFE), emissions from diesel engines in addition to those from gasoline engines were investigated.<sup>2)</sup> In the program, the relationship between fuel properties and many kinds of emissions were studied in detail, and the results of the study were reflected in the European fuel standards settled in 2000. These results are expected to be reflected in the fuel standards in 2005 as well. However, in this program, the detailed composition of fuel was not analyzed.

In an effort to follow these programs, a similar study, named Japan Clean Air Program (JCAP), was launched in Japan in 1997. In the JCAP, which consists of eight working groups (WGs), relationships between fuel properties and emissions from diesel engines were investigated by two WGs: Diesel WG and Combustion Analysis WG.<sup>3, 4)</sup>

On the other hand, we have been developing analytical methods of diesel fuel, which focus on the composition of aromatic hydrocarbons since 1993. In the course of this study, we identified a regression equation for estimating PM emissions<sup>5)</sup> and have developed precise analytical methods of diesel fuel in order to complement the regression equation.<sup>6)</sup>

At the time when the precise analytical methods were developed, the Diesel WG entrusted detailed analyses of the fuels prepared for the existing-step research and the model-step research in step-I of the JCAP to our laboratories. Therefore, the fuels tested in the step-I program were analyzed by precise analytical methods. In addition, the relationship between the fuel properties and PM emissions were regressively analyzed. This paper primarily

describes the results of the regression analyses.

## 2. Regression equation for estimating PM emissions

In a previous paper,<sup>5)</sup> exhaust gas and the soluble organic fraction (SOF) from a diesel engine, which was operated under several D13 mode engine conditions, were analyzed by gas chromatography/mass spectrometry (GC/MS). Then, the composition of the exhaust gas and SOF was compared with that of the fuel. Results indicated that, [1] the composition of the hydrocarbons in the exhaust gas was found to be nearly identical to that of the diesel fuel, [2] the components of the SOF correspond to the high boiling point components of the exhaust gas, [3] and the main components of the SOF were also found in the backend fraction at 310°C ( $R_{310}$ ) of the fuel in a distillation test. As a result,  $R_{310}$  of the fuel was thought to be associated with the SOF emission.

On the other hand, the H/C of the diesel fuel was thought to have a strong correlation with the soot in PM, since soot is a carbonization product of hydrocarbon. In addition, the composition of PM obtained under several engine conditions was analyzed. Results indicated that the ratio of SOF to insoluble fraction (ISF), in which soot was the main component, depends on the engine operating conditions (engine load and engine speed) as shown in **Fig. 1**.

Based on the above results, regression Eq. (1) was found to be useful for estimating the PM emission.

$$PM = a \times R_{310} + b \times (H/C) + c \dots\dots\dots(1)$$

Where, a, b, and c are coefficients that vary with the engine or the engine operating conditions. It was established that PM emissions from a direct-injection diesel engine operated with fuels that simulated market fuels under long-period emission regulations, were estimated by Eq. (1).<sup>5)</sup> It should be noted that Eq. (1) does not include a parameter for the sulfur content. This is because the fuels that simulated market fuels under long-period emission regulations and the fuels described in this paper had sulfur contents arranged in the same level.

### 3. Analyses of the fuels tested in the step-I study

The step-I study of the Diesel WG was divided into the existing-step study and the model-step study.<sup>3, 4)</sup>

In the existing-step study, in an effort to investigate the exhaust emission level of the present technologies, emissions from either the engines or vehicles on the market, operated with fuels prepared using refinery components so as to simulate the market fuels in 1997, were investigated. On the other hand, in the model-step study, in an effort to seek future technologies for reducing emissions, emissions from either advanced engines or vehicles operated with special fuels, prepared using solvents and chemicals, were investigated.

#### 3.1 Analyses of the existing-step fuels

Five kinds of fuels, either whose distillation characteristics or aromatic contents were varied within the range of the fuels on the market, were prepared, as shown in **Table 1**. These fuels were supplied into eight kinds of vehicles, with gross vehicle weights (GVWs) of less than 2.5 tons, and eight kinds of engines, with GVWs of more than 2.5 tons, for the emission test. **Table 2** shows the specifications of these vehicles and engines.

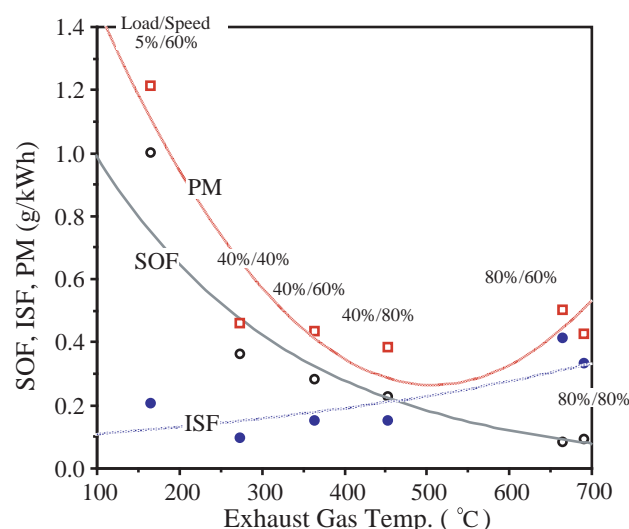
##### 3.1.1 Regression analyses for PM emissions

PM emissions, obtained under combinations of the fuels and either the vehicles or the engines mentioned above were analyzed using Eq. (1). **Table 3** shows the results and **Fig. 2** shows some of the results. As shown in Table 3 and Fig. 2, the PM emissions obtained in the existing-step fuels were explained by the backend fraction ( $R_{310}$ ) and H/C of the fuels, with the exception of the engines-DEOF and DEOG (Refer to Table 3).

##### 3.1.2 Relationship between fuel properties and SOF emissions

In a previous paper,<sup>5)</sup> the main components of SOF were observed to be the high boiling point components of the fuel, except under heavy load conditions or high speed engine conditions, both of which result in high exhaust gas temperatures, as shown in Fig. 1.

Therefore, the relationship between the products of hydrocarbon (HC) emissions and the backend fraction ( $R_{310}$ ):  $[HC \times R_{310}]$  and the SOF emissions was examined. The results are shown in the right column of Table 3. As shown in the right column of Table 3,  $[HC \times R_{310}]$  showed a positive correlation with SOF emissions, with the exception of the emissions from the engines-DEOG and DVOD



**Fig. 1** Relationship between exhaust gas temperature and PM composition.  
It turns out that the engine operation conditions expressed at an engine load and engine speed are replaced at the exhaust gas temperature measured just behind the exhaust valve.

**Table 1** Properties of existing-step fuels.

Item			D-1	D-2	D-3	D-4	D-5
		Unit	97-DAV	97-D10LA	97-10HA	97-50LA	97-50HA
Density	at 15℃	(g/cm3)	0.834	0.8151	0.8315	0.8324	0.8369
Distillation (JISK2254)	IBP	(℃)	181.0	156.0	157.0	188.0	160.0
	10%	(℃)	223.5	187.0	193.0	232.0	197.0
	30%	(℃)	258.0	212.0	229.0	262.5	241.5
	50%	(℃)	278.0	242.0	256.5	285.0	275.0
	70%	(℃)	300.0	272.0	280.0	309.0	307.5
	90%	(℃)	329.5	310.0	306.0	343.0	348.0
	95%	(℃)	344.0	324.0	315.0	357.5	367.0
	FBP	(℃)	360.0	336.0	326.0	368.0	382.0
Cetane Value	(JISK2280)		55.9	51.7	49.2	57.6	50.9
HPLC (JPI-Method)	Saturate	(vol.%)	75.8	79.1	70.6	79.0	71.7
	Unsaturate	(vol.%)	0.0	0.1	0.2	0.4	0.0
	Total Aromatics	(vol.%)	24.2	20.8	29.2	20.6	28.3
	Mono-Aromatics	(vol.%)	21.0	19.7	24.4	17.4	22.8
	Di-Aromatics	(vol.%)	2.4	0.8	3.4	2.2	3.8
	Tri-Aromatics	(vol.%)	0.8	0.3	1.4	1.0	1.7
Residue	R310*2)	(vol.%)	23.4	10.0	7.8	29.3	28.7
H/C *3)			1.96	2.02	1.94	2.00	1.95

\*1) Japan Petroleum Institute.

\*2) Read from reconstructed distillation curve, by TCRD.

\*3) Used for regression analyses (measured by TCRD).

TCRD: Toyota central R&D Labs.

(Table 3). Correlation coefficients greater than 0.8 were obtained between the  $[HC \times R_{310}]$  and the SOF emissions for four of the eight engines and five of the eight vehicles.

Changes in these SOF emissions (dSOFs) were

plotted in **Fig. 3**, against the correlation coefficients of the  $[HC \times R_{310}]$  and the SOF emissions. It can be observed that the correlation coefficients are greatly influenced by the changes in SOF emissions. Moreover, it was found that the errors in

**Table 2** Specifications of engines/vehicles for existing-step research.

Symbol	Vehicle or Engine	Regulation	G.W. (kg)	Displacement (L)	Intake System	Combustion	Injector Type	Others	Test Mode
E	Engine	S	-	9.2	NA	DI	E	-	D13
F	Engine	S	-	12.1	TI	DI	TICS	-	D13
G	Engine	S	-	3.6	NA	IDI	M	-	D13
H	Engine	S	-	10.5	TI	DI	TICS	-	D13
O	Engine	L	-	21.2	NA	DI	TICS	EGR	D13
P	Engine	L	-	8.2	NA	DI	TICS	EGR	D13
Q	Engine	L	-	4.8	T	DI	In-line/E	EGR	D13
R	Engine	L	-	8.0	NA	DI	C.R.	-	D13
A	Vehicle	S	2000	3.0	T	IDI	E	EGR	D10.15/11
B	Vehicle	S	1500	2.3	NA	IDI	M	EGR	D10.15
C	Vehicle	S	1250	2.0	NA	IDI	M	EGR	D10.15
D	Vehicle	S	1750	2.0	NA	IDI	M	EGR	D10.15/11
K	Vehicle	L	2500	3.0	TI	IDI	C. Rail	EGR+Cat.	D10.15
L	Vehicle	L	1500	2.2	NA	IDI	E	EGR	D10.15/11
M	Vehicle	L	1500	2.2	T	IDI	E	EGR+Cat.	D10.15
N	Vehicle	L	1500	2.0	T	IDI	E	EGR	D10.15

S: Short term emission regulation (1990-1994)

L: Long term emission regulation (1997-1999)

NA: Natural Aspiration

TI: Turbo-Intercooler

T: Turbo

DI: Direct Injection

IDI: Indirect Injection

E: Electrically controlled injector

M: Mechanically controlled injector

TICS: Timing & Injection rate Control System

**Table 3** Results of multiple regression analyses of PM emissions in existing-step research.

- D1-D5 -

Fuel	Multiple Regression*					EGR Catalyzer	R** SOF
	Multiple R	R <sup>2</sup>	a for H/C	b for R310	c		
Engine/D13-Mode							
DEOE	0.999	0.999	-366.290	7.533	1166.3	-	0.962
DEOF	0.689	0.475	-199.008	0.599	857.6	-	0.891
DEOG	0.772	0.596	-420.777	-0.124	1083.6	-	0.142
DEOH	0.996	0.991	92.263	3.316	90.3	-	0.972
DEOO	0.977	0.955	-119.813	2.734	422.1	EGR	0.656
DEOP	0.998	0.997	-234.054	4.360	611.8	EGR	0.953
DEOQ	0.771	0.594	-674.628	1.495	1373.0	EGR	0.598
DEOR	0.988	0.977	-725.148	3.058	1646.4	-	0.786
Vehicle/D10.15-Mode							
DVOA	0.809	0.654	-184.054	-0.361	495.7	EGR	0.901
DVOB	0.924	0.854	-175.128	0.912	364.3	EGR	0.961
DVOC	0.994	0.988	-248.737	1.240	547.4	EGR	0.935
DVOD	0.922	0.851	-578.568	3.890	1226.8	EGR	0.137
DVOK	0.987	0.976	-11.028	0.606	79.5	EGR+Cat.	0.663
DVOM	0.957	0.917	-136.049	0.754	302.8	EGR+Cat.	0.802
DVON	0.928	0.862	-213.000	0.649	471.9	EGR	0.841

\*:  $PM = a \times (H/C) + b \times (R_{310}) + c$

measurement of the SOF emissions had an influence on these correlations.

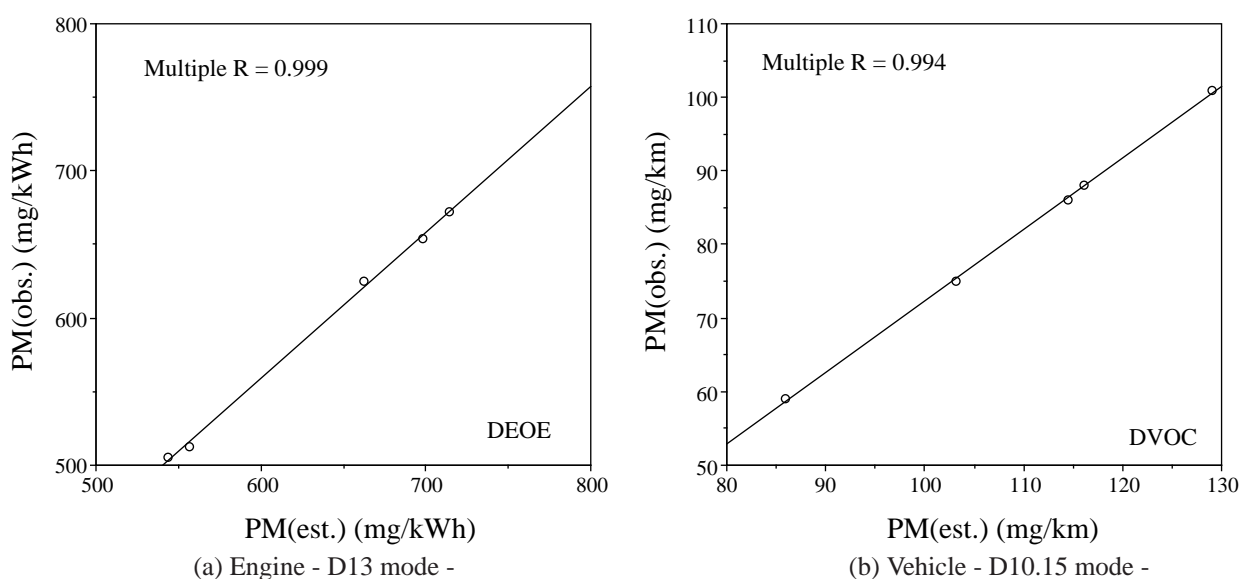
### 3.2 Analyses of model-step fuels

In the model-step study, the influence of the composition of aliphatic hydrocarbons and that of the composition of aromatic hydrocarbons on the emissions was investigated. The properties of the fuels prepared for the emission test are shown in **Table 4**. These fuels were evaluated using the emission test with either the engines or the vehicles

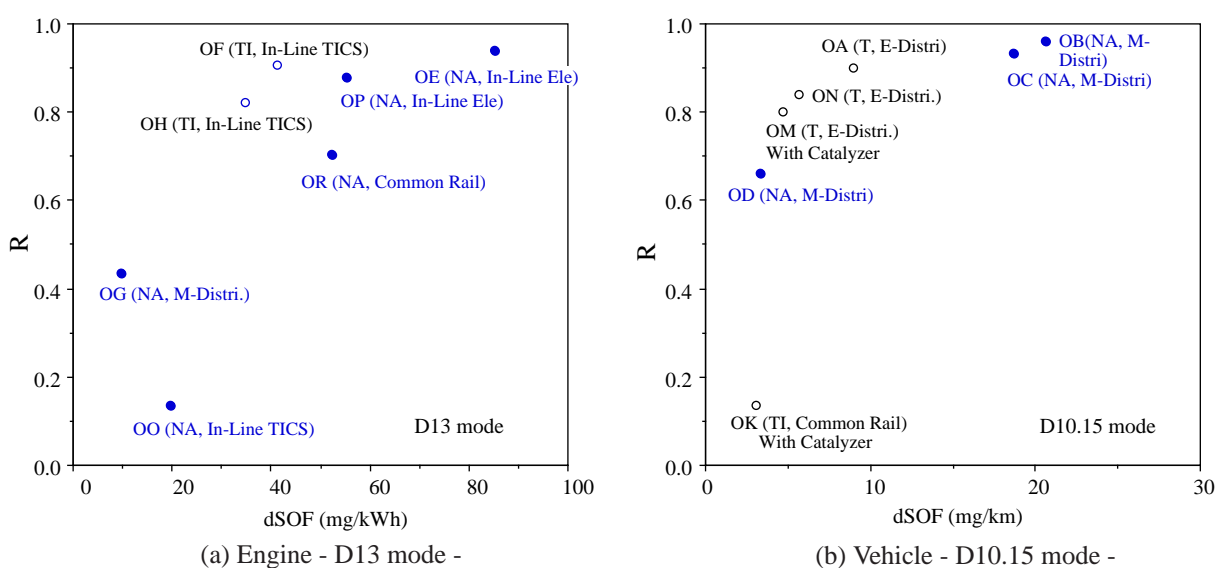
listed in **Table 5**.

#### 3.2.1 Regression analyses for PM emissions

The PM emissions from the model-step fuels were analyzed using regression equation (1). In these analyses, the backend fractions at 290°C ( $R_{290}$ ) were used instead of  $R_{310}$ , because the fuels from the model-step include MD-11 with an end point of 295°C in a distillation test. The results of the regression analyses are shown in **Table 6** and some of them are shown in **Fig. 4**. As shown in Table 6, multiple



**Fig. 2** PM emissions observed and estimated under D13 mode (a) and D10.15 mode (b).



**Fig. 3** Changes in SOF emissions (dSOF) and correlation coefficients between  $HC \times (R_{290})$  and SOF emissions under D13mode (a) and D10.15 mode (b) - Existing-step fuels -

**Table 4** Properties of model-step fuels.

Item		Unit	MD-8	MD-9	MD-10	MD-11	MD-12	MD-13
Density	at 15°C	(g/cm <sup>3</sup> )	0.835	0.833	0.818	0.815	8.835	0.8149
Distillation (JISK2254)	IBP	(°C)	177.5	177.0	186.0	172.0	182.5	187.5
	10%	(°C)	209.0	212.5	210.0	191.5	211.5	213.5
	30%	(°C)	260.0	258.5	248.0	205.0	256.0	252.5
	50%	(°C)	280.0	279.0	280.0	223.0	278.0	277.0
	70%	(°C)	295.0	298.0	299.0	244.0	297.0	297.0
	90%	(°C)	329.0	332.0	332.0	277.5	330.5	332.0
	95%	(°C)	351.0	350.0	350.5	286.5	349.5	352.0
	FBP	(°C)	359.0	363.0	362.0	295.0	362.5	359.5

Cetane Value	(JISK2280)		54.8	55.6	62.6	48.6	54.6	64
HPLC (JPI-Method)	Saturate	(vol.%)	64.6	91.5	97.5	75.5	75.8	99.6
	Unsaturate	(vol.%)	0.0	0.0	0.0	0.0	0.0	0.0
	Aromatics	(vol.%)	35.4	8.5	2.5	24.5	24.2	0.4
	1-Ring	(vol.%)	35.4	0.6	0.6	21.2	20.8	0.4
	2-Ring	(vol.%)	0.0	7.9	0.0	2.4	2.4	0
	3-Ring	(vol.%)	0.0	0.0	1.9	0.9	1.0	0
Residue	R290 *1)	(vol.%)	37.20	38.85	40.00	3.00	37.75	37.00
H/C*2)			1.857	1.889	1.986	1.889	1.841	2.052

\*1) Read from reconstructed distillation curve, by TCRD.

\*2) Measured by Advanced Technology Research Institute (ATRI).

**Table 5** Specifications of engines/vehicles for model-step Research.

Symbol	Vehicle or Engine	Technology	Outline
V	Engine	Highly Oxidative Catalyst	Engine P with Cat.
W	Engine	Oxidation Catalyst for 0.05%S	Engine P with Cat.
X	Engine	High Fuel Sensitivity	Engine R
Y	Engine	Low Fuel Sensitivity	Engine O
S	Vehicle	High Performance Catalyst	Vehicle C with Cat.
K	Vehicle	Direct Injection	Vehicle K
U	Vehicle	Low Fuel Sensitivity	Vehicle M
T	Vehicle	High Fuel Sensitivity	Vehicle N

Note) The engines or vehicles whose emission data are not cited in this paper were deleted.

**Table 6** Results of multiple regression analyses of PM emissions in model-step research.

MD6-MD11 & MD1 (DAV)							
Engine or Vehicle	Multiple Regression*					Catalyzer & EGR	R**
	Multiple R	R <sup>2</sup>	a for H/C	b for R290	c		
Engine/D13-Mode							
Engine OV	0.506	0.256	-75.122	1.130	688.82	High-Ox. Cata.	0.162
Engine OW	0.880	0.775	-235.326	0.495	624.48	0.05S Cata.	0.355
Engine OX	0.911	0.830	-461.853	2.208	1116.46		0.286
Engine OY	0.904	0.817	-153.296	1.290	458.71		0.591
Vehicle/D10.15-Mode							
Vehicle OS	0.925	0.857	-111.587	0.368	298.07	High Prfrm. Cata.	0.087
Vehicle OK	0.857	0.735	-88.791	0.187	227.8	Cata. & EGR	--
Vehicle OU	0.981	0.963	-76.973	0.278	178.65		0.467
Vehicle OT	0.962	0.926	-124.742	0.848	270.95		0.010

\*: PM= a × (H/C) + b × (R290) + c

\*\*: (HC) × (R290) vs. SOF

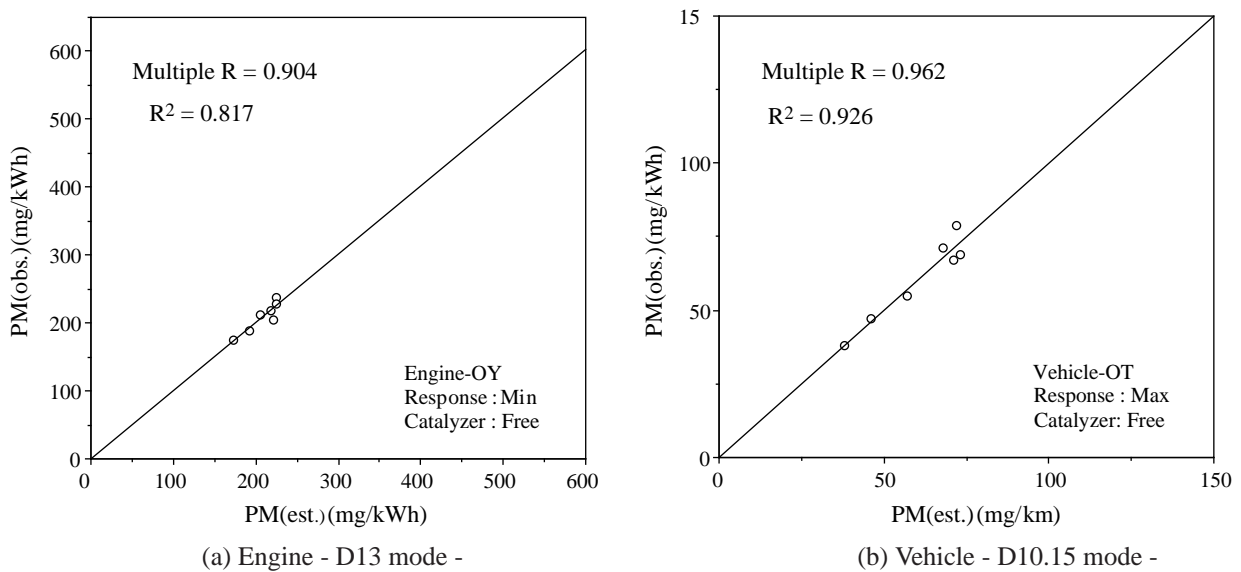
correlation coefficients greater than 0.9 were obtained in five sets of the eight sets of emission tests, and multiple correlation coefficients greater than 0.85 were obtained in seven sets of the eight sets of emission tests.

### 3.2.2 Relationship between fuel properties and SOF emissions

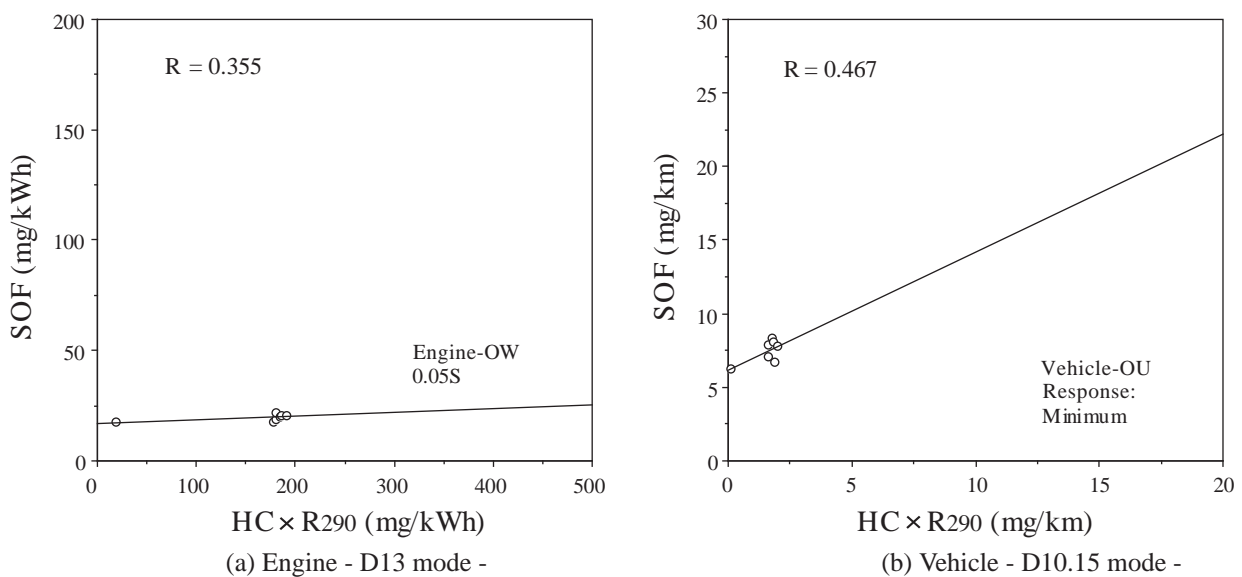
The relationship between the properties of the model-step fuels and either HC emissions or SOF emissions was determined, in the same manner as for the existing-step fuels. The relationship between the products of the HC emissions and the backend

fraction at 290 °C;  $[HC \times R_{290}]$  and the SOF emissions are shown in the right column of Table 6 and some of them are plotted in Fig. 5. From this data, the correlation between them is seen to be extremely low.

One of the reasons is thought to be that the 90% distillation temperatures ( $T_{90}$ ) for the model-step fuels were uniform at 330 °C, with the exception of the  $T_{90}$  for fuel-MD-11 (Refer to Table 7), which had an end point of 295 °C. Since the  $T_{90}$  of these fuels was uniform, the  $R_{290}$  of the model-step fuels, with the exception of that for MD-11, was also



**Fig. 4** PM Emissions observed and estimated from MD-Fuels under D13 mode (a) and D10.15 mode (b).



**Fig. 5** SOF Emissions observed and estimated from MD-Fuels under D13 mode (a) and D10.15 mode (b).

uniform at  $38.6 \pm 1.4\%$ . In addition, the difference in the  $R_{290}$  for these fuels was nearly the same as the error in reading of the  $R_{290}$  (1~2%). As a result, the error in measurement of  $R_{290}$  was thought to have a strong influence on these correlations.

Though, the backend fraction must be read directly

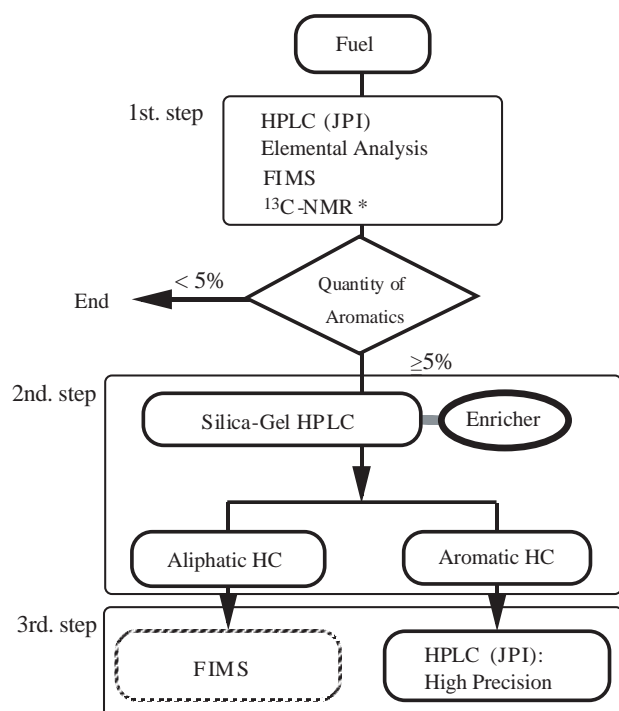
**Table 7** Comparison of MD-9 and MD-11.  
Properties and compositions of fuels and emissions.

Item	Unit	MD-9	MD-11	MD-9 vs. MD-11
R <sub>290</sub>	(vol.%)	38.85	3.00	1295:100*
H/C		1.889	1.889	100:100
Aroma.	(%)	8.5	24.5	
1-Ring	(%)	0.6	21.2	
2-Ring	(%)	7.9	2.4	
3-Ring	(%)	0	0.9	
Aromatic-C	(%)	10.48**	12.97**	81:100
HC(DEOV)	mg/kWh	131	173	73:100
HC(DEOW)	mg/kWh	464	647	
HC(DVOK)	mg/km	110	146	
SOF(DEOV)	mg/kWh	92.6	75.2	110:100
SOF(DEOW)	mg/kWh	18.9	17.3	
SOF(DVOK)	mg/km	23.7	17.6	
PM(DEOV)	mg/kWh	630	553	114:100
PM(DEOW)	mg/kWh	203	182	
PM(DVOK)	mg/km	71	61	

\*: Normalized by the value of MD-11.

\*\* : Amount of aromatic carbon in MD-9  $0.6\% \times (6/18) + 7.9\% \times (10/11)$

Amount of aromatic carbon in MD-11  $21.2(\%) \times (1/3) + 2.4(\%) \times (10/12) + 0.9(\%) \times (1/1)$



**Fig. 6** Scheme for precise analytical methods of diesel fuel.

from a distillation curve, the  $R_{290}$ s in this paper were read from the line graph reconstructed from the recovered temperatures and recovered volumes at every 10%.

#### 4. Relationship between fuel properties and SOF emissions in the model-step

The SOF emissions from four kinds of engines and four kinds of vehicles were averaged in an effort to analyze the relationship between the fuel properties and the SOF emissions in the model-step. The averaged SOF emissions are partially shown in Table 7. The observations can be made from Table 7. The H/C for fuels-MD-9 and MD-11 (Refer to Table 7) have the same value, 1.889. On the other hand, the  $R_{290}$ s for them are very different. The  $R_{290}$  for MD-9 was 38.85%, while that for MD-11 was 3.00%. Though the  $R_{290}$ s for MD-9 and MD-11 were very different, the SOF and PM emissions from MD-9 and MD-11 were nearly the same. Therefore, the causes for similar SOF and PM emissions from MD-9 and MD-11 with different  $T_{90}$ s, were considered by evaluating the precise analytical results for these fuels.

**Table 8** Precise analytical results of model-step fuels.

			MD-8	MD-9	MD-10	MD-11	MD-6	MD-7
Whole Fuel			MD-12 MD-13					
EA*			1.857	1.889	1.986	1.889	1.841	2.052
C-NMR	Branch(e)	mass %	29.68	30.27	35.64	26.46	32.06	34.45
	Branch(f)	mass %	49.62	54.27	59.46	47.20	52.72	61.12
	Aromatic	mass %	14.70	10.48	2.45	12.97	12.44	0.00
FIMS	DBE=0&7	a.u.	1000	1000	1000	1000	1000	1000
	DBE=1&8	a.u.	1492	693	1488	806	1058	1476
	DBE=2&9	a.u.	845	414	1020	440	684	1054
	DBE=3&10	a.u.	270	170	650	138	290	428
	DBE=4	a.u.	2586	13	114	726	914	127
	DBE=5	a.u.	18	0	19	4	7	40
	DBE=6	a.u.	0	0	14	0	0	26
Aliphatic Fraction								
FIMS	DBE=0	a.u.	**	1000	1000	1000	1000	**
	DBE=1	a.u.	**	1442	1293	1003	1371	**
	DBE=2	a.u.	**	940	870	540	910	**
	DBE=3	a.u.	**	404	348	100	328	**
	DBE=4	a.u.	**	170	198	22	92	**
	DBE=5	a.u.	**	31	48	0	26	**
	DBE=6	a.u.	**	27	52	0	14	**
Aromatic Fraction***								
HPLC (NH2-)	1 Ring	a.u.***	**	6.59	13.60	86.38	85.02	**
	2 Ring	a.u.***	**	93.41	1.67	7.02	9.03	**
	3 Ring	a.u.***	**	0.00	84.73	6.60	5.95	**

\*: Measured by Advanced Technology Research Institute.

\*\* : Aliphatic- and aromatic-fractions of MD-8&MD-13 were not measured.

\*\*\*: Not compensated.

#### 4. 1 Precise analytical methods for diesel fuel

**Figure 6** shows a flow chart for the precise analytical methods developed in a previous paper.<sup>6)</sup> Of the methods shown in Fig. 6, Field Ionization Mass Spectrometry (FIMS) and Carbon-13 Nuclear Magnetic Resonance Spectrometry (<sup>13</sup>C-NMR) of the whole fuel, and FIMS of the aliphatic and aromatic fractions was conducted. Elemental Analysis and High Pressure Liquid Chromatography (HPLC) of whole fuels were not conducted, since these analyses had already conducted by the Advanced Technology and Research Institute (ATRI) at the Petroleum Energy Center.

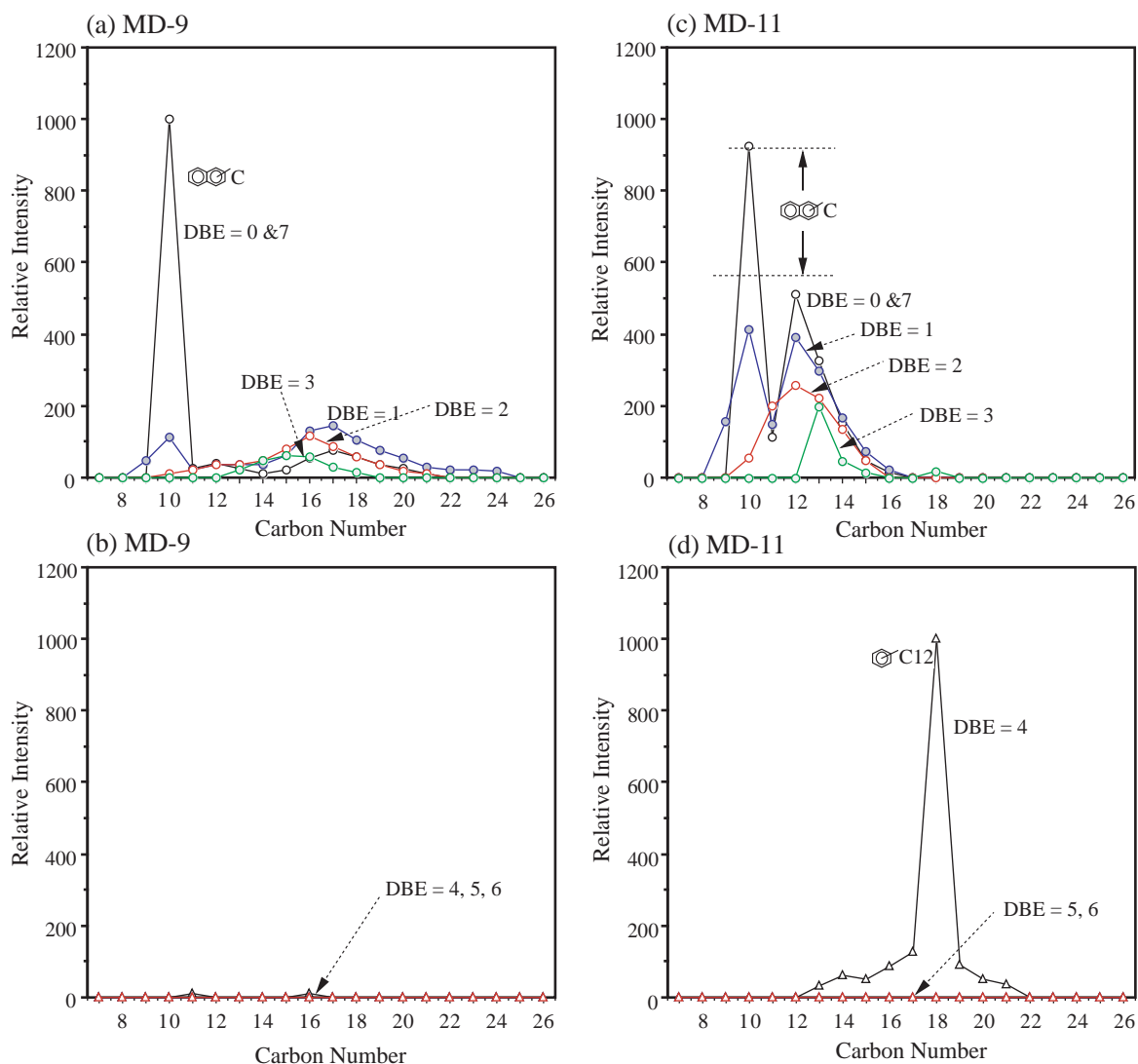
#### 4. 2 Results of precise analyses of the model-step fuels

**Table 8** shows some of the precise analytical

results for the model-step fuels.<sup>7)</sup> **Figure 7** shows carbon number distributions of hydrocarbons with the same double bond equivalent value (DBE). From these results, the following conclusions were made.

1) The molecular weight of the aliphatic hydrocarbons in MD-11 was lower than that of MD-9. It is well known that among the same DBE hydrocarbons, the smaller the carbon number in the hydrocarbons is, the lower the cetane number of the hydrocarbon. Accordingly, it is assumed that cetane number of aliphatic hydrocarbons in MD-11 is lower than that of the aliphatic hydrocarbons in MD-9.

2) The aromatic hydrocarbons in MD-9 consisted of 0.6% of C18 alkylbenzenes and 7.9% of methylnaphthalene. Accordingly, the amount of carbon in the aromatic-ring, that is, "aromatic



**Fig. 7** Carbon number distribution of MD-9 (a, b) and MD-11 (c, d).

carbon" is estimated to be about 7%, as explained in the footnote of Table 7.

3) On the other hand, the "aromatic hydrocarbons" in MD-11 consist of 21.2% C18 alkylbenzenes, 2.4% C13 and C14 alkyl naphthalenes, and 0.9% phenanthrene. Accordingly, the amount of "aromatic carbon" in MD-11 is estimated to be about 10.3%. As a result, the amount of "aromatic carbons" in MD-9 and MD-11 is in a ratio of 7:10.

4) It can be seen from the  $^{13}\text{C}$ -NMR results, shown in Table 8, that amount of "aromatic carbons" in MD-11 (12.97%) is more than that of MD-9 (10.48%).

5) From the results described in 2) and 3), the aromatic hydrocarbons in MD-9 were found to be more flammable than those in MD-11.

From the results described above, the relationship between the composition of MD-9 and MD-11 and their SOF and PM emissions were interpreted as follows:

1) Though MD-11 is a lighter fuel than MD-9, MD-11 is a less flammable fuel than MD-9.

2) Therefore, the HC emission from MD-11 is greater than HC emission from MD-9 by a factor of 1.4. Accordingly, though the  $R_{290}$  for MD-11 was smaller than that for MD-9, the SOF emissions from MD-11 amounts to about 9/10 of the SOF emission from MD-9.

PM emissions from the fuels studied in the Diesel WG of the JCAP can be estimated from the regression equation, consisting of the backend fraction and the H/C. In addition, a good fuel to reduce PM emissions was found to be a fuel with a high H/C and a fuel that does not contain high boiling point hydrocarbons. A paraffin mixture, which is distilled at  $310^\circ\text{C}$ , was proposed as an example. **Figure 8** shows an example of the composition of a low PM emission fuel.<sup>8)</sup>

## 5. Conclusions

The relationship between the fuel properties and the PM emissions studied in the existing-step and the model-step of the Diesel WG of the JCAP were regressively analyzed. The relationship between the fuel composition and the SOF and PM emissions were also analyzed using precise analytical methods, for a number of the fuels. Consequently, the

following results were obtained.

1) PM emissions from the fuels studied in the existing-step were estimated from the  $R_{310}$  and the H/C of the fuels, and most of the PM emissions from the model-step were estimated from the  $R_{290}$  and the H/C of the fuels.

2) SOF emissions from the fuels studied in the existing-step were estimated from the products of the HC emissions and backend fractions at  $310^\circ\text{C}$ :  $[\text{HC} \times R_{310}]$ .

3) SOF emissions from the fuels studied in the model-step were interpreted using the results of precise analyses.

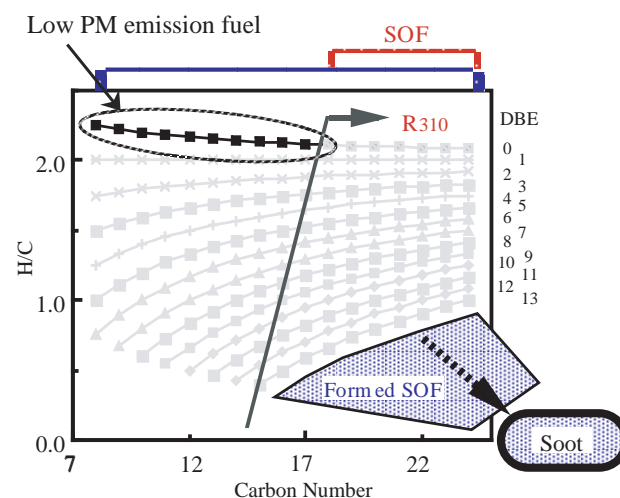
In summary, the regression equation, which established in a previous paper, was useful for estimating PM emission from the fuels studied in the existing-step and the model-step of JCAP.

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**Fig. 8** Composition of Diesel Fuel for Reduced PM Emission.

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