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Removal of Tar Model Compounds Produced from Biomass Gasification Using Activated Carbons

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Dry gas cleaning was performed using five different commercial activated carbons (ACs) at 150-300 °C. Phenol, *o*-cresol, naphthalene, and 1-methylnaphthalene were employed as the tar model compounds that produced from biomass gasification. The effect of the adsorption temperature and physical characteristics of ACs on the adsorption behaviors such as the breakthrough curves and adsorption capacities was investigated using a fixed-bed reactor. At 150 °C, *o*-cresol and naphthalene were effectively removed; the adsorption capacities of the ACs were 13.4-19.4 g-tar/(100 g-AC) and 19.9-23.7 g-tar/(100 g-AC) in *o*-cresol and naphthalene, respectively. For effective tar removal, a larger surface area, a smaller average particle size, and an appropriate pore diameter were necessary. The effect of the tar model compounds on the adsorption behavior was investigated using the same AC at 150 °C. The adsorption capacity was found to be 10.5-32.6 g-tar/(100 g-AC) in the following order: phenol < *o*-cresol < naphthalene < 1-methylnaphthalene. Tar compounds having methyl groups (*o*-cresol and 1-methylnaphthalene) were removed more effectively as compared to those having no methyl groups (phenol and naphthalene).

Key Words

Dry gas cleaning, Biomass, Tar, Breakthrough, Adsorption, Activated carbons

1. Introduction

Environment friendly and more efficient methods to produce energy are currently under intense research and development. Biomass resources have an economic advantage along with environmental benefits because they are renewable energy resources and offer the possibility to mitigate CO₂ accumulation in the atmosphere¹⁾. Biomass gasification has attracted significant interest since it provides efficient large-scale energy production by means of advanced technologies; for example, engines and turbines or conversion to liquid fuels such as Fischer-Tropsch synthesized oil or dimethyl ether²⁾. In general, product gases derived from biomass gasification contain several undesired contaminants such as particles, tars (polycyclic aromatic hydrocarbons), alkalis (Na and K), nitrogen com-

pounds (mainly NH₃), and sulfur compounds (mainly H₂S and COS); the amount of the contaminants should be controlled in order to avoid plugging and damaging the downstream equipment, which reduces the overall efficiency³⁾⁴⁾.

Tar removal technology can be broadly categorized into two methods: (1) physical methods^{1)~9)} that employ wet scrubbing, cyclones, filters, wet electrostatic precipitators, and activated carbons (ACs); and (2) chemical methods^{3)8)~14)} that employ catalytic and thermal cracking, partial oxidation, and plasma reactors. The wet gas cleaning method that employs a scrubber has been widely used in the last two decades; however, wastewater has to be treated in order to avoid environmental pollution using a large plant and this incurs a relatively high cost. The catalysts are extremely sensitive to contaminants such as sulfur, chlorine, and nitrogen compounds; they can also get deactivated due to coke formation. Tar can be effectively removed by using a Rh/CeO₂/SiO₂ catalyst at 550 °C¹³⁾, while the high cost should be considered during its usage. On the contrary, the dry gas cleaning method using commercial ACs was con-

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sidered to be advantageous due to its higher energy efficiency and lower costs. Tar compounds produced from biomass gasification could be removed using ACs with a large specific surface area and large average pore diameter at 300–400 °C⁷⁾. However, in order to enhance the tar removal efficiency when using ACs, a qualitative study must be conducted.

Tar compounds derived from biomass gasification can be classified according to their boiling point (b.p.) fractions: light (b.p. <150 °C), medium (b.p. between 150 and 250 °C), and heavy (b.p. >250 °C) compounds¹⁵⁾. Medium tar compounds of phenol, *o*-cresol, naphthalene, and 1-methylnaphthalene are the main compounds derived from biomass gasification¹⁶⁾. Phenol and cresol (acidic compounds) are corrosive when used in internal combustion (IC) engine applications. Some of the light tars (such as benzene or toluene) cannot be considered as harmful components in gases since these compounds are found in major quantities in gasoline¹⁷⁾. In this study, phenol, *o*-cresol, naphthalene, and 1-methylnaphthalene with not more than two aromatic rings were used as the tar model compounds. The removal of such tar model compounds was systematically investigated using commercial ACs.

2. Experimental

The physical characteristics of five different ACs used as tar adsorbents in this study are listed in Table 1. AC-1, AC-3, AC-4, and AC-5 had similar specific surface areas, while AC-1 had the smallest particle size. The particle size

Table 1 Physical property of activated carbons

Activated carbons	Specific surface Area (m ² /g)	Average pore diameter (nm)	Average particle size (mm)
AC-1	1150	1.2	1.0
AC-2	490	1.0	4.0
AC-3	1100	1.9	4.1
AC-4	1100	1.9	2.2
AC-5	1250	2.7	2.0

Table 2 Molecular structure and physical characters of model tar compounds in this study

Compounds	Structure	Molecular Weight	Boiling Point (°C)
Phenol		94	181.8
<i>o</i> -cresol		108	190.95
Naphthalene		128	217.9
1-Methylnaphthalene		142	244.8

of AC-3 was greater than that of AC-4. AC-5 had the largest average pore diameter, which was in the mesoporous range. AC-2 had the smallest specific surface area and an average pore diameter with a large particle size. Phenol, *o*-cresol, naphthalene, and 1-methylnaphthalene were used as the tar model compounds derived from biomass gasification. Their physical characteristics are shown in Table 2.

Dry gas cleaning was carried out using a laboratory-scale rig, as shown in Fig. 1. Approximately 0.4 g of AC was used in each experiment. Each tar model compound was vaporized by heating at the desired temperature using a mantle heater (2). The nitrogen flow rate was controlled at 200 ml (STP)/min using a mass flow controller (1). The tar concentration (C_0) was approximately 2000 ppmv. In order to adjust the value of C_0 , its value was measured via a bypass using a gas chromatograph equipped with a flame ionization detector (GC-14B, Shimadzu). The entire vaporous tar paths are indicated by black bold lines in Fig. 1; the temperatures of these paths were maintained at 100 °C using ribbon heaters in order to avoid condensation. Simultaneously, an AC bed was heated at the reaction temperature in a nitrogen atmosphere. When the desired tar concentration was steadily obtained, the vaporous tar was derived in the AC bed. The space velocity on an AC weight basis was maintained at 30 L-N₂ (STP)/(h g-AC).

The adsorption capacity of the AC can be defined as follows:

$$w \text{ (g-tar/100 g-AC)} = \frac{\text{the weight change in the AC}}{\text{initial weight of AC}} \quad [1]$$

Here, the initial weight of the AC was the amount of the AC before adsorption at the desired temperature in a nitrogen atmosphere, and it was calculated from the weight loss of the AC under the same conditions by using a thermogravimetric analysis (Thermo Plus, TG8120, Rigaku). The weight change in the AC was regarded as the adsorbed amount of the tar model compound, and it was evaluated from the difference in the weight of the AC before and after adsorption.

Fig. 1 Schematic diagram of experimental apparatus for tar removal

3. Results and Discussion

Phenol and naphthalene with one or two aromatic rings are the representative compounds of light or medium tar derived from woody biomass gasification. Hanaoka et al. demonstrated that AC-3 with a large specific area and large average pore diameter was effective in tar removal at 300–400 °C⁷⁾. They used actual tar derived from woody biomass gasification; however, the qualitative behavior of the tar compound was not clarified. Initially, we investigated whether phenol and naphthalene were removed or not at 300 °C for AC-3. This breakthrough behavior is shown in Fig. 2. Phenol and naphthalene easily broke through AC-3 at the beginning. This result suggests that at 300 °C, such medium tar compounds (b.p. between 150 and 250 °C) would be difficult to remove by using ACs. Therefore, the removal of tar compounds having one or two aromatic rings was investigated in order to improve the tar removal efficiency using ACs.

3.1 Effect of the adsorption temperature

Tar compounds can be conveniently removed at lower temperatures because they condense easily. However, dry gas cleaning has to be carried out at temperatures higher than 150 °C since a near-liquid layer is formed on the surface of the filtering material at temperatures lower than 150 °C; further, the stickiness of this layer would cause considerable mechanical problems and frequent failures⁹⁾. In this study, the adsorption temperature was between 150 and 250 °C.

The breakthrough curves of *o*-cresol and naphthalene at 150 and 250 °C are shown in Fig. 3 and Fig. 4, respectively. Apparently, *o*-cresol and naphthalene were efficiently removed at 150 °C as compared to their removal at 250 °C. It can be explained that the intermolecular forces such as van der Waals forces become weaker with an increase in the temperature. Accordingly, at 150 °C, the removal of tar compounds with one or two aromatic rings, which were difficult to remove at 300 °C, would be effective with dry gas cleaning using ACs.

Fig. 2 Breakthrough curves of phenol (A) and naphthalene (B) at 300 °C for AC-3

Fig. 3 (a) Breakthrough curves of *o*-cresol at (A) 150 °C and (B) 250 °C

Fig. 3 (b) Breakthrough curves of *o*-cresol at (A) 150 °C and (B) 250 °C

Fig. 4 (a) Breakthrough curves of naphthalene at (A) 150 °C and (B) 250 °C

Fig. 4 (b) Breakthrough curves of naphthalene at (A) 150 °C and (B) 250 °C

Table 3 Adsorption capacity at 150 °C for activated carbons

Sample	<i>o</i> -cresol		Naphthalene	
	C ₀ (ppmv)	w (g/100g)	C ₀ (ppmv)	w (g/100g)
AC-1	2420	16.1	2035	23.0
AC-2	2345	14.4	2217	19.9
AC-3	2420	17.5	1939	22.3
AC-4	2412	19.4	2276	23.7
AC-5	2403	13.4	1914	19.9

Table 3 shows the values of the adsorption capacities at 150 °C. The adsorption capacities in *o*-cresol and naphthalene were 13.4–19.4 g-tar/(100 g-AC) and 19.9–23.7 g-tar/(100 g-AC), respectively. They depended on the type of ACs. These results indicate that the characteristics of ACs would influence the tar removal efficiency.

3.2 Effect of the physical characteristics of ACs

AC-2 and AC-3 had identical particle sizes, while their specific surface areas were different. The breakthrough curves of *o*-cresol and naphthalene for these two samples are shown in Fig. 3(a) and Fig. 4(a), respectively. The results show that *o*-cresol and naphthalene easily broke through AC-2 as compared to that of AC-3. In general, micropores would result in larger surface areas of the ACs. In the adsorption of aromatic compounds at 150 °C over the ACs, adsorption took place easily on AC-3 because larger pores are essential for making the micropores accessible to the aromatic molecules. In the case of AC-2, although it has a low surface area less than 500 m²/g, almost pores are micropores. Moreover, the adsorption capacities are similar.

AC-3 and AC-4 had the same specific surface areas and average pore diameters. However, the average particle size of AC-4 was less than that of AC-3. Fig. 3(a) and Fig. 4(a) show that when the C/C₀ values were in the range of 40–50%, the tar concentration in AC-4 was less than that in AC-3; at higher C/C₀ values, the tar concentration values in AC-3 was less than that in AC-4. Table 3 shows that the adsorption capacities of *o*-cresol and naphthalene were greater for AC-4 as compared to AC-3. It is assumed that in AC-4 with a smaller particle size, there were more adsorption sites exposed to the tar model compounds in the initial adsorption process than those in AC-3. However, for AC-3 with a larger particle size, the tar model compounds required further diffusion to reach the new adsorption sites. As a result, a greater amount of time was required to reach the adsorption equilibrium.

AC-4 and AC-5 had similar specific surface areas and average particle sizes, while AC-4 was categorized as a microporous material with an average pore diameter of <2 nm and AC-5 was categorized as a mesoporous material

with an average pore diameter of 2–50 nm. Fig. 3(a) and Fig. 4(a) show that the adsorption behaviors were influenced by the average pore diameters of the ACs, depending on the tar model compounds. In *o*-cresol, the adsorption behavior of AC-4 was similar to that of AC-5 until 50 min; however, in the case of naphthalene, the C/C₀ value for AC-5 was less than that for AC-4 until 130 min, while both the times required reaching the equilibrium for AC-5 was lesser than that of AC-4. The adsorption capacity of AC-4 (shown in Table 3) was greater than that of AC-5. Mastral¹⁸⁾ had showed that the proper carbon materials for naphthalene adsorption will be the ones showing a higher micropore volume with a micropore diameter large enough to avoid diffusional effects. Consequently, the adsorption capacity of AC-4 with a relatively large micropore diameter and a large specific surface area was higher than that of AC-5.

For tar adsorbents, the ACs required a large amount of time to breakthrough and a larger adsorption capacity. In *o*-cresol, AC-4 was the most favorable for tar removal; for naphthalene, AC-1 was the most favorable. By considering the characteristics of these ACs, it was found that a larger specific surface area, a smaller particle size, and an appropriate pore diameter are required for effective tar removal.

3.3 Effect of the type of tar model compound on their adsorption behavior

The effect of the type of the tar model compound on their adsorption behavior was investigated using AC-1 at 150 °C. Fig. 5 shows the breakthrough curves of each tar model compound. Table 4 lists the adsorption capacities. Phenol, *o*-cresol, naphthalene, and 1-methylnaphthalene were almost completely adsorbed by AC-1; the adsorption behavior was dependent on the type of the tar compounds. The adsorption capacity was 10.5–32.6 g-tar/(100 g-AC) in the following order: phenol < *o*-cresol < naphthalene < 1-methylnaphthalene. Table 2 shows that the tar compounds having methyl groups (*o*-cresol and 1-methylnaphthalene) were

Fig. 5 Breakthrough curves of model tar components for AC-1 at 150 °C (A=phenol, B=*o*-cresol, C=naphthalene, D=1-methylnaphthalene)

Table 4 Adsorption capacity of AC-1 at 150 °C for tar model compounds

Tar	C ₀ (ppmv)	w (g/100g)
Phenol	2160	10.5
<i>o</i> -cresol	2420	16.1
Naphthalene	2035	23.0
1-methylnaphthalene	2083	32.6

removed more effectively as compared to those having no methyl groups (phenol and naphthalene). This can be attributed to the fact that the interactions between the methyl groups of the tar compounds and the hydrophobic functional group on the surface of the ACs or the high b.p. of the tar compounds having a methyl functional group resulted in an increase in the adsorption capacity. However, in order to effectively explain the effect of the functional groups on the adsorption capacity, a more detailed investigation must be conducted in the near future.

The adsorption rate in mesopores was faster, and the time required to reach the adsorption equilibrium was shorter in comparison to those in the micropores. The specific surface area attributed to the micropores was higher; therefore, the breakthrough curves B and C levels off at approximately 90% C/C₀ because it would require considerable time to reach the equilibrium.

The removal efficiency of tar compounds was also affected by the presence of steam in the gas stream¹⁹. Moreover, the removal of VOCs from humidified gas streams using ACs depends on the temperature, concentration, and components of the tar²⁰. We will further investigate the influence of steam on the removal of tar model compounds using ACs. The regeneration of ACs is necessary to obtain a renewable resource²¹. In this study, a preliminary experiment was performed; almost the same breakthrough curves were obtained without any loss in the adsorption capacity of the used ACs when they were treated several times by thermal regeneration in a stream of nitrogen at 400 °C. The detailed investigation is still under study.

4. Conclusions

Medium tar compounds with not more than two aromatic rings that were difficult to be removed at 300 °C were identified, and they were easily removed by ACs at 150 °C. Further, *o*-cresol and naphthalene were effectively removed, and the adsorption capacities of ACs were 13.4–19.4 g-tar/(100 g-AC) in *o*-cresol and 19.9–23.7 g-tar/(100 g-AC) in naphthalene. A larger specific surface area, a smaller average particle size, and an appropriate pore diameter were required for effective tar removal. The average pore diameter influences the tar removal process, depending on the type of the tar model compounds. Using AC-1, the ad-

sorption capacity was 10.5–32.6 g-tar/(100 g-AC) in the following order: phenol < *o*-cresol < naphthalene < 1-methylnaphthalene. Tar compounds having methyl groups (*o*-cresol and 1-methylnaphthalene) were removed more effectively as compared to those having no methyl groups (phenol and naphthalene).

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