

Effect of Fuel Properties of Kerosene on Deposit Accumulation* (Deposit Accumulation on Wick during Wick Combustion)

Kazuhiro HAYASHIDA**, Katsuhiko HAJI***, Hiromi ISHITANI**
and Masataka ARAI****

**Department of Mechanical Engineering, Kitami Institute of Technology,
165 Koen-cho, Kitami, Hokkaido 090-8507, Japan
E-mail: hayashka@mail.kitami-it.ac.jp

***Advanced Technology and Research Institute, Petroleum Energy Center (PEC),
1-4-10 Ohnodai, Midori-ku, Chiba 267-0056, Japan
(Present address: Research & Development Division, JX Nippon Oil & Energy Corporation,
8 Chidori-cho, Naka-ku, Yokohama 231-0815, Japan)

****Department of Mechanical System Engineering, Gunma University,
1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

Abstract

Effect of fuel properties of kerosene on deposit accumulation was studied experimentally. Five types of kerosene, which distillation and composition properties were different, were used as the test fuel. Deposit accumulation processes were investigated by using wick combustion burner. Deposit accumulation rate was estimated from the mass of deposit which accumulated on wick and the fuel consumption. As the results, it was confirmed that the deposit accumulation rate increased with the content of aromatic hydrocarbons and naphtho benzenes. Main component of the deposit was heavy hydrocarbons formed by thermal decomposition and polycondensation of the fuel within the wick. To estimate the effect of peroxide on deposit accumulation, test fuels which contain peroxide generated by sun exposure were used. The peroxide-containing fuels significantly increased the deposit mass than normal fuels.

Key words: Liquid Fuel, Diffusion Combustion, Combustion Products, Kerosene, Deposit, Fuel Property, Peroxide

1. Introduction

Household combustion appliances, such as space heaters and boilers, emit exhaust gas, which must be extremely clean because it is discharged either directly into an interior room or immediately outside of the house. However, as many household combustion appliances are small and portable, the installation of an exhaust aftertreatment system is difficult. Thus, to reduce the quantity of the air pollutants contained in the exhaust gas, improvements to combustion technology are indispensable.

Adjustment of the properties of the fuels is an effective way to improve the combustion characteristics so that minimize pollutant emissions. Basic knowledge between the fuel properties and practical combustion performances is necessary to make effective adjustments corresponding to the ongoing diversification of fuels, such as newly-introduced crude oil, sulfur-free fuel, and synthetic fuel⁽¹⁾⁽²⁾. Therefore, the effects of fuel properties on the diffusion combustion of kerosene have been investigated in a previous study⁽³⁾.

When combustion appliances are used for a long time, deposits gradually accumulate

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on the parts of the appliance that are exposed to high temperatures, such as the fuel nozzle and the combustion chamber wall. Excessive deposit accumulation can cause malfunctions of combustion appliances, such as decreased output and degradation of exhaust emissions. Deposits can be broadly classified into two categories: soot-like deposits and tar-like deposits. Soot-like deposits are formed by the accumulation of soot particles generated by combustion. Conversely, tar-like deposits are formed by the thermal decomposition and polycondensation of fuels. Therefore, the accumulation characteristics of tar-like deposits should be strongly affected by changes in the properties of the fuel used; however, this relationship has not been investigated in detail.

In this study, the effects of fuel properties on deposit accumulation were investigated through deposit accumulation on wick during wick combustion. Several types of kerosene, which have different fuel properties, were used as the test fuels. Moreover, to estimate the influence of peroxide on deposit accumulation, test fuels containing peroxides generated by oxidative degradation were used.

2. Test Fuel and Experimental Apparatus

2.1 Test Fuels

Five types of kerosene, with different distillation and compositional properties, were used as test fuels. The physical properties of the test fuels are shown in Table 1. Regarding fuel E, the end point (246.5 °C) and density (0.7547 g/cm³) were lower than those of the other fuels. Furthermore, its smoke point (>50 mm) implies that the sooting tendency of

Table 1 Physical properties of test fuels

Test item		Test method	A	B	C	D	E
Density (15°C)[g/cm ³]		JIS K2249	0.7910	0.7895	0.7884	0.7980	0.7547
Distillation characteristics	Initial boiling point [°C]	JIS K2254	153.5	147.0	146.5	145.5	156.0
	5vol% [°C]		166.0	161.0	161.5	158.0	164.5
	10vol% [°C]		167.5	165.5	165.0	160.5	165.5
	20vol% [°C]		174.5	172.5	171.5	167.0	168.5
	30vol% [°C]		181.0	179.5	178.0	174.0	172.5
	40vol% [°C]		187.5	187.0	184.5	182.0	177.5
	50vol% [°C]		194.5	194.5	192.0	191.5	182.5
	60vol% [°C]		202.5	204.0	201.0	201.5	190.5
	70vol% [°C]		212.0	214.0	210.5	211.5	201.0
	80vol% [°C]		223.0	227.0	225.5	223.0	215.0
	90vol% [°C]		236.0	244.5	239.0	238.5	232.5
	95vol% [°C]		246.0	259.5	254.0	249.0	242.0
	97vol% [°C]		252.0	270.5	264.0	256.0	246.5
	End point [°C]		256.0	276.5	270.0	259.5	246.5
Percent recovery [vol%]	98.5	98.5	98.5	98.5	98.5		
Percent residue [vol%]	1.0	1.0	1.0	1.0	1.0		
Percent loss [vol%]	0.5	0.5	0.5	0.5	0.5		
Kinematic viscosity (30°C) [mm ² /s]		JIS K2283	1.347	1.365	1.335	1.373	1.334
Net calorific value [J/g]		JIS K2279	43380	43430	43440	43390	44100
Smoke point [mm]		JIS K2537	23.0	24.0	24.0	26.0	>50
Freezing point [°C]		JIS K2276	-48.5	-45.5	-49.0	-68.0	-66.0
Flash point [°C]		JIS K2265	45.0	43.5	44.0	39.5	46.0
Elemental analysis	Sulfur [mass ppm]	JIS K2541	8	4	2	<1	<1
	Nitrogen [mass ppm]	JIS K2609	<1	<1	<1	<1	<1
	Carbon [mass%]	JPI Method	85.8	85.9	85.6	85.8	84.6
	Hydrogen [mass%]	JPI Method	14.0	14.1	14.1	14.2	15.4
CH ratio		—	0.51437	0.51132	0.50953	0.50713	0.46107

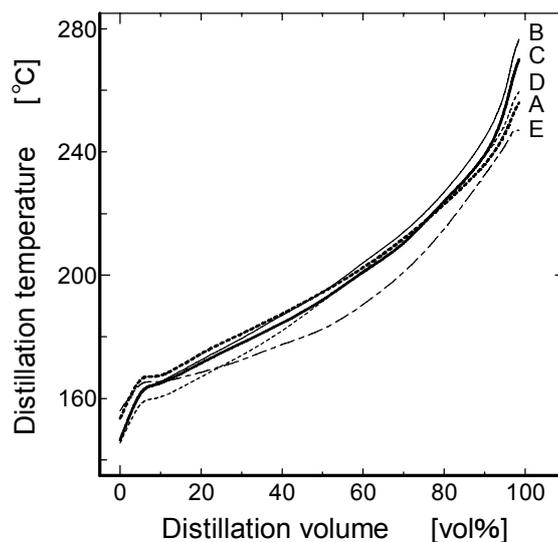


Fig. 1 Distillation characteristics of test fuels

fuel E was much smaller than that of the other fuels. Figure 1 shows the distillation characteristics of the test fuels; the lower distillation temperatures of fuel E indicate its light quality.

Table 2 shows the results of the composition analyses of the test fuels. The results confirmed that fuel E consisted only of saturated hydrocarbons (i.e., paraffins and naphthenes). In contrast, other fuels contained between 7.6~19.5 vol% aromatic hydrocarbons. Although a small amount of unsaturated hydrocarbons (0.1 vol%) are indicated in Table 2 for fuel A, the value was within the range of analytical error, so the result may be inaccurate. Most of the aromatic components of the fuels were one-ring aromatics; two-ring aromatics were very rare. In addition, the following low-stability components are also shown in Table 2: naphtheno benzenes, olefin hydrocarbons (bromine number), dienes (diene value), and organic peroxides (peroxide number)⁽⁴⁾. Naphtheno benzenes, compounds that consist of naphthene and aromatic rings, were contained in higher concentrations in fuel A (5.4 vol%); these molecules were not contained in fuel E. The bromine number was largest in fuel D (28.8 mgBr₂/100g) and lowest in fuel E (4.4 mgBr₂/100g). The diene values of fuels D and E indicated 0.05 gI₂/100g and 0.01 gI₂/100g, respectively; dienes were not detected in other fuels. The peroxide numbers demonstrate that none of the fuels contained organic peroxides.

Table 2 Composition of test fuels

Component	A	B	C	D	E
Aromatic HC [vol%]	19.5	17.2	16.9	7.6	0.0
Unsaturated HC [vol%]	0.1	0.0	0.0	0.0	0.0
Saturated HC [vol%]	80.4	82.8	83.1	92.4	100.0
1-aromatics [vol%]	19.1	17.0	16.7	7.5	0.0
2-aromatics [vol%]	0.4	0.2	0.2	0.1	0.0
3 ⁺ -aromatics [vol%]	0.0	0.0	0.0	0.0	0.0
1-naphtheno benzenes [vol%]	5.0	4.8	4.2	2.5	0.0
2-naphtheno benzenes [vol%]	0.4	0.5	0.3	0.0	0.0
3 ⁺ -naphtheno benzenes [vol%]	0.0	0.0	0.0	0.0	0.0
Bromine number [mgBr ₂ /100g]	9.4	9.0	10.1	28.8	4.4
Diene value [gI ₂ /100g]	0.00	0.00	0.00	0.05	0.01
Peroxide number [mg/kg]	0.0	0.0	0.0	0.0	0.0

2.2 Wick Combustion Burner

A wick flame was formed with a wick combustion burner, as shown in Fig. 2. The burner was equipped with a pool filled with fuel, and a wick was put in the pool. Fuel was supplied from a tank to the pool through a float chamber under the fuel tank. To form a steady flame, the fuel level within the pool was kept constant by the float. The fuel flow rate was derived from the weight loss of the burner, measured by an electronic balance. The pool was made of aluminum. The pool had an outer diameter of 20 mm, an inner diameter of 16 mm, and a depth of 6 mm. The wick, made of sintered bronze metal (39 % porosity), was placed in the center of the pool. The wick was cylindrical (8 mm diameter, 18 mm length, 6 mm wall thickness) with a flat bottom (8 mm diameter, 2 mm thickness). The wick was put in the pool so that the bottom protruded 7 mm from the pool rim. The distance from the fuel surface to top of the wick was 10 mm.

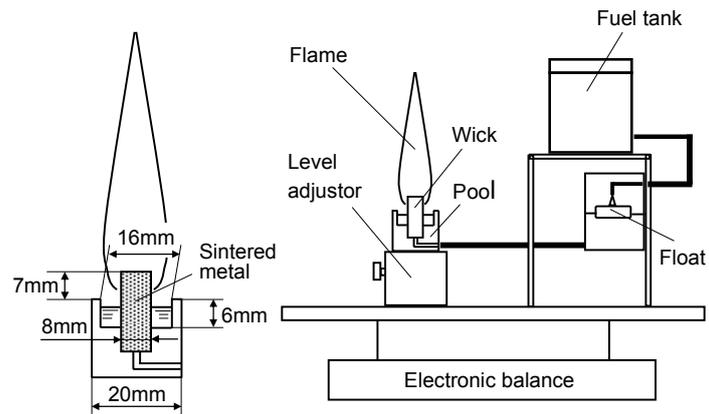


Fig. 2 Schematic of wick combustion burner

3. Results and Discussion

3.1 Relationship between Fuel Properties and Deposit Accumulation

Tar-like deposits, formed by the thermal decomposition and polycondensation of the fuel, adhered to and accumulated on the upper part of the wick during combustion. To investigate the effects of fuel properties on tar-like deposit accumulation, tar-like deposits were accumulated on the wick by prolonged combustion. The deposit mass was obtained by subtracting the mass of unused wick from the mass of the wick that had accumulated deposits. In this process, if unburnt fuel remained in the wick with deposits, an accurate deposit mass could not be obtained. To eliminate remaining fuel, the wick was pulled up from the pool with a flame, and combustion was continued until all fuel was used. Obtained deposit was visually confirmed as tar-like deposit, but soot particle might have slightly adhered on the wick.

Figure 3 shows temporal change of deposit mass. In this experiment, one wick was sequentially used in the measurement of one test fuel. As seen in the figure, the deposit growth rate decreased after a certain period of time except fuel E. This result implies that the accumulation of deposits proceeded in two stages. Deposits were first rapidly accumulated in voids of the wick, which gradually saturate over time; we called this period the "internal accumulation mode". Once the voids became saturated with deposits, deposits subsequently accumulated on the outer surface of the wick; we called this phase the "surface growth mode". Although the deposit growth rate in the internal accumulation mode varied somewhat due to individual differences of the wick, the growth rate of the surface growth mode had reproducibility. Regarding fuel E, the deposit accumulation would not have attained to the surface growth mode owing to its extremely low deposit growth rate.

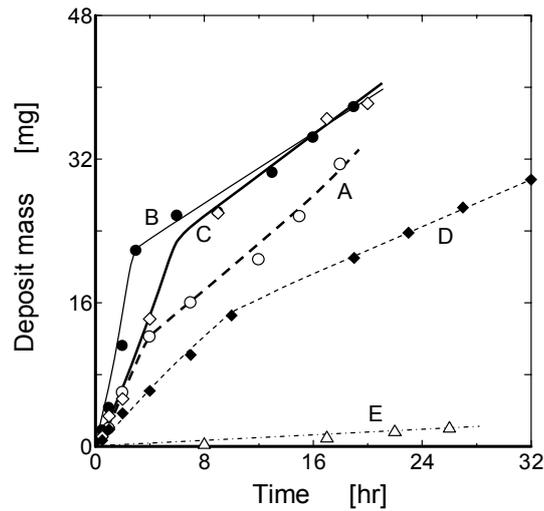


Fig.3 Temporal change of deposit mass

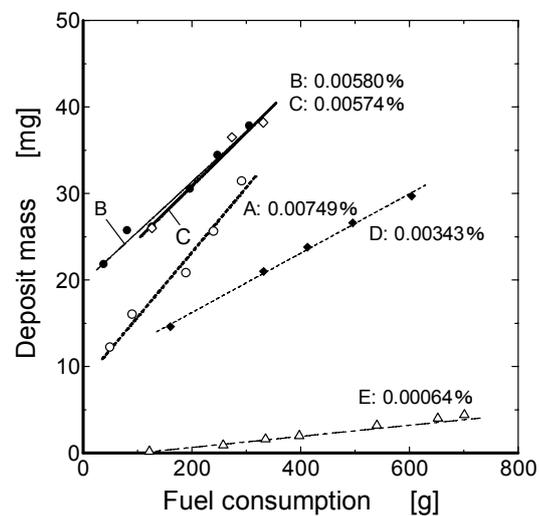


Fig. 4 Relationship between fuel consumption and deposit mass

As the deposit growth rate in the internal accumulation mode was influenced by individual differences of the wick, the relationship between deposit mass and fuel consumption was investigated in the surface growth mode. The results are shown in Fig. 4. Note that the results reported here for fuel E are not for the surface growth mode. Straight lines in the figure were obtained by the least-squares method, and the slopes correspond to the deposit accumulation ratio (the percentage of conversion from fuel to deposit). Deposit accumulation ratios are also indicated in the figure. Obtained results indicate that the deposit mass of each fuel increased proportionally with increasing fuel consumption. Fuel A displayed the highest deposit accumulation ratio (0.00749 %), followed by fuel B (0.00580 %) and C (0.00574 %). Fuel E (0.00064 %) exhibited an extremely small accumulation ratio. Compared with the fuel compositions shown in Table 2, fuel A, with its high deposit accumulation ratio, was found to contain higher levels of aromatics and naphtheno benzenes; conversely, fuel E, with its low deposit accumulation ratio, contained no aromatics or naphtheno benzenes. Note that there was no correlation between the bromine number, diene value, and accumulation ratio. The extremely low accumulation ratio of fuel E might be caused by several factors: (1) the amount of low-stability components in fuel E was very low, (2) pyrolysis of saturated hydrocarbons was hard to

occur within the range of the internal temperature of the wick, and (3) deposits formation from the pyrolysis products of saturated hydrocarbons took relatively long time.

The relationship between aromatic hydrocarbons, naphtho benzenes and the deposit accumulation ratio is presented in Fig. 5. The deposit accumulation ratio was strongly associated with the content of aromatics and naphtho benzenes. As naphtho benzenes are one of the aromatics, more naphtho benzenes may be contained in the aromatic-rich fuel. It is well known that naphtho benzenes are more susceptible to thermal decomposition at lower temperatures than other hydrocarbons; thus, pyrolysis and polycondensation of naphtho benzenes would be performed within the wick. Finally, naphtho benzenes were transformed into tar-like deposits. Conversely, because the pyrolysis of aromatics was difficult to perform due to their high thermal stability, initial aromatics contained in the fuel transformed into heavy molecules and tar-like deposit without pyrolysis. Note that the sooting tendency became stronger with increasing aromatic content in the fuel⁽³⁾; soot adherence to the wick possibly affected the results shown in Fig. 5. Although the deposits did not necessarily originate from aromatics and naphtho benzenes, the deposit accumulation ratio of fuel E was extremely low and no correlation was found between the bromine number, diene value, and deposit accumulation ratio. These results suggested that most of the deposits originated from the naphtho benzenes and/or aromatic hydrocarbons.

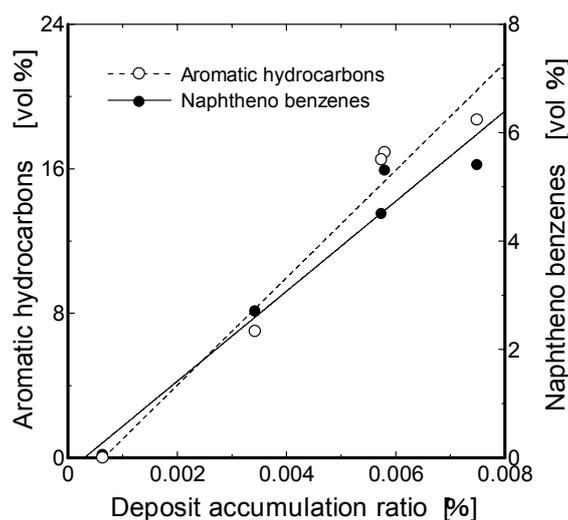


Fig. 5 Relationship between aromatic hydrocarbons, naphtho benzenes and deposit accumulation ratio

3.2 Deposit Analysis

Deposits that accumulated on the wick were extracted by diethyl ether and chloroform solutions and dried after evaporation of the solutions. The collected deposits were then analyzed with a simultaneous thermogravimetry/differential thermal analysis (TG-DTA) instrument (TA Instruments, SDT2960). Analysis was performed by the following steps:

- (1) The sample was held at room temperature for 5 minutes and then heated to 250 °C.
(atmosphere: N₂, flow rate: 100 mL/min)
- (2) The sample was held at 250 °C for 10 minutes and then heated to 550 °C.
(atmosphere: N₂, flow rate: 100 mL/min)
- (3) The sample was held at 550 °C for 20 minutes.
(atmosphere: air, flow rate: 100 mL/min)

[heating rate; 50°C/min]

Table 3 shows the mass loss of the deposits in each step. Considering the boiling point of hydrocarbons, the mass loss of each step corresponds to (1) the kerosene fraction, (2) the

Table 3 Results of TG-DTA analysis

Mass loss	A	B	C	D	E
Room temp.~250°C (N ₂) [wt%]	15.0	12.5	12.5	15.1	14.2
250~550°C (N ₂) [wt%]	22.2	23.2	18.0	21.4	26.4
550°C (air) [wt%]	49.5	51.1	61.4	62.8	60.0
Residue [wt%]	13.4	13.2	8.1	0.8	0.0

heavy kerosene component and light polycondensation products of low molecular weight, and (3) the heavy polycondensation product. The residue was considered to be a carbonized deposit and soot particles.

The results of TG-DTA analysis suggested that most of the deposit components were heavy polycondensation products formed by thermal decomposition and polycondensation of the fuel within the wick. Residues of fuel A, B and C, which contained higher amounts of aromatics and naphtheno benzenes, were higher than that of the other two fuels; this result is probably due to an increase in the carbonized deposit formed at the wick surface and/or soot adhesion on wick. Additionally, some sulfur compounds might be contained in the residue because these fuels contain sulfur, as indicated in Table 1. In contrast, the deposits of fuel E contained no residue, and the mass loss in the range of 250~550 °C was relatively high. This fact demonstrates the very low deposit growth rate of fuel E, as described previously. The deposits of fuel D, with its very high bromine number and diene value, displayed a relatively large mass loss of the heavy polycondensation product; this observation may be due to the contribution of a tar-like deposit that originated from olefins and dienes⁽⁵⁾.

3.3 Relationship between Organic Peroxide and Deposit

Organic peroxides, which form by oxidative degradation of fuel, easily cause thermal decomposition owing to the relatively weak -O-O- bond. To estimate the influence of organic peroxide on deposit accumulation, peroxide-containing fuel was applied to the wick combustion burner. To prepare the peroxide-containing fuel, the test fuels were placed outdoors in a white polyethylene tank and were exposed to sunlight. Fuel properties of the peroxide-containing fuels were also analyzed concerning the same items in Table 1. As a result of the exposure to sunlight, few variations in the physical properties were detected other than a small decrease in the aromatics (up to 0.8 vol %) in each fuel.

The amounts of peroxide in the peroxide-containing fuels are listed in Table 4. Normal fuels did not contain any peroxide, while the peroxide-containing fuels contained different amounts of peroxide; fuels A~D contained around 200 mg/kg and fuel E contained 3 mg/kg. Generally, because these fuels contained both constituents that could form peroxides and inhibit peroxide generation⁽⁶⁾⁽⁷⁾, peroxide production would be influenced by the fuel composition. Fuel E potentially had extremely high oxidation stability as the peroxide production was very little.

Table 4 Peroxide number

Peroxide number	A	B	C	D	E
Normal [mg/kg]	0	0	0	0	0
Sun exposure [mg/kg]	216	199	183	247	3

Deposit masses of the normal and peroxide-containing fuels were investigated after four hours of combustion. The results are shown in Fig. 6. Note that data for fuel E were not obtained due to its extremely low deposit growth rate. As seen in the figure, the deposit masses of peroxide-containing fuels were much larger than those of the normal fuels. The deposit growth rate in the internal accumulation mode was influenced by individual

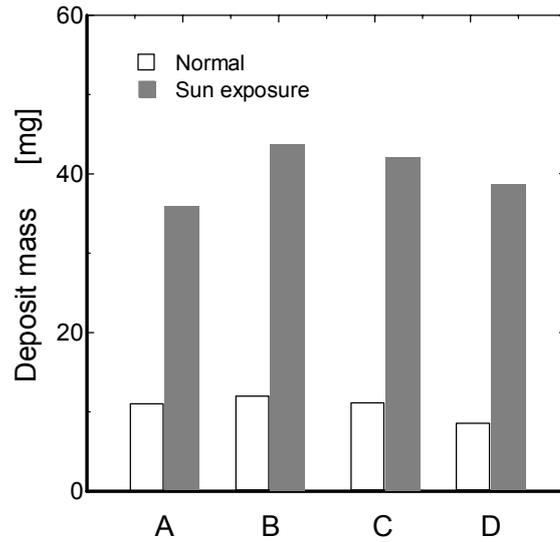


Fig. 6 Influence of peroxide on deposit mass

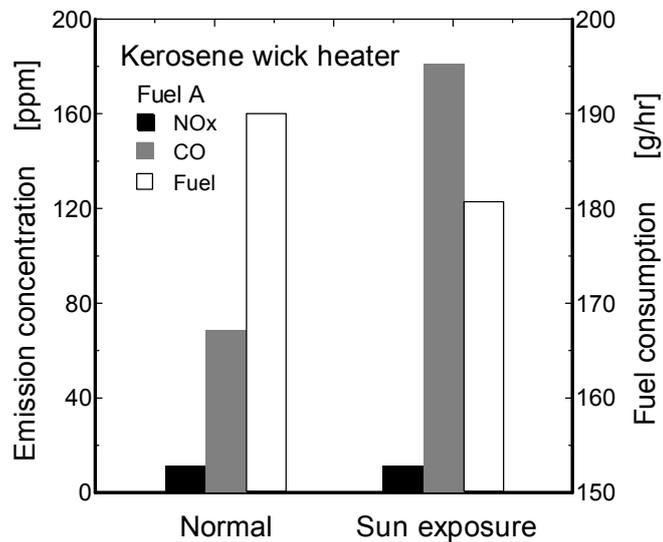


Fig. 7 Performance comparison between normal fuel and peroxide-containing fuel

differences of the wick, as described previously. However, it was confirmed that the error resulting from individual differences of the wick was approximately $\pm 15\%$ during four-hour combustion of fuel A, thus we believe that the results did not vary so much by the wick. The deposit mass significantly increased by a small amount peroxide (about 200 ppm), so the results suggest that peroxides have the strongest tendency to form deposits. Furthermore, peroxides possibly accelerated deposit formation by synergistic interactions between other fuel components.

Normal and peroxide-containing fuels were supplied to a commercially available radiant kerosene wick heater which combustion system resembled that of our wick combustion burner. Figure 7 shows the fuel consumption rate and emission concentrations of NOx and CO after one hour of operation. The heater was operated at maximum heating output with fuel A. Exhaust gas was sampled from the exhaust stack and was analyzed with gas analyzers (NOx; HORIBA, MEXA-1160CLT-H, CO; HORIBA, COPA-2000); concentrations of NOx and CO in the exhaust gas were investigated. Fuel consumption was obtained from the weight loss of the heater measured by an electronic balance. As seen in the figure, the NOx concentration was mostly unchanged, while the CO concentration of

peroxide-containing fuel increased about 2.7 times from normal fuel. Deposit accumulation on a heater wick that is enhanced by peroxides may cause inhomogeneous fuel vaporization from the heater wick; increase in CO concentration would be caused by inhomogeneous fuel distribution and combustion. Moreover, because the fuel supply performance of the wick was suppressed by the deposits, the fuel consumption of peroxide-containing fuel was approximately 5 % lower than normal fuel. Note that the results similar to fuel A were also obtained from other fuels. These results reveal that the peroxide causes problems with combustion appliances, even after operation for a short period of time.

4. Conclusions

The effects of the fuel properties of kerosene on deposit accumulation were investigated with a wick combustion burner and a commercially available radiant kerosene wick heater. The main results are summarized as follows:

1. Except for fuel E, deposit accumulation per unit time (deposit growth rate) decreased after a certain time after ignition.
2. The conversion percentage from fuel to deposit (deposit accumulation ratio) increased with greater contents of aromatics and naphtho benzenes in the fuels.
3. The primary components of deposits were heavy polycondensation products (50~60 wt%). Heavy kerosene components, light polycondensation products (about 20 wt%), and kerosene fractions (about 15 wt%) were also identified in the deposits.
4. Deposit masses were greatly increased in the combustion of the peroxide-containing fuels, with peroxide numbers of approximately 200 mg/kg, relative to normal fuels.
5. By applying the peroxide-containing fuels to a commercially available radiant kerosene wick heater, a decrease in fuel consumption and an increase in CO concentration were confirmed after one hour of operation.

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