Control for Pollutant Emission from Diesel Engine Vehicles by Fuel Modification (Part 4)

Effect of Fuel Composition on the Emission of Benzo(a)pyrene

Akira OBUCHI*, Akihiko OHI, Hyogoro AOYAMA, and Hideo OHUCHI

National Research Institute for Pollution and Resources,
Onogawa 16-3, Yatabe-cho, Tsukuba-gun, Ibaraki 305

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Effects of the composition of the fuel on the emission of benzo(a)pyrene (B(a)P) from a diesel engine were investigated using a single cylinder test engine and 1) pure hydrocarbon-mixed fuels composed of *n*-cetane, heptamethylnonane(HMN), α -methylnaphthalene and a cetane number improver and 2) subfraction-mixed fuels composed of *n*-cetane, HMN and subfractions of diesel fuels prepared by fractional distillation and chromatographic separation. Aromaticity (aromatic carbon content) of the fuel was the principal factor for B(a)P emission, that is, B(a)P emission rate generally increased with the aromaticity of the fuel. Further effects by cetane number, boiling range and the content of B(a)P in the fuel were also considered.

1. Introduction

Control of pollutant emission, especially the particulate matter and nitrogen oxides, from diesel-powered vehicles is becoming an urgent problem for the protection of the atmospheric environment.¹⁾ The authors have been conducting fundamental experiments for reducing pollutant emissions from diesel engines by fuel modification and have already reported on structural analysis of diesel fuels using proton and carbon-13 nuclear magnetic resonance spectroscopy(NMR)²⁾, and on combustion experiments of pure hydrocarbon-mixed fuels³⁾ and subfraction-mixed fuels⁴⁾ using a CFR F-5 single cylinder test engine.

The results of these experiments are summarized as follows: The average number of structural components in a diesel fuel molecule, such as methyl group(-CH₃), paraffinic or naphthenic methylene group(-CH₂-), aromatic carbon, can be determined by combining the NMR method with the traditional oil analysis method. From the combustion experiments using pure hydrocarbon-mixed fuels, of which molecular structures are fully known, it was found that the increase in the aromatic carbon content in the fuel results in increases in the emission of carbon monoxide, nitrogen oxides and particulate matter. From the combustion experiments

using the subfraction-mixed fuels, boiling range of the fuel was found to have little effect on gaseous emission.

Recently much attention has been focused on the emission of organic substances contained in diesel exhaust particulate matter, because some of them are suspected to be carcinogenic substances.⁵⁾ Polycyclic aromatic hydrocarbons(PAH) and their nitro substitutes⁶⁾ are presently of particular concern. Therefore, it is necessary not only to measure the total amount of the particulate matter but also to determine the amount of these harmful substances when a new device or countermeasure for reducing diesel exhaust emission is developed.

The authors have developed a method to determine the amount of PAH contained in the particulate matter or diesel fuel, using high performance liquid chromatography(HPLC) with fluorescent spectroscopic detection.⁷⁾ In this paper, we will report the effect of certain fuel properties, such as cetane number, boiling range and the content of aromatic carbon, B(a)P itself and a cetane number improver on the emission of B(a)P, which is the most representative substances in many carcinogenic PAHs.

2. Experimental

2.1 Sample

Two sets of fuels, pure hydrocarbon-mixed fuels

* To whom correspondence should be addressed.

and subfraction-mixed fuels, were used as the sample. Details of the preparation method and the properties of these fuels were explained in the previous papers.^{2)~4)} The pure hydrocarbon-mixed fuels were composed of *n*-hexadecane (*n*-cetane), 2,2,4,4,6,8,8-heptamethylnonane(HMN), α -methyl-naphthalene(α -MN) (Tokyo Kasei Co., Ltd, Special Grade) and/or Diesel Ignition Improver 2 (DII-2, Ethyl Corp.), and were tested in order to find the effects on emissions of ternary or quaternary paraffinic carbon, aromatic carbon and a cetane number improver in the fuel. The composition and the cetane number of these fuels are summarized in **Table 1**. The subfraction-mixed fuels were composed of *n*-cetane, HMN and subfractions of diesel fuels, which were of particular

boiling ranges (200–240, 240–280, 280–320 and 320–360°C, symbolized as 20, 24, 28 and 32, respectively) and structural types (saturates and aromatics, symbolized as S and Ar, respectively). This set of fuels was tested in order to find the effects of aromatic carbon content and the boiling range of the fuel on the emissions. The composition and some properties of these fuels are summarized in **Table 2**. The aromatic-rich gas oil, whose properties were investigated previously²⁾, is an equivalent mixture of an Arabian Light rerun and direct distillate of a Sumatran oil. The content of B(a)P was measured using the HPLC.⁷⁾

2.2 Analysis of B(a)P

The analytic procedure for B(a)P is shown in **Fig. 1** as a flow chart. The diesel exhaust partic-

Table 1 Composition and Properties of Pure Hydrocarbon-mixed Fuels

Fuel	<i>n</i> -C ^{a)}	Composition HMN ^{b)}	(vol%) α -MN ^{c)}	DII-2 ^{d)}	Cetane Number	Specific Gravity (20/4° C)	Aromaticity
H0 α 0	100.00	0.00	0.00	0.00	100	0.7745	0
H20	80.00	20.00	0.00	0.00	83	0.7763	0
H35	64.71	35.29	0.00	0.00	70	0.7777	0
H53	47.06	52.94	0.00	0.00	55	0.7797	0
H82	17.65	82.35	0.00	0.00	30	0.7835	0
α 5	95.00	0.00	5.00	0.00	95	0.7872	0.064
α 15	85.00	0.00	15.00	0.00	85	0.8113	0.184
α 30	70.00	0.00	30.00	0.00	70	0.8495	0.347
α 45	55.00	0.00	45.00	0.00	55	0.8850	0.492
α 70	30.00	0.00	70.00	0.00	30	0.9473	0.700
H47 α 5	47.94	47.06	5.00	0.00	55	0.7913	0.064
H35 α 15	49.71	35.29	15.00	0.00	55	0.8150	0.184
H18 α 30	52.35	17.65	30.00	0.00	55	0.8491	0.346
H80D4	16.34	79.81	0.00	3.85	55	0.7911	0
H88D8	4.59	87.15	0.00	8.26	55	0.8005	0
H85D15	0.00	85.47	0.00	14.53	55	0.8130	0

^{a)} *n*-cetane, ^{b)} 2, 2, 4, 4, 6, 8, 8-heptamethylnonane, ^{c)} α -methyl-naphthalene, ^{d)} Diesel Ignition Improver 2

Table 2 Composition and Properties of Subfraction-mixed Fuels

Fuel	Composition (vol%)			Cetane Number	Specific Gravity (20/4°C)	Concentration of Benzo (a) pyrene (mg/l)	Aromaticity
	Σ ^{a)}	<i>n</i> -C ^{b)}	HMN ^{c)}				
F (Σ 20S) 25	25.0	35.7	39.3	—	0.7850	0.008	0.005
F (Σ 20S) 50	50.0	24.3	25.7	54	0.7904	0.016	0.011
F (Σ 24S) 25	25.0	32.1	41.9	—	0.7848	0.010	<0.001
F (Σ 24S) 50	50.0	18.2	31.8	54	0.7902	0.019	<0.001
F (Σ 28S) 25	25.0	29.3	45.7	—	0.7861	0.007	<0.001
F (Σ 28S) 50	50.0	11.4	38.6	54	0.7927	0.013	<0.001
F (Σ 32S) 25	25.0	28.0	47.0	—	0.7895	0.009	<0.001
F (Σ 32S) 50	50.0	8.9	41.1	54	0.7997	0.019	<0.001
F (Σ 20Ar) 25	25.0	47.1	27.9	—	0.8107	0.011	0.168
F (Σ 20Ar) 50	50.0	47.2	2.8	48	0.8435	0.022	0.318
F (Σ 24Ar) 25	25.0	47.2	27.8	—	0.8207	0.010	0.169
F (Σ 24Ar) 50	50.0	47.3	2.7	—	0.8627	0.019	0.316
F (Σ 28Ar) 25	25.0	45.1	29.9	—	0.8224	0.007	0.142
F (Σ 28Ar) 50	50.0	43.2	6.8	—	0.8656	0.013	0.282
F (Σ 32Ar) 25	25.0	41.9	33.1	—	0.8197	0.012	0.126
F (Σ 32Ar) 50	50.0	36.8	13.2	48	0.8606	0.024	0.237
A ^{d)}	—	—	—	29	0.8629	5.38	0.360
A 55 ^{e)}	63.4 ^{f)}	36.6	0.0	54	0.8293	3.41	0.240
F ^{g)}	—	—	—	52	0.8307	1.91	0.130

^{a)} subfraction, ^{b)} *n*-cetane, ^{c)} 2, 2, 4, 4, 6, 8, 8-heptamethylnonane, ^{d)} aromatic-rich gas oil,

^{e)} cetane number-adjusted aromatic-rich gas oil, ^{f)} content of the aromatic-rich gas oil, ^{g)} commercial diesel fuel

* Pallflex Prod. Corp. TX40HI20-WW, 142 mmφ

Fig. 1 Pretreatment Procedure for B(a)P Analysis

ulate matter, which contains B(a)P, was trapped on a Teflon-coated glass fiber filter (Pallflex Corp., TX40HI20-WW, 142 mmφ). The loaded filter was extracted with dichloromethane for 12 hours, and the extract was concentrated and dried. Then acetonitrile was added to the residue and the solution was passed through a preparation column (Waters Associates., Sep-Pak C-18). Finally, the eluate was analyzed using a HPLC with a fluorescent spectroscopic detector. The chromatographic conditions for B(a)P analysis are summarized in **Table 3**. Details of this analytic procedure have been reported elsewhere.⁷⁾

2.3 Engine System

The engine used was a CFR F-5 single cylinder

Table 3 Chromatographic Conditions for PAH Analysis

pump	: Altex Scientific Inc. 101 A
injection device	: Kyowa Seimitsu Co., Ltd., Autosampler KSST-60J, sample volume=40 μl
column	: Beckman, ODS column Ultrasphere-ODS 4.6×250 mm
mobile phase	: 70/30 (v/v) acetonitrile/water at 1.0 ml/min, deoxygenated by bubbling with helium
detector	: Shimadzu Corp., Fluorescence spectrometer RF-530, ex. wave length=330 nm, em. wave length=430nm
data collection	: System Instruments Co., Ltd., Chromatogram processor 7000 AS

test engine for measuring cetane number (ASTM D 613 or JIS K 2280). The exhaust was lead to a dilution tunnel (Horiba Seisakusho Co. Ltd., DLT-09S), obtaining a 1 in 13 dilution, approximately. The diluted exhaust was filtrated with 47 mmφ and 142 mmφ filters, by which the emission rate of the particulate matter and its content of B(a)P were measured. This system was also equipped with an automobile exhaust gas analyzer (Horiba, MEXA 2000) for measuring concentrations of total hydrocarbon(THC), carbon monoxide (CO), nitrogen oxides (NO_x) and carbon dioxide (CO₂), and an electrostatic aerzol analyzer (Nihon Kagaku Kogyo, MODEL 3030) for measuring the size and number of the particulate matter. The schematic diagram of the engine system is shown in **Fig. 2**. The results of the measurements, except those for B(a)P, were reported in the previous papers.

The operating condition of the engine was the

Fig. 2 Schematic Diagram of the Engine and Sampling Systems

Table 4 Reproducibility of B(a)P Measurement

No.	B(a)P Emission Rate (ng/min)	
	H53	F
1	4.8	34.3
2	6.4	64.0
3	7.4	22.8
4	4.9	29.9
5	6.8	53.6
6	5.8	49.9
7	7.1	20.9
8	4.0	53.0
9	4.7	
10	2.5	
mean	5.4	41.1
s. d. ^{a)}	1.5	16.1
c. v. ^{b)} (%)	29	39

a) s. d. : standard deviation

b) c. v. : coefficient of variation

same as that for measuring cetane number, except for the compression ratio and the fuel flow rate. The compression ratio was set at 16.0. The fuel flow rate was set at 15 ml/min for the experiments on pure hydrocarbon-mixed fuels, and varied from 14.6 to 16.0 ml/min for the subfraction-mixed fuels by keeping the excess air ratio constant at 1.35, which was estimated by real time measurement of CO₂, CO and THC exhaust concentrations and calculation according to Holl's equation.⁸⁾ The engine was warmed up for more than 3 hours before the experiment. In addition, about 15 min of preliminary operation with each test fuel always preceded the sampling of the particulate matter, which lasted 20–25 min.

The total reproducibility of the B(a)P measurement from engine operation to the HPLC analysis was examined using fuel H53 and F (Table 4), which was estimated to be 29% and 39%, respectively, as the coefficient of variation. The engine

condition is thought to be the principal factor for the variation.

3. Results

3.1 B(a)P Emission from the Pure Hydrocarbon-mixed Fuels

All the results concerning particulate and B(a)P emissions by combustion of pure hydrocarbon-mixed fuels are summarized in Table 5, where B(a)P emission rates were estimated from particulate emission rates and B(a)P contents in the particulate matter.

Fuels H0 α 0 to H82 are binary mixtures of *n*-cetane and HMN so that these fuels are purely paraffinic. As the content of HMN increases, ternary and quaternary carbon structure increases and cetane number decreases (see Table 1). As shown in Table 5, B(a)P emission rates ranged from 5 to 12 ng/min for these fuels, and there is no definite tendency towards HMN content.

Fuels α 5 to α 70 are binary mixtures of *n*-cetane and α -MN. As α -MN content increases, aromaticity of the mixture increases and the cetane number decreases (see Table 1). The particulate emission rate was maximum at α 30, while B(a)P content in the particulate matter roughly increased with the α -MN content in the fuel. B(a)P emission rates ranged from 7 to 210 ng/min, one order of magnitude larger than those for the purely paraffinic fuels, except for α 5.

Fuels H47 α 5 to H18 α 30 are ternary mixtures of *n*-cetane, HMN and α -MN, keeping the cetane number constant at 55. For fuel H18 α 30, B(a)P emission rate was definitely large compared with the purely paraffinic fuels, due to the increase in both the particulate emission rate and the B(a)P

Table 5 Particulate and B(a)P Emissions by Combustion of Pure Hydrocarbon-mixed Fuels

Fuel	Particulate Emission Rate (mg/min)	B(a)P Content in the Particulate Matter (ppm)	B(a)P Emission Rate (ng/min)
H0 α 0	27.2	0.26	7.1
H29	20.8	0.59	12.3
H35	22.7	0.20	4.5
H53	24.5 $\pm$ 2.7	0.22 $\pm$ 0.06	5.4 $\pm$ 1.5
H82	13.2	0.77	10.1
α 5	29.8	0.25	7.4
α 15	53.6	1.77	94.8
α 30	67.9	3.09	210
α 45	52.0 $\pm$ 5.1	2.10 $\pm$ 0.51	111 $\pm$ 37
α 70	25.6	3.25	83.2
H47 α 5	28.9	0.48	13.8
H35 α 15	36.0	0.37	13.3
H18 α 30	54.8	1.14	62.5
H80D4	24.5	0.35	8.6
H88D8	24.4	0.29	7.1
H85D15	21.6	0.40	8.6

Table 6 Particulate and B(a)P Emissions by the Combustion of Subfraction-mixed Fuels

Fuel	Particulate Emission Rate (mg/ min)	B(a)P Content in the Particulate Matter (ppm)	B(a)P Emission Rate (ng/ min)
F (Σ20S) 25	23.5	0.36	8.4
F (Σ20S) 50	22.0	0.46	10.1
F (Σ24S) 25	24.3	0.21	5.1
F (Σ24S) 50	23.7	0.22	5.2
F (Σ28S) 25	23.7	0.27	6.4
F (Σ28S) 50	23.5	0.33	7.7
F (Σ32S) 25	25.9	0.14	3.6
F (Σ32S) 50	29.3	0.13	3.8
F (Σ20Ar) 25	30.8	0.20	6.2
F (Σ20Ar) 50	51.1	0.67	34.3
F (Σ24Ar) 25	35.8	0.18	6.4
F (Σ24Ar) 50	51.4	1.61	82.8
F (Σ28Ar) 25	32.6	0.45	14.7
F (Σ28Ar) 50	54.2	1.97	106.8
F (Σ32Ar) 25	27.5	0.37	10.2
F (Σ32Ar) 50	39.1	0.60	23.4
A a)	18.3	0.88	16.1
A 55 ^{b)}	38.4	0.23	8.8
F c)	42.2±3.3	0.96±0.35	41.1±16.1

a) aromatic-rich gas oil
b) cetane number-adjusted aromatic-rich gas oil
c) commercial diesel fuel

content.

Fuels H80D4 to H85D15 are purely paraffinic fuels doped with the cetane number improver, setting the cetane number around 55. As shown in the table, the cetane number improver had no influence on the particulate and B(a)P emissions, since these values are in the same order as those for the non-doped fuels (H0α0–H82).

3.2 B(a)P Emission from the Subfraction-mixed Fuels

All the results concerning particulate and B(a)P emissions by the combustion of the subfraction-mixed fuels are summarized in Table 6, in which the results for the commercial (F) and the specially prepared aromatic-rich fuels (A, A55) are also listed.

Fuels F(Σ20S)25 to F(Σ32S)50 are mixtures of *n*-cetane, HMN and 25 or 50 vol% of saturate subfractions of diesel fuels. These fuels, therefore, are almost purely paraffinic. The results for these fuels were almost equal to those for the pure hydrocarbon-mixed, paraffinic fuels (H0α0–H82), and there is no significant tendency towards boiling range or content of the subfractions.

Fuels F(Σ20Ar)25 to F(Σ32Ar)50 are mixtures of *n*-cetane, HMN and 25 or 50 vol% of the aromatic subfractions of diesel fuels. The emissions were mostly great compared with the saturate subfraction-mixed fuels or H53 in Table 5. Both particulate emission rate and B(a)P content were increased with the content of the aromatic subfraction for all the boiling ranges. As for the ef-

fect of the boiling range, the emissions were maximum at F(Σ28Ar)50, which contained the aromatic subfraction having a boiling range from 280 to 320°C. We will consider this point later.

4. Discussion

There are several reports concerning the relationship between the fuel composition and the B(a)P or PAH emission from diesel engines.^{9)~11)} Henderson et al. studied PAH emission using 0.01–1% *n*-cetane solution of some PAHs as fuel and found that the content of pyrene in the exhaust particulate matter increased with its content in the fuel.⁹⁾ They pointed out that PAH species are liable to be emitted unburnt because their boiling points are higher than *n*-cetane. In our study, experiments to add known amounts of B(a)P purposely to the fuel and observe its emission rate were not conducted. However, B(a)P was found in the subfraction-mixed fuels and some original diesel fuels (see Table 2) so that it was possible to examine the effect of B(a)P contained in the fuel on its emission. Fig. 3 shows the B(a)P emission rate as a function of B(a)P supply rate with the fuel. There is no meaningful correlation between the two values in this figure. In addition, in the higher range of B(a)P supply rate, B(a)P is being greatly reduced during the combustion. On the other hand, in the case of pure hydrocarbon-mixed fuels, the fuels were free from B(a)P so that the B(a)P emitted in this instance was clearly the combustion-derived pro-

The supply and emission rates are equivalent on the dotted line.

Fig. 3 Relationship between the B(a)P Supply Rate with the Fuel and the B(a)P Emission Rate

duct in the engine. At any rate, it is concluded from these considerations that the content of B(a)P was not the principal factor for its emission in such low concentration range of B(a)P as in the case of our experiments and the emission level was more affected by other fuel and combustion characteristics.

As for the fuel properties, aromaticity was found to be the principal factor increasing B(a)P emission. In Fig. 4, B(a)P emission rates are exhibited as a function of aromatic carbon supply rate (r_a) with the fuel. B(a)P emission rate is increased roughly exponentially with r_a . When the fuel is almost purely paraffinic, neither branching struc-

ture of the molecule, addition of the cetane number improver nor the boiling range had any effect on the particulate and B(a)P emissions as shown in Table 5 (H0 α 0–H82, H80D4–H85D15) and Table 6 (F(Σ 20S)25–F(Σ 32S)50).

In Fig. 4, the result for α 30 (cetane number=70) deviates to upper side and that for α 70 (cetane number=30) to lower side, so that cetane number of the fuel is thought to be another factor affecting the emission of B(a)P. However, further experiments are necessary to clarify this effect.

Mills et al. reported the effect of diesel fuel aromaticity on PAH emissions using a 2-cylinder engine. They tested specially blended gas oils which ranged in aromatic content from 10 to 70 %, and found that the PAH emission rate (the sum of each amount of PAH examined, mainly

- : Pure hydrocarbon-mixed fuels, cetane number=55
- : Pure hydrocarbon-mixed fuels, cetane number=30
- △ : Pure hydrocarbon-mixed fuels, cetane number=70
- : The subfraction-mixed fuels, cetane number=55
- : Commercial diesel fuel (F), cetane number=55

Fig. 4 Relationship between the Aromatic Carbon Supply Rate and the B(a)P Emission Rate

Fig. 5 The Results of the 50 vol% Subfraction-mixed Fuels

Table 7 Properties of Aromatic Subfraction

Subfraction	Specific Gravity (15/4° C)	Aromatic Carbon Number in a Molecule	Aromaticity
$\Sigma 20\text{Ar}$	0.9102	6.33	0.574
$\Sigma 24\text{Ar}$	0.9474	7.52	0.537
$\Sigma 28\text{Ar}$	0.9565	8.01	0.499
$\Sigma 32\text{Ar}$	0.9453	7.49	0.423

composed of smaller PAHs than chrysene) increased monotonously with the aromaticity of the fuel. Our results are in agreement with theirs.

Fig. 5 shows the results of B(a)P emission rate for the fuels containing 50 vol% of the subfraction. As for the fuels containing the aromatic subfractions, the variation range is great. In order to find the cause of this tendency, some fuel properties were considered, which are listed in **Table 7**. The Maxima of the specific gravity and average aromatic carbon number in a molecule (C_a) are at $\Sigma 28\text{Ar}$, which agree with the tendency of the B(a)P emission. C_a must be six for aromatic substances which contain only one benzene ring. The fact that C_a exceeds six means that there exist certain aromatic substances which contain some fused ring or plural number of benzene rings. The greater the C_a is, the higher is the content of such substances. These substances are thought to be more liable to change into B(a)P than simple benzene derivatives. It will be our next aim to clarify this point or to attempt to identify certain substance which especially participate in the formation of B(a)P.

5. Conclusion

Effects of the fuel composition on the emission of benzo(a)pyrene (B(a)P) were investigated using

a CFR F-5 engine under an operating condition of a fixed fuel injection timing, revolution and fuel flow rate or excess air ratio, and using pure hydrocarbon-mixed fuels or subfraction-mixed fuels.

B(a)P emission rate generally increased with aromaticity of the fuel. Additional effects by cetane number and molecular structure were suggested for the fuels containing aromatics. In the case of almost purely paraffinic fuels, neither branching structure of the molecules, addition of the cetane number improver nor the boiling range had any effect on the particulate and B(a)P emissions. There was no evident relationship between the content of B(a)P in the fuel (0.03–5 mg/liter) and its emission rate.

References

- 1) Greeves, G., Wang, C.H.T., Soc. Automotive Eng. Paper No. 810260, (1981).
- 2) Ohuchi, H., Ohi, A., Aoyama, H., *Sekiyu Gakkaishi*, **25**, (4), 205 (1982).
- 3) Ohi, A., Aoyama, H., Obuchi, A., Ohuchi, H., *Sekiyu Gakkaishi*, **27**, (4), 303 (1984).
- 4) Ohi, A., Aoyama, H., Obuchi, A., Ohuchi, H., *Sekiyu Gakkaishi*, **27**, (4), 313 (1984).
- 5) Barth, D. S., Blacker, S. M., *J. Air Pollut. Contr. Assoc.*, **28**, 769 (1978).
- 6) Tejada, S. B., Zweidinger, R. B., Sigsby, Jr, J. E., Soc. Automotive Eng., Paper No. 820775, (1982).
- 7) Obuchi, A., Aoyama, H., Ohi, A., Ohuchi, H., *J. Chromatogr.*, **312**, 247 (1984).
- 8) Holl, W. H., Soc. Automotive Eng., Paper No. 730533, (1973).
- 9) Henderson, T. R., Sun, J. D., Li, A. P., Hanson, R. L., Bechtold, W. E., *Environ. Sci. Technol.*, **18**, 428 (1984).
- 10) Mills, G. A., Howarth, J. S., Howard, A. G., *J. Inst. Energy*, **57**, (430), 273 (1984).
- 11) Mills, G. A., Howard, A. G., *J. Inst. Energy*, **56**, (428), 131 (1983).

要 旨

ディーゼル機関の燃料組成の改善による排出物質の低減
(第4報) 燃料組成のベンゾ(a)ピレン排出に及ぼす影響

小 瀧 存, 大井 明彦, 青山兵五郎, 大内日出夫

公害資源研究所, 305 茨城県筑波郡谷田部町小野川 16-3

ディーゼル車は、燃料経済性が優れているために近年増加の傾向にあるが、粒子状物質（黒煙）と窒素酸化物の排出量が多く、これらの有害物質による大気汚染が問題となりつつある。¹⁾とりわけ、粒子状物質については、発がん性の疑いのある有機物質の存在が確認されており、その排出の実態を定量的に把握することが望まれている。^{2), 3)}中でも、ベンゾ(a)ピレン (B(a)P) は、発がん性を有する種々の多環芳香族炭化水素の代表的な物質で、これの定量方法や生物化学的な性質は詳しく調べられている。著者らは、ディーゼル燃料の組成、性状と排出物質との間の詳細な関係を明らかにすることにより排出物質低減対策に寄与するディーゼル燃料の改変の方向を提示することを目的とした研究を進めてきたが^{2)~4)}、上述の理由により、新たに、粒子状物質に含まれる B(a)P を分析の対象に加え、燃料組成とその排出量との関係を調べた。

二組の燃料を試験に供した。第一は、3種類の単一成分炭化水素 *n*-セタン、ヘプタメチルノナン (HMN)、1-メチルナフタレン (α -MN) とセタン価向上剤 (DII-2, Ethyl 社製) を適宜混合したもので (Table 1)、燃料の芳香族成分およびセタン価向上剤の含有量、セタン価が B(a)P の排出量に及ぼす影響を調べた。第二は、軽油相当留分の油を分留および分取クロマトグラフィーにより沸点範囲別、さらに飽和成分、芳香族成分別に分けた試料を、セタン価 55 に合わせたもので (Table 2)、燃料の芳香族成分含有量および沸点が B(a)P の排出量に及ぼす影響を調べた。B(a)P の分析手順は Fig. 1 に示す通りで、ディーゼル機関の排出ガスを約 13 倍に希釈した後、142 mmφ のガラス繊維円板ろ紙を通して粒子状物質を採取し、抽出、前処理の後、蛍光検出器付の高速液体クロマトグラフィーで定量を行った (Tables 3, 4)。使用した機関は、セタン価測定用 CFR F-5 ディーゼル機関 (ASTM D613 または JIS K 2280) で、圧縮比 16.0、燃料消費量 15 ml/min (単一成分炭化水素混合燃料の場合) または 空気過剰率 1.35 (分割試料混合燃料の場合) 以外の条件は、セタン価測定時のものと同じとした。機関を含む装置系を Fig. 2 に示す。

Table 5 に、単一成分炭化水素混合燃料の燃焼における粒子状物質および B(a)P 排出量の結果をまとめた。

n-セタンと HMN を混合した純パラフィン系燃料 H0 α 0~

H82 の場合、B(a)P の排出量は 5~12 ng/min で、2成分の混合比による変化は認められなかった。一方、*n*-セタンと α -MN を混合した燃料 α 5~ α 70 の場合、B(a)P 排出量は α 5 を除くと 80~210 ng/min で、純パラフィン系燃料に比べて著しく増加した。H47 α 5~H18 α 30 は、セタン価を 55 に保ったまま *n*-セタン、HMN、 α -MN の混合比を変えたもので、粒子状物質および B(a)P 排出量は α -MN を 30% 含む H18 α 30 のとき、純パラフィン系の H0 α 0~H82 と比べて明らかな増加が認められた。H80D4~H85D15 は *n*-セタンと HMN の混合物にセタン価向上剤を添加した燃料で、H0 α 0~H82 との比較からわかるように、セタン価向上剤の使用は粒子状物質、B(a)P の排出量に何ら影響を及ぼさなかった。

Table 6 に、分割試料混合燃料の燃焼における粒子状物質および B(a)P 排出量の結果をまとめた。

F(Σ 20S)25~F(Σ 32S)50 は、飽和成分の分割試料、*n*-セタン、HMN から成る燃料で、純パラフィン系に近い性状のものである。これらの場合、B(a)P 排出量は単一成分炭化水素混合燃料における純パラフィン系の H0 α 0~H82 と同様の小さい値となり、また、分割試料ごとやその混合率による変化も認められなかった。一方、F(Σ 20Ar)25~F(Σ 32Ar)50 は芳香族成分の分割試料、*n*-セタン、HMN から成る燃料で、B(a)P の排出量は、飽和成分を混合した燃料に比べて一般に大きく、分割試料の混合率とともに増加した。また、分割試料ごとの変化も著しかったが、沸点範囲と単調な関係にはなかった。

以上の結果について次のような考察を行った。まず、燃料中に含まれる B(a)P とその排出量の関係を調べたところ (Fig. 3)、報告例にあるような正の相関関係⁵⁾は認められなかった。これは、本研究における燃料中の B(a)P 排出量が報告例よりも極端に低いためと思われる。次いで、燃料の芳香族性と B(a)P 排出量の関係を調べ (Fig. 4)、B(a)P 排出量が芳香族成分の供給量とともに指数関数的に増大することを見出した。この際、セタン価も B(a)P 排出量に影響を及ぼすことが示唆された。さらに、芳香族成分の分割試料における試料ごとの B(a)P 排出量の違い (Fig. 5) は、燃料中の芳香族成分の構造の違いとよく対応すること (Table 7)、などを明らかにした。

Keywords

Benzo(a)pyrene, Diesel fuel, Emission