Formation of PM and Soot Precursor in Diffusion Flame Generated by Thermally Decomposed Diesel Fuel

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Particulate matter (PM) and soot precursor formation by thermally decomposed n-paraffin and iso-paraffin fuels were studied in a high temperature atmosphere to simulate diesel combustion. Thermally decomposed hydrocarbons were generated using a plug flow reactor. They were immediately introduced into a co-flow diffusion burner as fuel. Both fuels produce thermally decomposed hydrocarbons having different compositions that affect PM and soot formation. Branched molecular structure fuel causes more exhaust PM concentration than n-paraffin fuel because of increasing first aromatic ring concentrations and PAHs. PAHs fluorescence wavelength in SOF features a 464nm peak when soot appears.

Key words: Thermal Decomposition, Diesel Fuel, Soot Formation, Soot Precursor, PAHs, Spectroscopic Measurement

1. Introduction

At high load, diesel engines tend to produce particulate matter (PM) including soot that negatively affects the environment and human health. To reduce PM, diesel engine combustion has been investigated extensively with particular focuses on improving fuel and lubricants and developing after treatments such as catalyst technology and Diesel Particulate Filters (DPFs) [1].

Diesel fuel injected into engine cylinder with high temperature and high pressure soon vaporizes and chemically decomposes before initial burning. The decomposed fuel is supplied to the diffusion flame during the combustion. Authors have been studied thermal decomposition of the fuel in the diesel combustion using a rapid compression machine and a plug flow reactor [2],[3], suggesting light hydrocarbons (LHCs) produced by the thermal decomposition affect the combustion and emission formation.

Soot is produced when hydrocarbon fuel is exposed to high temperature and inadequate oxygen vapor phase [4]. There might be effects due to thermal decomposition on soot formation. Soot formation is affected by the molecular branched structure of fuel [5] and thermal decomposition of fuel with different chemical structure may cause other effects.

The present experiment fundamentally investigates PM and soot precursor formation during diesel combustion by using a plug flow and a co-flow diffusion burner.

2. Experimental methods

The experimental setup (Fig.1) consisted of a plug flow reactor and a co-flow diffusion burner. Immediately after fuel was thermally decomposed in the flow reactor, the fuel was fed to the co-flow diffusion burner. A plug flow reactor was used to analyze thermal decomposition of two high molecular liquefied fuels that are main components of diesel fuel:

(1) n-paraffin (Normal saturated paraffin, $C_{12}H_{26}$: 27wt.%, $C_{13}H_{28}$: 47wt.%, $C_{14}H_{30}$: 26wt.%)

(2) iso-paraffin (Iso-alkyl structure of saturated paraffin, $C_{11}H_{24}$: 9.7wt.%, $C_{12}H_{26}$: 12.8wt.%, $C_{13}H_{28}$: 16.1wt.%, $C_{14}H_{30}$: 44.1wt.%, $C_{15}H_{32}$: 17wt.%, $C_{16}H_{34}$: 0.2wt%, Olefin: 0.1vol.%, Aromatics(1R): 0.2vol.%)

Thermally decomposed hydrocarbons produced in the plug flow reactor were used as fuels in a co-flow diffusion burner. A gas sampling method was used to analyze PM in the exhaust gas from the co-flow diffusion

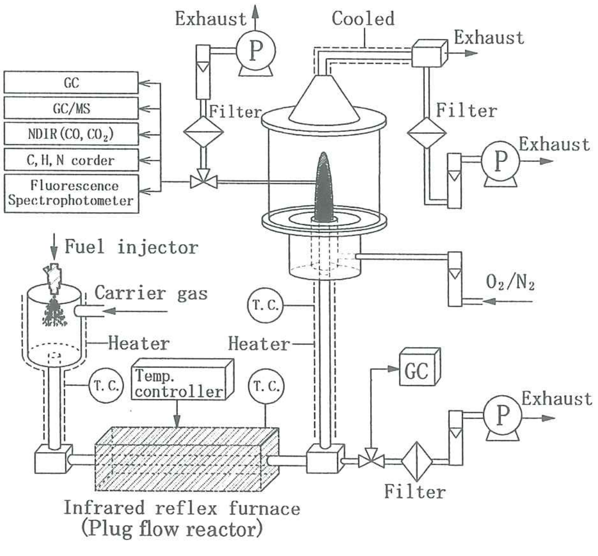

Fig.1 Schematic diagram of experimental setup

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burner. PM and gas compositions in the flame centerline were also analyzed. A fluorescence spectrophotometer was used to measure polycyclic aromatic hydrocarbons (PAHs) included in SOF (Soluble Organic Fraction) extracted from PM.

Plug flow reactor

Residence time (tr) of the fuel-nitrogen mixture in the reactor was relatively long 40ms and controlled furnace temperatures (Tr) of 1350K and 1500K were high because such conditions were needed to decompose enough high molecular liquefied fuel in nitrogen atmosphere. A high temperature gas sampler (Yanaco GHS-50) was used to inject some thermally decomposed fuels into a gas chromatograph (GC: Yanaco G3800) equipped with FID and TCD. Thermally decomposed hydrocarbons were sampled on a teflon filter (MILLIPORE FHLP04700 d=47mm hole=0.45μm). Soluble organic fraction (SOF) was eluted into dichloromethane 5000 (DCM) by a Soxhlet extractor. PAHs in the DCM were injected by a micro syringe into a gas chromatography / mass spectrometry device (GC/MS: Finnigan MAT GCQ). Standard samples (Naphthalene, Acenaphthene, Phenanthrene, Anthracene, Fluoranthene, Pyrene) and the NIST library were used for qualitative analysis.

Co-flow diffusion burner

Thermally decomposed hydrocarbons produced in the flow reactor were introduced into the co-flow diffusion burner as fuel. Atmospheric pressure and axisymetric co-flow diffusion flames were generated using the burner in which fuel and nitrogen flowed from a centerline tube (22.65mm i.d.). Oxygen and nitrogen co-flowed through the outer tube (38mm i.d.) Oxidizer velocity was adjusted to the fuel carrier gas mixture using a ring plate on the outer tube. The burner outlet was surrounded by a cylindrical quartz tube to prevent excess air inflow.

In the combustion vessel, equivalence ratio (ϕ_b=(Air/Fuel)$_{theory}$ / (Air/Fuel)$_{real}$) was kept at 1.0, 1.5, 2.0. Experimental data of exhaust PM concentration, carbon and hydrogen weight ratio C/H in PM were obtained. SEM (Scanning Electron Microscopy) images of PM and types of PAHs in SOF were analyzed. PM was sampled at 4*l*/min with a diaphragm pump on the teflon filter, which was dried at least 12 hours before and after collection. PM concentration was determined by weight. SOF was extracted from PM using the Soxhlet method. An elemental analyzer (Yanaco MT-6) for C/H analysis was used with a quartz filter (Whatman QM-A) that was dried at least 12 hours before and after collection. PM was captured on a micro grid (Oukenshoji TypeA) attached to the teflon filter when PM was sampled. SEM (Hitachi S-4700) was used to observe PM structures. GC/MS, UV-Visible spectroscopy (UV-VIS: Hitachi U-2010) and fluorescence spectrophotometer (FL: Hitachi F-2500) were used to analyze PAHs in SOF.

PM, light molecular weight hydrocarbons (LHCs), PAHs, CO and CO_2 in the vertical centerline of the flame were extracted using an alumina sampling tube (1mm i.d. 2mm o.d., length 235mm) with a flow rate of 0.9 l/min inserted via one of the holes placed on vertical line at 15mm intervals in the cylindrical quartz tube. Surface temperature of the alumina sampling tube was kept at 300℃ to prevent PAHs condensation. PAHs extracted from the flame were eluted directly into 50ml DCM ice-cooled at 0℃. DCM samples were analyzed by GC/MS, UV-VIS and FL. Quantitative analysis using GC/MS calibration-curve method was applied to standard samples. The total ionization cross section method [6] was used to quantify non-standard PAHs samples. CO and CO_2 concentrations were measured by NDIR (Yanaco ALTAS-12F).

3. Results and Discussion

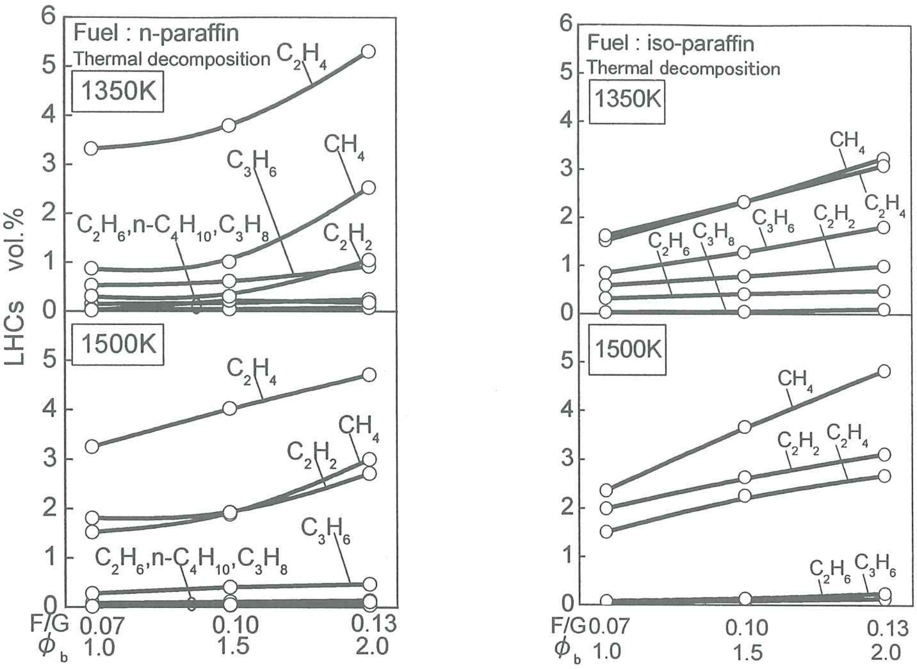
Thermal decomposition of n-paraffin and iso-paraffin fuels

LHCs formation

LHCs are produced in the order $C_2H_4>CH_4>C_3H_6>C_2H_2$ from n-paraffin at fuel-carrier gas mass flow rate F/G=0.07 and F/G=0.10 in 1350K nitrogen atmosphere (Fig.2). At F/G=0.13, C_2H_2 concentration increases. In all F/G conditions at 1500K. LHCs are produced in the order $C_2H_4>C_2H_2 \fallingdotseq CH_4>C_3H_6$. C_2H_4 concentration is highest at both temperatures because of the β rule for n-paraffin [7]. Chemical reaction at 1350K is slower than at 1500K. According to Gibbs free energy map of hydrocarbons [8], CH_4, C_2H_2 and C_2H_4 tend to increase at higher temperature and thus C_2H_4 concentrations differ between 1350K and 1500K, but the concentration of C_2H_4 was similar at both temperatures.

At 1500K, there are additional chemical reactions on C_2H_4, the βrule comes into effect and C_2H_4 reacts to more lighter weight hydrocarbons such as CH_4 and C_2H_2.

LHCs are produced in the order $C_2H_4=CH_4>C_3H_6>C_2H_2>C_2H_6$ from iso-paraffin at 1350K and $CH_4>C_2H_2>C_2H_4$ at 1500K. In addition to



(a) n-paraffin (b) iso-paraffin

Fig.2 LHCs production during thermal decomposition of n-paraffin and iso-paraffin in the plug flow reactor

C_2H_4, there is high concentration of CH_4 originated from C-C bond dissociation of iso-paraffin fuel.

Figure 3 is one of examples of C-C bond dissociation with thermal decomposition of 2-methylbutane. Large amounts of C-C bond are weaker than the small amounts of C-C bond, favoring such fission. CH_3 abstracts H-atoms that have weaker bond, producing a lot of CH_4. At 1500K, alkane such as C_3H_8 and C_2H_6 tend to be decomposed to alkene and alkyne, producing C_2H_4, C_2H_2 and CH_4.

PAHs formation

Figure 4 shows chromatograms of thermally decomposed n-paraffin and iso-paraffin fuels. For n-paraffin fuel at 1350K, two aromatic rings of naphthalene appear along with remaining fuel C_{12}, C_{13}, C_{14}. At 1500K, 2-5 fused aromatic rings are formed and there are no detectable fuel constituents. For iso-paraffin fuel, 2-4 fused aromatic rings are produced at 1350K and 2-5 fused aromatic rings are produced at 1500K.

Aromatic ring formation

Benzene formation in n-paraffin and iso-paraffin fuels is shown in Fig.5. Benzene concentration in n-paraffin is lower than in iso-paraffin. Benzene is formed via LHC reactions [9] and many branched molecular bonds of iso-paraffin promote the reactions. Iso-paraffin fuel tends to form benzene and first aromatic rings. Pathways through the first aromatic rings (e.g. benzene, toluene and phenyl radicals) probably affect PAHs formation and growth.

These thermal decomposition of the fuels can contribute the construction of pyrolysis kinetic reaction mechanism used in the numerical analysis that predicts diesel combustion.

PM and soot precursor generation by thermally decomposed n-paraffin and iso-paraffin fuel

Exhaust PM analysis using a co-flow diffusion burner

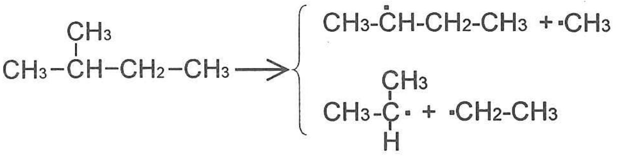
Thermally decomposed hydrocarbons produced in the flow reactor were supplied to the co-flow diffusion burner as fuel.

Figure 6 shows exhausted PM concentration containing soot and SOF related to equivalence ratio (ϕ_b). Using decomposed n-paraffin fuel, PM increases with increase in reactor temperature (Tr) and ϕ_b. Soot appears at ϕ_b>1.5 or soot formation is promoted at higher equivalence ratio. Using decomposed iso-paraffin fuel, soot is produced at high equivalence ratio and high temperature. PM formation at ϕ_b=1.5~2.0 differs significantly between 1350K and 1500K. At 1500K, simultaneous increase of soot and SOF is remarkable.

SEM images of exhausted PM were taken under soot conditions of ϕ_b =2.0 at 1350K and 1500K. Figure 7 shows aggregated PM. For decomposed n-paraffin at 1350K, PM aggregates less and disperses. At 1500K, PM forms large chain-like aggregations. For decomposed iso-paraffin, even if sampling time was shorter than when using n-paraffin, much more PM is produced, therefore PM formation is much faster. Generally, diesel soot has extremely small 30-50nm particles that agglomerate in a chain-like structure.

Decomposed n-paraffin at 1350K has the least diesel soot formation, but there appears diesel soot feature in the other conditions (Fig.7).

For decomposed n-paraffin (sampling time=1min), PM elemental measurements are C/H=7.6 at 1350K and



$$CH_3\text{-}\overset{CH_3}{CH}\text{-}CH_2\text{-}CH_3 \longrightarrow \begin{cases} CH_3\text{-}\dot{C}H\text{-}CH_2\text{-}CH_3 + \cdot CH_3 \\ CH_3\text{-}\underset{H}{\overset{CH_3}{C}}\cdot + \cdot CH_2\text{-}CH_3 \end{cases}$$

Fig.3 Thermal decomposition pathways of 2-methylbutane

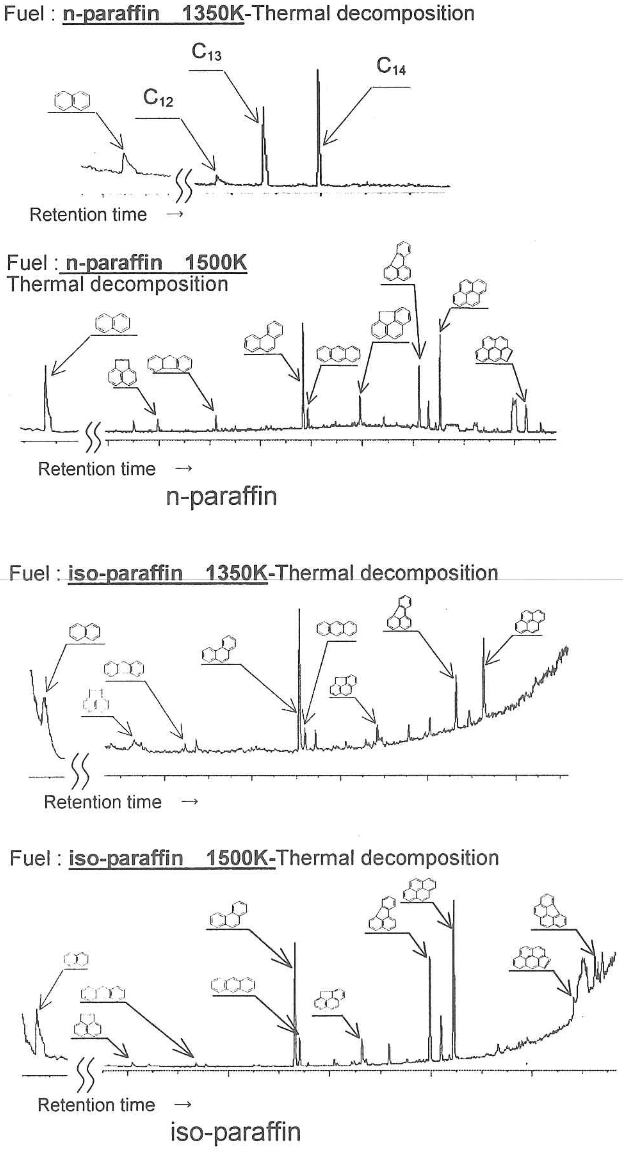


Fig.4 PAHs production during 1350K and 1500K thermal decomposition of n-paraffin and iso-paraffin in the plug flow reactor

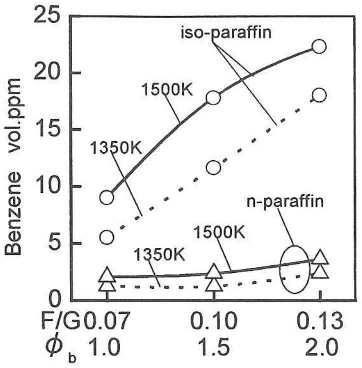


Fig.5 Benzene production during 1350Kand 1500K thermal decomposition of n-paraffin and iso-paraffin in the plug flow reactor

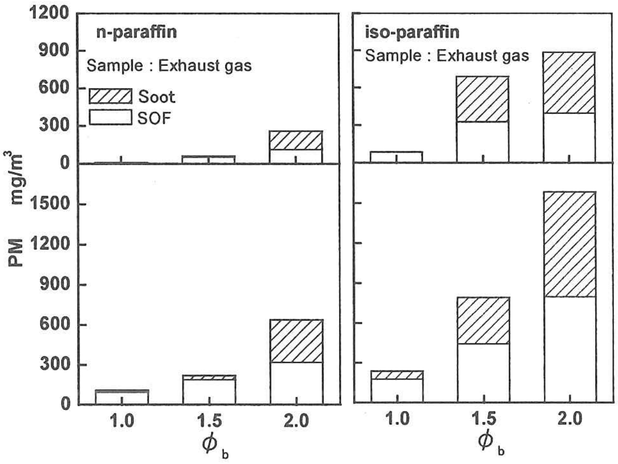
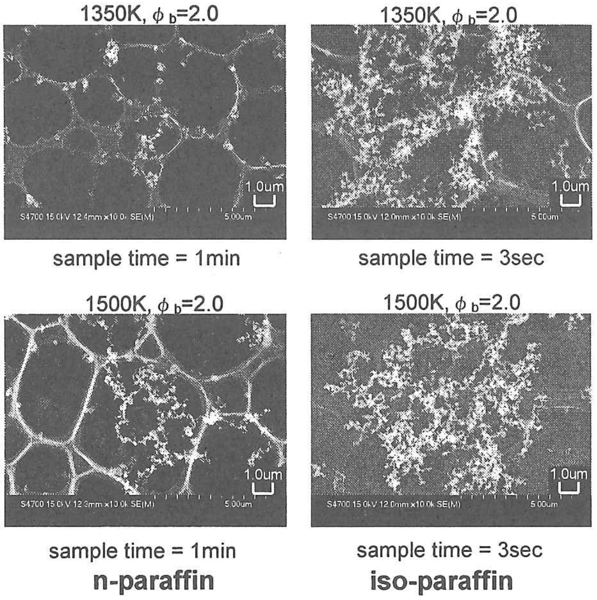


Fig.6 Exhaust PM formation of n-paraffin and iso-paraffin



1350K, ϕ_b=2.0 1350K, ϕ_b=2.0

sample time = 1min sample time = 3sec

1500K, ϕ_b=2.0 1500K, ϕ_b=2.0

sample time = 1min sample time = 3sec

n-paraffin **iso-paraffin**

Fig.7 PM aggregate structure in SEM images

C/H=13.7 at 1500K. For decomposed iso-paraffin (sampling time = 3sec), PM elemental measurements are C/H=3.72 at 1350K and C/H=5.7 at 1500K. Carbonization develops at high temperature, even though the PM produced via decomposed iso-paraffin at 1350K and 1500K looks similar structures in SEM images.

Analysis of PM and gas composition in the flame

PM concentration and gas composition in the flame were examined at sooting condition of ϕ_b =2.0 at 1500K. Figure 8 shows PM concentrations in the flame centerline at the position z/h, where z is the distance from the burner outlet and h is the flame height. The difference between PM and SOF concentrations is defined as soot. For decomposed n-paraffin, small quantities of PM are produced and PM concentrations are almost constant at all sampling points. For decomposed iso-paraffin, soot formation is clearly identified and PM concentration varies depending on the position. PM is produced at about z/h=0.2, reaching maximum concentration at about z/h=0.5. PM in the flame reduces after peaking, but soot increases to about 50vol.% of PM at about z/h=0.9. For decomposed iso-paraffin, both formation and oxidation of PM and soot are active in the flame.

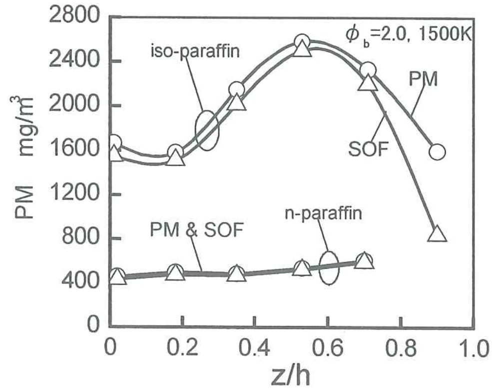


Fig.8 PM formation in the flame centerline for n-paraffin and iso-paraffin

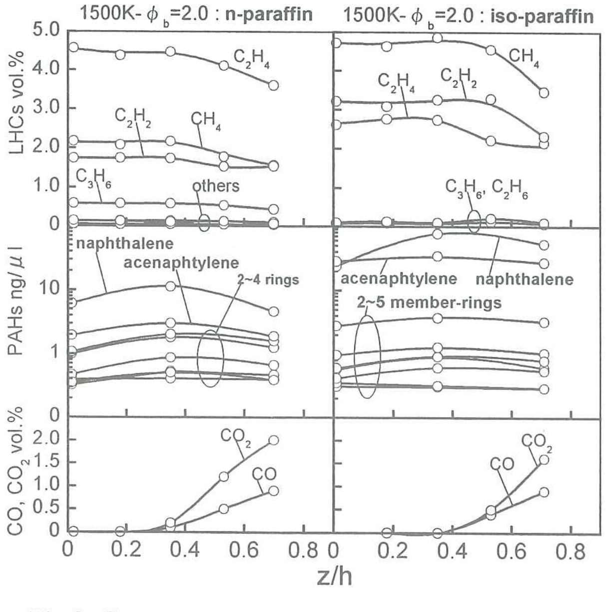


Fig.9 Concentrations of LHC, PAHs and CO, CO_2 in the flame centerline for n-paraffin and iso-paraffin

Figure 9 shows concentrations of LHCs, PAHs, CO and CO_2 in the flame. For decomposed n-paraffin, LHC concentrations keep constant from the burner outlet to z/h=0.4, but those concentrations reduce at z/h>0.5. PAH concentrations increase gradually to z/h=0.4, but the concentrations are lower at about z/h=0.75~0.8. CO and CO_2 are produced at z/h>0.4, probably showing oxidation of LHCs and PAHs.

For decomposed iso-paraffin, LHC concentrations are constant until the middle of the flame and reduce downstream. Except for naphthalene concentration fluctuates, PAH concentrations are constant at all sampling positions. Acenaphtylene and naphthalene are produced about ten times more than other PAHs. As in decomposed n-paraffin, CO and CO_2 increase at z/h>0.4, but CO_2 concentration is lower or combustion is restrained in the decomposed iso-paraffin. Soot concentration increases in the decomposed iso-paraffin fuel downstream shown in Fig.8, suggesting that LHCs such as C_2H_2, benzenoid aromatic ring and PAHs having strong soot tendency are not oxidized sufficiently and are probably soot formation materials.

Spectra of fluorescence for PAHs included in SOF extracted from PM

GC/MS analysis of SOF samples of the decomposed n-paraffin fuel at ϕ_b=1.0, 1350K shows no soot but at ϕ_b=2.0, 1500K there is soot formation. Qualitative PAHs contain 2-5 aromatic rings in both SOF samples, but there is no qualitative difference in chromatographic detection of PAHs or in the number of aromatic rings.

UV-VIS measurements of PAHs absorbance for wavelengths are in Fig.10. 321nm and 337nm wavelengths are of pyrene, judged from standard

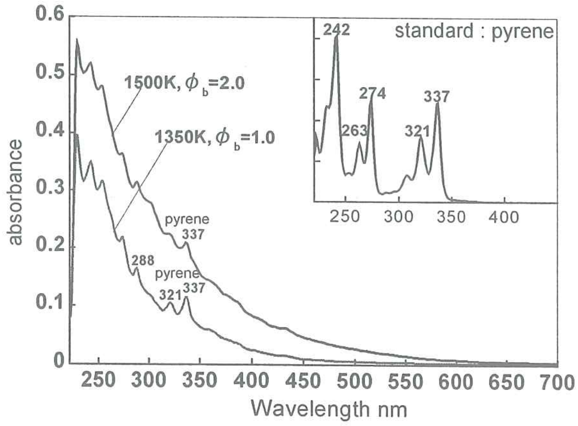


Fig.10 UV-VIS spectra of PAHs in SOF extracted from exhaust PM

material. Many PAHs have wide range of wavelength absorbance and are mixed together, so SOF sample wavelengths have gentle peaks.

GC/MS and UV-VIS analyses suggest that the relationship between PAHs and soot formation is not well understood. Considering pyrene wavelength peaks detected by UV-VIS, PAHs in SOF having wavelength peaks higher than pyrene were excited using FL. Strong peaks detected in high wavelength regions might be a signal for high molecular weight PAHs.

Figure 11 shows fluorescence wavelength excited at λ_{ex}=337nm. Only pyrene peaks appear at ϕ_b=1.0, 1350K, but an accompanying 464nm wavelength peak with strong fluorescence intensity appears at ϕ_b=2.0, 1500K. When pyrene concentration is high or pyrenes approach each other, they may sympathize and excimer luminescence (about 475nm) may emit. In this experiment, under usual measurement conditions 50ng/µl pyrene concentration is relatively high. However, the excimer disappears, indicating that the 464 nm wavelength peak might show PAH development.

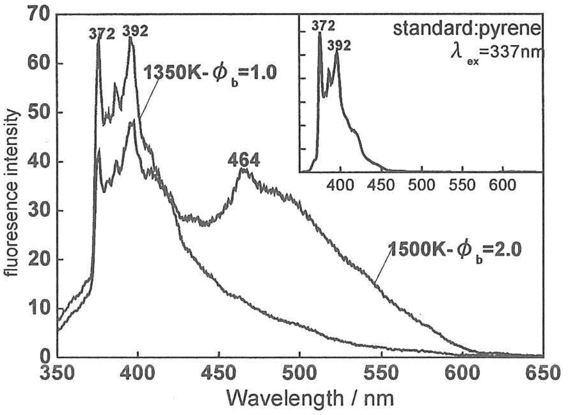


Fig.11 Fluorescence spectra of PAHs in SOF extracted from exhaust PM

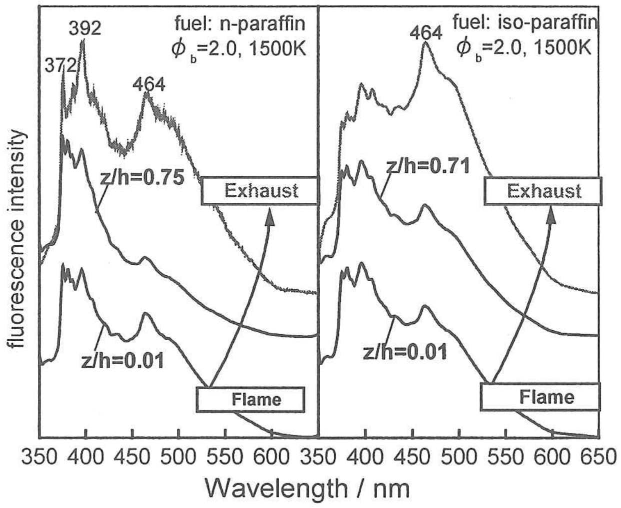


Fig.12 Fluorescence spectra of PAHs in SOF sampled in the flame centerline and the exhaust for n-paraffin and iso-paraffin

Measurements of fluorescence caused by PAHs in exhaust PM and PM in the flame centerline show 464nm wavelength peaks in the sooting flame at ϕ_b=2.0, 1500K (Fig.12). In both decomposed n-paraffin and iso-paraffin fuels, the 464nm appears in any sampling position. The 372nm and 392nm peaks of pyrene appear specifically on decomposed n-paraffin, but the intensity reduces and the 464nm peak fluorescence is much stronger in decomposed iso-paraffin. When the 464 nm wavelength peak is strong intensity, soot is produced further. This peak relates to soot precursor.

4. Conclusion

The effects of the molecular structure of n-paraffin and is-paraffin on soot formation were investigated at an atmospheric pressure. The following conclusions have been drawn.

(1) N-paraffin and iso-paraffin fuels thermally decomposed in high temperature nitrogen atmosphere produce PAHs as well as LHCs such as CH_4, C_2H_4, C_2H_2. Iso-paraffin fuel forms a lot of PAHs even at low temperature.

(2) For decomposed n-paraffin fuel, soot concentration increases at rich condition of equivalence ratio over 1.5 and soot forms in chain-like aggregates. Carbonization progresses using the decomposed n-paraffin and iso-paraffin fuels produced in a high temperature reactor.

(3) Compared to decomposed n-paraffin, PM and soot are formed and oxidized relatively fast in decomposed iso-paraffin. In a high temperature, soot forms even at low equivalence ratio. High equivalence ratio causes PM production and PM carbonization.

(4) For both decomposed n-paraffin and iso-paraffin fuels, a 464nm fluorescence wavelength peak appears in SOF sampled in the flame and the exhaust gas at soot formation condition of rich fuel and high temperature. This 464nm peak is related to soot precursor.

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