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An improvement of thermal conduction of activated carbon by adding graphite

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This study was performed to improve thermal conduction of granular activated carbon by adding graphite powder. Granular activated carbons were fabricated from anthracites and graphite powders using a binder pitch, and then activated in a nitrogen-carbon dioxide gas at 850°C. Additions of graphite from 20 to 30 wt% were considered to be suitable for thermal conductivity and n-butane adsorption power. The thermal conductivities of such granular activated carbons were 20 times those of activated carbons without graphite. A fixed bed filled with the granular or powder activated carbons containing graphite were never ignited even though the inside of the bed was directly heated.

1. Introduction

Activated carbons characteristically have many small pores effective for adsorption and have been widely applied for decolorizing, refining reagents, recovering solvents, eliminating pollutants, and so on. Recently, activated carbons have also been used to eliminate organic halogenides, which are thought to be harmful to organisms (environmental hormones) in drinking water. Adsorption is conducted under different working conditions corresponding to the objectives. In general, adsorption occurs at low temperatures because the adsorption process is exothermic. Disposal of dioxins has recently become a worldwide problem, and these dioxins must be adsorbed from incinerator exhaust gases. Dioxins should generally be adsorbed at as low a temperature as possible. However, to eliminate dioxins from combustion exhaust gases, they must be adsorbed at relatively high temperatures of 200°C or so at which facilities are to be protected from acid gases produced during combustion [1–3].

Utilization of natural gas containing mainly methane as a fuel for automobiles and fuel cells has been investigated due to the global demand for clean energy. A gas cylinder filled with activated carbon to sufficiently occlude methane gas at pressures of 3MPa is currently receiving attention [4–6].

A cooling system based on cyclic adsorption-desorption processes by a particular adsorbent using water vapor or alcohols instead of chlorofluorocarbons is also being considered. G. Cacciola *et al.* produced activated carbon bricks using PTFE (polytetrafluoroethylene) as a binder. The samples presented an effective thermal conductivity ranging between 0.13 and 0.20 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [7].

For these reasons, the future demand of activated carbons is anticipated to increase. However, some problems must be solved before utilizing activated carbons for new purposes. The first problem is the temperature rise due to heat of adsorption and the subsequent reduction of adsorption capacity and efficiency. The second problem is the temperature rise due to reaction of adsorbate with functional groups on activated carbon, and the third is reduced adsorption efficiency due to the delay of heat supply for desorption. Thermodynamically, adsorption is considered exothermic because entropy decreases [8]. Therefore, temperature rise of activated carbon must be prevented, if activated carbon is employed in a large packed tower. To regenerate spent carbon, heat required to desorb substances must be promptly supplied from outside the adsorption tower.

The numerical value of thermal conductivity for activated carbon is required, but there is almost no information available. A thermal conductivity value of activated carbon of 0.17 to 0.28 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ is found from a handbook [9]. This is less than the diffusion value of general refractory bricks, so activated carbon may be classified as a non-thermal conductive material, indicating that such low thermal conductivity delays thermal diffusion of adsorption heat and lowers adsorbability. Activated carbon may also ignite through an accumulation of heat of adsorption and oxidation of adsorbates. Activated carbon is estimated to ignite from 200°C to 500°C [10].

Thus, careful attention must be paid since the thermal conductivities of granular activated carbons seem to be around one thousandth of that of graphite (50 to 150 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [11]. There are two processes

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TABLE I Approximate analyses of coals (dry basis)

Item	Daxi-China	HongGaiVietNam
Volatile matter (%)	8	7
Ash (%)	2	3
Fixed carbon (%)	90	90
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	0.20–0.29	

TABLE II Approximate analysis of artificial and natural graphites

Item	Artificial graphite	Flaky graphite
Fixed carbon (%)	99	87
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	120	–

for manufacturing granular activated carbons. In one process, char crushed after carbonization of precursors such as fruit shells is activated. In the other, granules made from pulverized char with a size of ca. 0.05 mm and using tar pitch as a binder are activated [12]. Activated carbon produced by the former process has voids originally intrinsic to the char and many cracks derived during carbonization in addition to many pores developed by activation. Thus, the bulk density is essentially low, which means low thermal conductivity.

Accumulation of adsorption heat tends to increase when the equipment has a large amount of activated carbon. Virgin activated carbon treated with acid to eliminate minerals is known to increase the ignition point. However, activated carbon, on which substances such as alkali earth metals and fly ash adhere, ignites at relatively low temperatures because of their catalytic effect. Thus, there are some problems regarding thermal conduction [10].

We investigated the improvement of thermal conductivity of granular activated carbon by adding graphite powder as a thermal conductive material. The adsorption performance and thermal conductivity of the activated carbons with graphite added were assessed. This paper describes the thermal conductivities of activated carbons with graphite and the thermal conduction in a fixed bed.

2. Experimental

2.1. Specimens

Daxi (China) and Hon Gai (Vietnam) anthracites were chosen as raw materials for activated carbon preparation. Thermal conductivity values for coal of 0.20 to 0.53 $W \cdot m^{-1} \cdot K^{-1}$ [13] were reported. The coals were ground in a ball mill and the powder with diameter from 0.025 to 0.045 mm was sieved. The approximate analysis for anthracite is listed in Table I. Artificial graphite (Toyo Tanso, IG-11) and a kind of natural graphite (flaky graphite of reagent grade) were used as thermal conductive materials. Artificial graphite ground in a ball mill and the powder with diameter from 0.025 to 0.045 mm was sieved. Flaky graphite was ground in the same ball mill for a short time so that the flaky shape remained. The size was 0.18 mm or under. However, we did not investigate in details the effect of the shape of flaky graphite. The properties of these graphite are shown in Table II.

2.2. Preparing of granular activated carbons with graphite powder

Columnar activated carbons (5 mm diameter and 5 to 10 mm long) were prepared as follows. Anthracite and graphite powder were kneaded with a binder of coal tar pitch of 20 to 30% in weight, followed by forming using a molding machine at a pressure of 167 MPa. The granules were carbonized at 600°C for 2 h in nitrogen. The chars were activated at 850°C for 3 or 4 h in nitrogen containing carbon dioxide (50 vol%) using a rotary kiln. The raw materials, the contents of graphite, and activation times are summarized in Table III. Burn off (wt%) was calculated from dry basis weight loss through the activation. The products with graphite and the commercial activated carbons were ground and sieved to 200 mesh after which when the thermal conduction of powder specimens were examined.

2.3. Measuring thermal conductivity

The thermal conductivity of the granular activated carbons prepared in this work was assessed by the laser-flash method using an instrument developed by Shinku Richo Co. (TC-300Type) [14, 15]. For this measurement, large activated carbon specimens

TABLE III Preparation condition and properties of activated carbons

Specimen	Coal	Graphite	Graphite (wt%)	Activation time (h)	Burn off (wt%)	Surface area (m^2/g)	n-Butane activity (wt%)	κ ($W \cdot m^{-1} \cdot K^{-1}$)
RAG-23	Daxi	Artificial	20	3	33	748	14.2	1.65
RAG-33	Daxi	Artificial	30	3	31	669	13.3	2.61
RAG-43	Daxi	Artificial	40	3	29	628	9.3	3.61
RAG-24	Daxi	Artificial	20	4	38	761	15.1	1.41
RNG-23	Daxi	Flake	20	3	32	745	16.3	1.53
RNG-33	Daxi	Flake	30	3	30	730	14.5	2.33
RNG-24	Daxi	Flake	20	4	37	792	16.7	1.37
RNG-14	Daxi	Flake	15	4	38	843	19.8	0.86
VAG-24	HongGai	Artificial	20	4	33	786	17.1	1.55
VNG-24	HongGai	Flake	20	4	32	774	16.6	1.31
R-03	Daxi		0	3	36	859	20.4	0.27
R-04	Daxi		0	4	42	987	21.1	0.17
V-04	HongGai		0	4	38	960	21.8	0.19

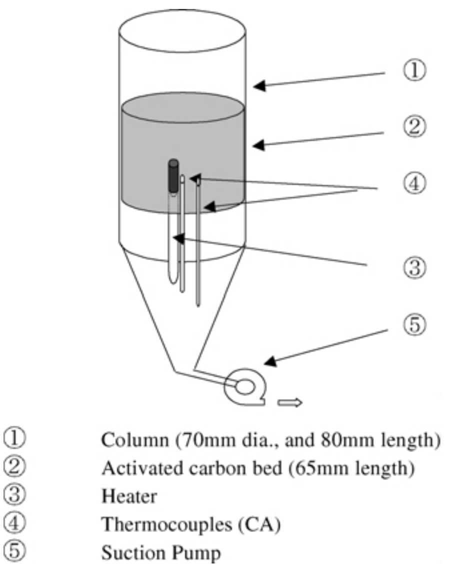

Figure 1 Schematic diagram of apparatus for measurement of thermal conduction in bed filled with activated carbon.

(10 mm diameter and 5 mm length) were fabricated according to the manufacturing method described in Section 2.2. Thermal diffusivity, $\alpha(\mathrm{m}^2 \cdot \mathrm{s}^{-1})$, was calculated from Equation 1 based on a datum on time dependence of temperature on the reverse side of the disk-like activated carbon specimen.

$$\alpha = 0.1388 L^2 k \cdot t_{1/2}^{-1} \tag{1}$$

Here, $t_{1/2}$ (s) is half of the time required to reach the maximum temperature. L (m) is the thickness of the disk-like activated carbon, and k is a coefficient in the equation. Thermal conductivity, $\kappa(\mathrm{W} \cdot \mathrm{m}^{-1} \cdot \mathrm{K}^{-1})$, can be obtained from Equation 2 using specific heat C $(\mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1})$ and density $\rho(\mathrm{kg} \cdot \mathrm{m}^{-3})$.

$$\kappa = \alpha \cdot C \cdot \rho \tag{2}$$

We adopted 840 as the specific heat of activated carbon [11]. The apparent densities measured by weighing the specimens were used.

2.4. Thermal conductivity in fixed bed

In order to evaluate the performance of the activated carbons developed in this work, we examined the thermal conduction in a fixed bed as shown in Fig. 1. The fixed bed has two CA thermocouples and a heater. One thermocouple was set near the heater and the other 10 mm away. A 100 W-nichrome wire covered with a 5 mm diameter aluminum tube was used as the heater. We performed thermal conductive tests by supplying electric power of 68 and 88 W to the granular activated carbon bed. Data on the powder were needed, so we also checked the thermal conduction in the bed filled with powdered activated carbon by applying electric power of 51 W. The changes of temperature reflecting the thermal conductivities of the activated carbons were measured in air flow rates of 0.1 $\mathrm{m} \cdot \mathrm{s}^{-1}$ (granular activated carbons) and 0.02 $\mathrm{m} \cdot \mathrm{s}^{-1}$ (powdered activated carbons) introduced from the upper side and flowing toward the bottom using a suction pump. In this study, we compared the properties of two kinds of commercial powdered activated carbons, one made from coal and the other from coconut shells.

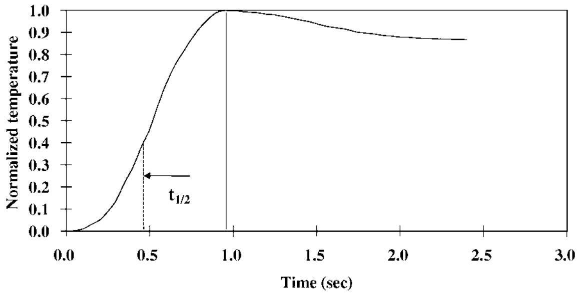

Figure 2 Time dependence of temperature of specimen measured by the laser flash method.

2.5. Measuring surface areas and adsorption power

The surface area of the activated carbon specimen was measured by the BET method and n-Butane activity was evaluated according to ASTM (D5742-95).

3. Results and discussion

3.1. Properties of activated carbon with and without graphite

Fig. 2 illustrates a typical pattern of the time dependence of temperature measured by the laser flash method. Before analyzing the thermal properties, we examined the values of nickel and graphite as standard materials. The measured values were the same as those in references [11, 16]. $t_{1/2}$ of these standard materials was observed in a region of 10 to 20 ms. $t_{1/2}$ of the activated carbons developed in this study required a much longer time, 5 s. The various items derived from the patterns shown in Fig. 2 are listed in Table IV. The

TABLE IV Thermal properties analyzed by laser flash method

		Specimen		
Item	Unit	RAG-33	RNG-14	R-03
L	m	3.22×10^{-3}	3.54×10^{-3}	3.80×10^{-3}
$t_{1/2}$	s	0.450	1.425	4.458
k		0.822	0.811	0.801
Thermal diffusivity	$\mathrm{m}^2 \cdot \mathrm{s}^{-1}$	2.6×10^{-6}	9.9×10^{-7}	3.6×10^{-7}
Density	$\mathrm{kg} \cdot \mathrm{m}^{-3}$	1180	1040	880
Specific heat	$\mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$	840	840	840
Thermal conductivity	$\mathrm{W} \cdot \mathrm{m}^{-1} \cdot \mathrm{K}^{-1}$	2.60	0.86	0.27

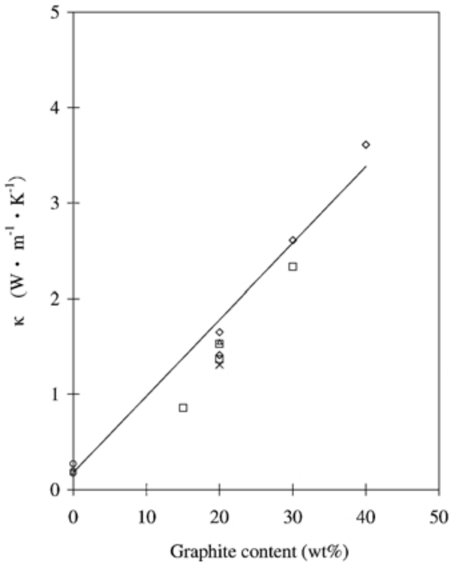

Figure 3 Thermal conductivities of activated carbons as a function of adding graphite. Composition of activated carbon. ◇: Daxi coal with artificial graphite, □: Daxi coal with flaky graphite, △: Hong Gai coal with artificial graphite, ×: Hong Gai coal with flaky graphite, and ○: Daxi and Hon Gai coals without graphite.

relationship between the added graphite content and the value of κ is shown in Fig 3. κ increases almost linearly with increasing graphite content. κ of the specimen with 40% in weight graphite added is 20 times as great as that of activated carbon without graphite. Table III shows thermal conductivity and adsorption properties of activated carbons. The table indicates a tendency for κ to decrease with increasing activation time. The surface area and adsorption amount of n-butane increase with increasing activation time. This is considered due to an increase in porosity during activation. No serious reduction of n-butane adsorption or surface area is observed between the specimens with 20 and 30 wt% of graphite, although those items decreased with an increase in graphite whereas κ increased. The decrease of adsorption tends to be small, so the role of graphite through activation is not thought to change. Since the increase in activation time increased adsorption capability, adding graphite did not seem to disturb the activation of coal and char. Thus, we concluded that adding 20 to 30 wt% graphite is suitable in view of the κ value and the n-butane adsorption power. We expected that κ values would differ with the shape and size distribution of graphite. In this study, we did not investigate details related to the effect of grain shape and size.

3.2. Thermal conduction in a fixed bed

In order to clarify the effect of adding graphite, we examined the thermal conduction in the fixed bed shown in Fig. 1 using the activated carbons adding 20 wt% graphite (RAG 23). Fig. 4 depicts the changes in temperatures of the activated carbons installed in the bed when 68 W was supplied and indicates a steep increase in temperature of the activated carbon near the heater. However, it is noteworthy that the temperature reaches a maximum of 366°C. The temperature sensed by the other thermocouple farther from the heater gradually increased and reached a maximum of 64°C after 2 min. The results when 88 W was supplied were similar to those in Fig. 4, although the maximum attained temperature exceeded that with 68 W by about 70°C. However, no evidence of ignition was found. Fig. 5 illustrates the temperature-increase curves of granular commercial activated carbons made from coal and coconut shells (Tsurumi coal Co. of Japan). These were supplied in sieving-size of 2.36 to 4.75 mm. The temperature steeply rose after heating of 180s and 360s, indicating that the activated carbons near the heater began to ignite at those temperatures. A temperature increase was sensed at the thermocouple farther from the heater at about 100°C and seems to be due to the heat conduction from ignition and burning. We ground the granules with graphite to powders and sieved to less than 0.074 mm in size to examine the thermal conduction.

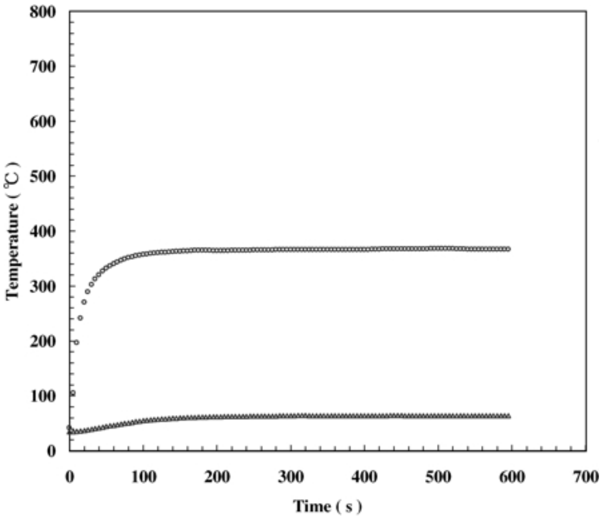

Figure 4 Changes in temperature of the two points in the activated carbon bed shown in Fig. 1. ○: Thermocouple installed close to the heater and △: Thermocouple installed displaced from the heater by 10 mm.

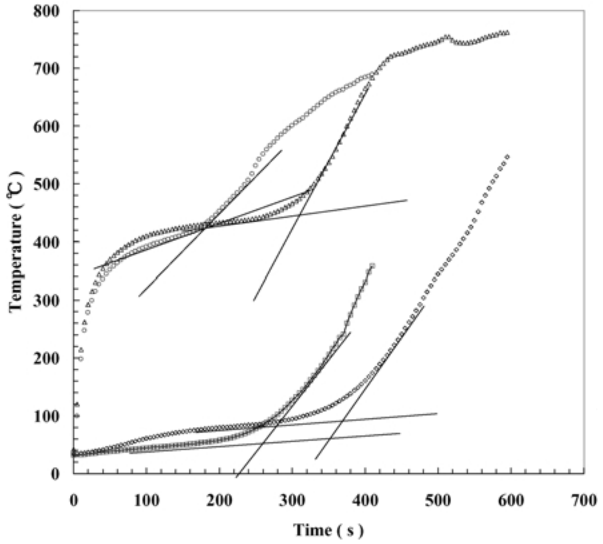

Figure 5 Comparison of temperature rises in the bed filled with commercial granular activated carbons. Thermocouple installed close to the heater: ○: Activated carbon made from coconut shell and △: Activated carbon made from coal. Thermocouple installed displaced from the heater by 10 mm: □: Activated carbon made from coconut shell and ◇: Activated carbon made from coal.

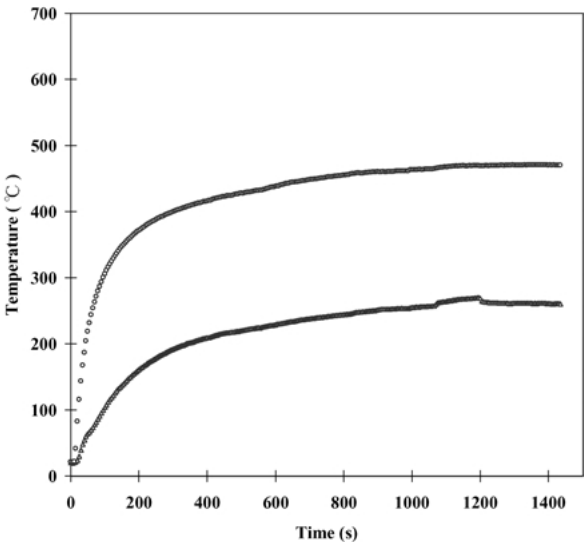

Figure 6 Changes in temperature in the bed filled with pulverized activated carbon. ○: Thermocouple installed close to the heater and △: Thermocouple installed displaced from the heater by 10 mm.

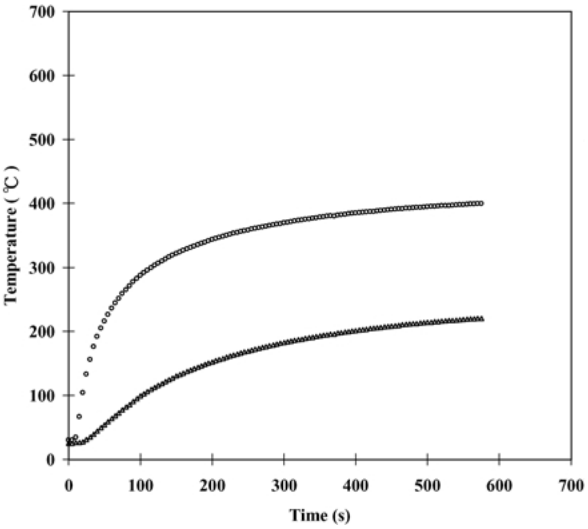

Figure 7 Changes in temperature in the bed filled with artificial graphite powder. ○: Thermocouple installed close to the heater and △: Thermocouple installed displaced from the heater by 10 mm.

Fig. 6 shows the rising curves of temperature in the bed filled with a powder. In this case, 51 W power was supplied. The maximum temperature attained was 470°C. This is considered high compared to that when 68 W was applied (see Fig. 4), but there was no ignition. The effects of adding graphite on the thermal conductivity are compared in Fig. 7 (artificial graphite) and Fig. 8 (flaky graphite). We could find no difference between the two types. Both of the powders reach a maximum temperature of 400°C. Figs 9 and 10 illustrate the temperature-increase curves in the powders of the activated carbon made from coal and coconut shells without graphite. A steep rise of temperature near the heater is observed at around 450°C in both activated powders. The temperature farther from the heater in the former powder also rises more steeply than that near the heater, indicating that the area is burnt by the spreading fire. Red-hot spots in the powders produced from activated carbons without graphite were observed

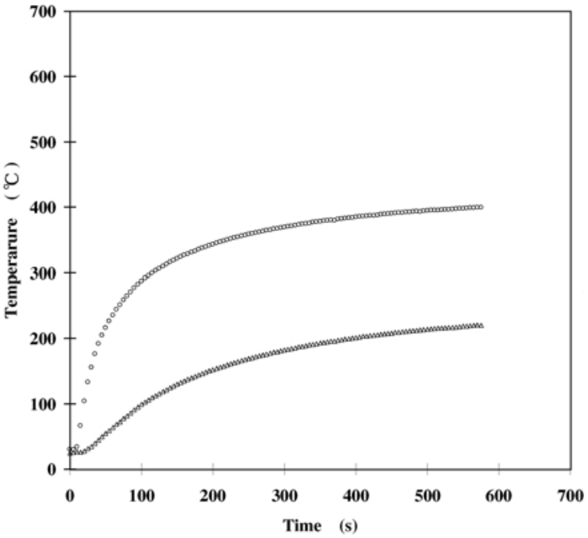

Figure 8 Changes in temperature in the bed filled with flaky graphite. ○: Thermocouple installed close to the heater and △: Thermocouple installed displaced from the heater by 10 mm.

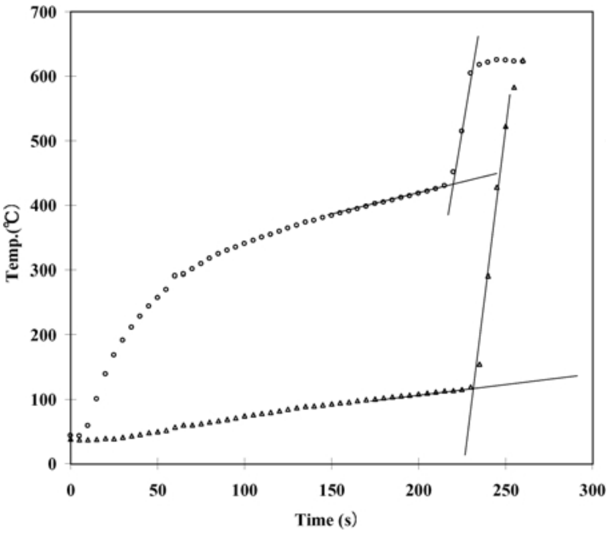

Figure 9 Changes in temperature in the bed filled with commercial coal activated carbon powder. ○: Thermocouple installed close to the heater and △: Thermocouple installed displaced from the heater by 10 mm.

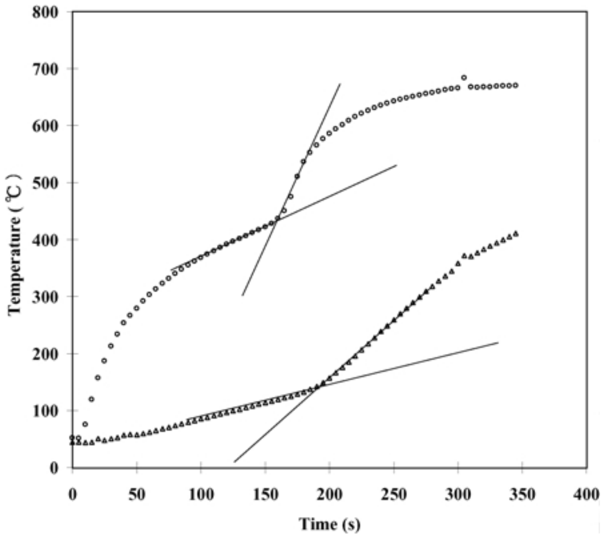

Figure 10 Changes in temperature in the bed filled with commercial coconut activated carbon powder. ○: Thermocouple installed close to the heater and △: Thermocouple installed displaced from the heater by 10 mm.

in some places of the fixed bed surface with the naked eye. The entire fixed bed became red hot when the air supply was increased. Based on the above, we must monitor the fixed bed carefully to ensure there is no ignition since the thermal diffusion of activated carbon is extremely low.

This work confirmed an important role of graphite in improving thermal conduction. We are now conducting a detailed thermal analysis in the fixed bed for a practical application of activated carbon with graphite.

4. Conclusion

This study investigated the effect of adding graphite to granular activated carbons to improve the extremely low thermal conductivity. The results are summarized below.

The thermal conductivities of activated carbons fabricated from precursors such as coal and coconut shells, followed by activating at 850°C for 3 or 4 h, were found to be 20 times higher than those of activated carbons without added graphite.

We examined a fixed bed of activated carbon with graphite and containing a heater and thermocouples. We found that the temperature attains a maximum but there is no ignition in fixed bed of activated carbon with graphite. Therefore, we concluded that the addition of graphite to activated carbon effectively improves thermal conductivity.

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