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Abstract: Two methods, pyrolysis and steam regeneration, were used to investigate the regeneration efficiencies of two types of activated carbons that were exhausted by the phenol compound in the liquid phase. NaOH titration and temperature program deposition indicated that the two carbons exhibit different surface acidities, oxygen group distributions, and oxygen populations on the carbon surface. After treating by pyrolysis and steam regeneration, the surface recovery of spent carbons gradually increased with the regeneration temperature. Pyrolysis at 700–900°C cannot completely remove all phenol molecules from the spent carbons, thereby having a lower surface recovery than steam regeneration. Comparing the two methods, steam regeneration is an efficient method in not only recovering the porosity, but also enlarging and deepening the pore structure of carbons. In comparison with the two carbons, the higher oxygen population on the carbon surface would decrease the surface recoveries and cause a more serious carbon weight loss. This could be attributed to the fact that a greater amount of surface groups would promote the possibility of chemisorbed fraction, thus leaving more degradation species in the pores. This study would shed

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one light on how oxygen groups existed on carbon surface act as cracking sites in diminishing the removal efficiency.

Keywords: Activated carbon, phenol, thermal regeneration, steam gasification, oxygen surface groups

INTRODUCTION

Activated carbons have been extensively employed to remove volatile organic compounds (VOCs) and other contaminants from wastewaters and waste-gases. Due to its high specific surface area and porosity, activated carbon possesses an excellent capability for adsorption of various pollutants in liquid- or vapor-phase (1–7). Generally, the usage quantity of carbons is an important factor in applying the adsorption treatment. One possible way to reduce the cost is to efficiently desorb the retained substances by regeneration methods. These methods enable reuse by maintaining the carbon's adsorption capability and extending its cycle life. Thus, the regeneration of porous carbons is a crucial issue and requires a detailed investigation to ascertain if such procedures are economically attractive. Pioneer studies have indicated that this regeneration can be carried out by several treatments such as chemical regeneration, thermal regeneration, electrochemical treatment, and so on. Among these methods, thermal regeneration is by far the most commonly used because of its simplicity, high efficiency, and solvent-free property (8–11).

In general, thermal regeneration can be performed on a variety of devices including fluidized beds, rotary kilns, and multiple-furnaces. During this thermal process, it involves not only thermal desorption such as dehydration, but also several chemical reactions such as pyrolysis and gasification (10–14). This sequence is as follows: dehydration at 105°C to 150°C, desorption of volatile organic and pyrolysis of adsorbed organic by heating to 700–800°C, and gasification of pyrolytic residues at a high temperature of 800–900°C. The thermal reactions that occurred at sufficient temperatures would produce a large amount of oxidants such as water vapor, oxygen, carbon monoxide, and so on (10). From an economical point of view, it is vital to reduce the loss of carbons in the gassing stage.

Basically, commercial activated carbons possess a high removal capability; however, this cannot guarantee to prevent a critical carbon loss during thermal regeneration. Therefore, selecting suitable carbon types and thermal regeneration conditions are quite crucial based on the above point. This study intends to examine regeneration efficiencies of two types of commercial carbons with different amounts of oxygen surface functional groups. A commonly VOC, phenol, was employed as an adsorbate in this study. In comparison, thermal regeneration under inert and steam atmospheres at high temperatures (700–900°C) were also investigated into their recovery efficiencies.

EXPERIMENTAL PROCEDURE

Materials

Two granular activated carbons used here were made of bituminous coal (ACB, Calgon Carbon Co., USA) and coconut shell (ACC, Ho-Tai Co., Taiwan), respectively. Here ACB carbon was prepared by physical activation, whereas ACC carbon was prepared by using ZnCl_2 as activating agent, i.e., chemical activation. The carbons are of industrial grade and are widely used for the removal of organic pollutants from municipal and industrial wastewaters. Prior to adsorption/desorption tests, the two carbons were ground and sieved to 1–2 mm in diameter. Then all carbon samples were washed with distilled water and dried at 120°C in a vacuum oven for one day. A phenol solution (GR grade, Nacalai Tesque Co., Japan) was prepared by diluting the adsorbate in distilled water. The initial concentration was set at 1000 mg/L.

Essentially, adsorption of phenol is a significant index that evaluates the capability of carbons in removing the small organic compound (molecular size: 30.2 \AA^2) from the liquid phase (4, 7).

Analysis of Porous Characteristics

An automated adsorption apparatus (Micromeritics, ASAP 2010) was used to analyze surface characteristics of carbons, including specific area, total pore volume, and pore size distribution. Adsorption of N_2 , as a probe species, was performed at -196°C . Before any such analysis, the sample was degassed at 120°C under a vacuum atmosphere (about 10^{-3} Torr). Surface areas and micropore volumes of the samples were determined from the application of the BET and Dubinin-Radushkevich (D-R) equations, respectively, to the N_2 adsorption isotherms at relative pressures between 0.06 and 0.2. For type I isotherms (1), the amount of N_2 adsorbed at relative pressures near unity corresponds to the total amount adsorbed in both micropores (filled at low relative pressures) and mesopores (filled by capillary condensation at relative pressures above 0.2); consequently subtracting the micropore volume (determined from the D-R equation) from the total amount (determined at $p/p_0 = 0.98$ in this case) will provide the volume of the mesopore (15).

Analysis of Surface Chemistry

A selective neutralization technique is applied to estimate acidic oxygen groups present on the carbon surface. In this case, a carbon sample (0.25 g) was immersed in 25 ml of 0.12 N NaOH solution, then sealed and

mechanically oscillated for 24 h. The concentration of Na^+ ions, which did not participate in exchange with protons associated with the acidic oxygen complex, was measured by titrating aliquots of the supernatant liquid against a standard 0.12 N HCl solution. Thus, the amount of acidic complexes neutralized by NaOH solution could be estimated.

To analyze the surface oxide population on the carbon surface, a temperature program desorption (TPD) experiment was carried out in a fixed bed reactor that contains a quartz tube with a diameter of 14 mm. All spent carbons (weight: 0.1 g) were poured into the quartz tube, and the flow rate of helium is controlled at $310 \text{ cm}^3/\text{min}$ by a mass flow controller. Before entering the carbon bed, the inert gas is preheated by passing a zone filled with quartz beads. Then the carbon samples were heated at a ramp rate of $10^\circ\text{C}/\text{min}$ up to 900°C . An infrared spectrometer (California Analytical Instruments, Model 300) is used to measure the concentration of CO and CO_2 .

Batch Adsorption Procedure

Liquid-phase adsorption experiments were conducted by placing a certain amount of carbon and 100 cm^3 aqueous solution into a 250 cm^3 glass-stopped flask. These flasks were put in a constant-temperature (40°C) bath with an oscillating speed of 100 rpm. Upon achieving equilibrium (after 24 h), all slurries were filtered through nylon filters prior to analysis, so that interference from the carbon could be minimized.

The concentrations of residual solutions were analyzed by an UV/visible spectrophotometer (Shimazu, Model UV-1201) at a appropriate wavelength ($\lambda = 268$). The amount of phenol captured by the carbon can be determined as follows:

$$Q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where Q_e is the amount of adsorbate on carbon at equilibrium, in units of mg adsorbate/g carbon, C_0 is the initial concentration of adsorbate in the aqueous solution; C_e is the residual concentration, V is the volume of the aqueous solution, and m is the amount of carbon used in the adsorption. The equilibrium adsorption capacities of ACB and ACC were measured to be 2.8 mmol/g and 3.1 mmol/g, respectively. This indicated that both of the carbons have an excellent capability in removing phenol from the liquid phase. The saturated carbons with phenol are used to examine their regeneration efficiencies later.

Thermal Regeneration Procedure

A standard thermogravimetric analyzer (TGA; Perkin-Elmer TGA 7) was used to observe the thermal desorption of phenol. A small thermocouple

probe (type K) placed within a few millimeters of the sample pan served to indicate the sample temperature. The spent carbons were placed in the sample pan and suspended in the heated zone of the TGA. Experiments were performed under an extra-high helium flow of $60 \text{ cm}^3/\text{min}$ at a heating rate of $10^\circ\text{C}/\text{min}$ up to 900°C .

The spent carbons were thermally regenerated at various temperatures under inert and steam atmospheres. These treatments started upon the completion of adsorption from phenol solution. The carbons were collected by filtration and dried at 120°C for 24 h. The spent carbons were first pyrolyzed in a pure helium atmosphere to determine the amount of residue and to compare samples with the steam regeneration. These regenerations were performed in a crucible placed in a horizontal tubular furnace. A stainless steel tube ($\text{Ø}46 \times \text{L}450 \text{ mm}$) was placed in the furnace as a reactor for thermal regeneration. Two kinds of thermal regenerations were performed in this study: pyrolysis in inert and steam activation. For the pyrolysis process, the samples were heated from ambient temperature to various pyrolytic temperatures ($700\text{--}900^\circ\text{C}$) at $10^\circ\text{C}/\text{min}$, and then were kept in the hot zone for 10 min. A highly-purity helium gas flow was introduced and fixed at $250 \text{ cm}^3/\text{min}$ during this process. After that, the treated carbons were allowed to cool before being removed and weighed.

To promote the regeneration efficiency, the steam regeneration was performed at various regeneration temperatures from 700°C to 900°C . This activation was operated under a steam pressure of approximately 2 atm for 10 min. The weight loss of carbon, W_L , is used to evaluate the regeneration efficiency of each carbon. The definition of regeneration efficiency, R_S , was employed to quantify the recovery of the surface area after thermal regeneration.

RESULTS AND DISCUSSION

Surface Characteristics of Carbons

Nitrogen adsorption isotherms of carbons were used to deduce the surface properties, including surface areas, total pore volumes, and pore size distributions. The average pore diameter can be determined according to the surface area and total pore volume (the sum of the micropore and mesopore volumes), if the pores are assumed to be cylindrical and have no intersection. The surface characteristics of the original activated carbons are shown in Table 1. The results show that both the carbons have a great surface area, higher than $950 \text{ m}^2/\text{g}$. The surface areas are not proportional to the total pore volumes, since the pore size distribution is different. ACB has a higher mesopore fraction of 18%, whereas the pore volume of ACC has a slight contribution to the mesopore. It is expected that the average pore diameter (D_p) of ACB is larger than that of ACC.

Table 1. Surface characteristics of different carbons determined by nitrogen physisorption at -196°C

Carbon type	S_{BET} (m^2/g)	Pore vol. (cm^3/g)	Pore size distribution		
			Micro (%)	Meso (%)	D_p (\AA)
Original carbons					
ACB	955	0.55	82	18	23
ACC	1025	0.50	98	2	19
Spent carbons					
ACB-P	578	0.37	75	25	26
ACC-P	585	0.29	97	3	19

Surface characteristics of carbons exhausted with phenol are also listed in Table 1. All spent carbons are designated by using its nomenclature and then followed by a P letter, i.e., after adsorption of “phenol”. It is observed from Table 1 that both surface areas and total pore volumes of the spent carbons significantly decreased, compared to their fresh carbons. A decreasing proportion of 40–43% in their BET surface areas is observed, indicating a large amount of porosity blocked by phenol. It is also found that the mesopore fraction and the mean pore size of spent carbons exhibit a slight increase. These results reflect the fact that phenol molecules may mainly hinder inner and narrow pores, i.e., micropores, thus giving the larger values.

Surface Chemistry of Carbons

To verify acid-base properties of carbons, the amounts of acidic groups on fresh carbons determined by NaOH titration are collected in Table 2. Those results provide a rough estimation to identify the surface acidity of carbons. It is found that a larger number of oxygen groups and a lower pH value for ACB carbon, comparing with ACC. A TPD experiment is also used to identify the surface chemistry of carbons, by heating up to 920°C under a He environment. The corresponding integrations of different TPD profiles are collected and shown in Table 3. Typical oxygen-containing groups on

Table 2. Acid-base properties of original activated carbons by titrating KOH solution

Carbon	pH value	Acidic group (mmol/g)
ACB	6.4	1.28
ACC	7.5	0.71

Table 3. Amount of light compound liberated from spent carbons heated to 920°C under a helium environment

Carbon type	CO (mmol/g)	CO ₂ (mmol/g)	Total O (mmol/g)
ACB	1.61	0.68	2.97
ACC	0.85	0.41	1.67

carbon would be characterized as four types: a strongly acidic carboxyl group, a weaker acidic carboxyl group, a hydroxyl group, and a carbonyl group (16). It can be suggested that carboxylic groups and their derivatives, such as lactones, are decomposed to produce carbon dioxide; ketone, quinone, hydroquinones, and phenolic groups produce carbon monoxide and water (2, 17, 18). As shown in Table 3, CO and CO₂ evolutions of ACB have greater amounts than those of ACC, resulting in a higher total oxygen population. This TPD result for oxygen evolution is quite identical with the analysis of surface acidity in Table 2.

These findings observed from Tables 1–3 evidence that the two types of carbons behave different heterogeneous surfaces caused by pore structure and surface acidity. Basically, the activated carbons employed here have a heterogeneity that is contributed from various pore size and surface group distributions, especially for the existence of surface groups. These surface groups are probably implanted in the early stages of carbon preparation, i.e., when porosity is still relatively narrow, or chemisorbed under an oxygen-containing atmosphere (15). These characteristics may affect their regeneration efficiencies. In general, physical adsorption belongs to a weaker affinity that is mainly related to pore size (19, 20). Otherwise, chemical adsorption of phenolic compounds leads to a stronger bonding between acidic groups and adsorbate molecules. This bonding may play a major role in affecting the efficiency of thermal regeneration. The influence of surface groups on thermal regeneration of carbons will be discussed later.

Analysis of TGA on Spent Carbons

Figure 1 illustrates derivative thermogravimetry (DTG) patterns for ACB-P and ACC-P carbons. These curves have been updated against the DTG curves of fresh carbons. It is obvious that two major peaks at different temperatures in ACB-P curve, concentrated at 200°C and 650°C, correspond to the presence of phenol physisorbed and chemisorbed on the carbon surface. At temperature below 300°C, the physisorbed fraction was initially removed from ACB-P carbon, thus forming phenol and/or heavy degradation byproducts. As for a comparison of physisorbed evolution, the maximum evolved temperature of ACB-P (210°C) has a lower value than that of ACC-P (270°C).

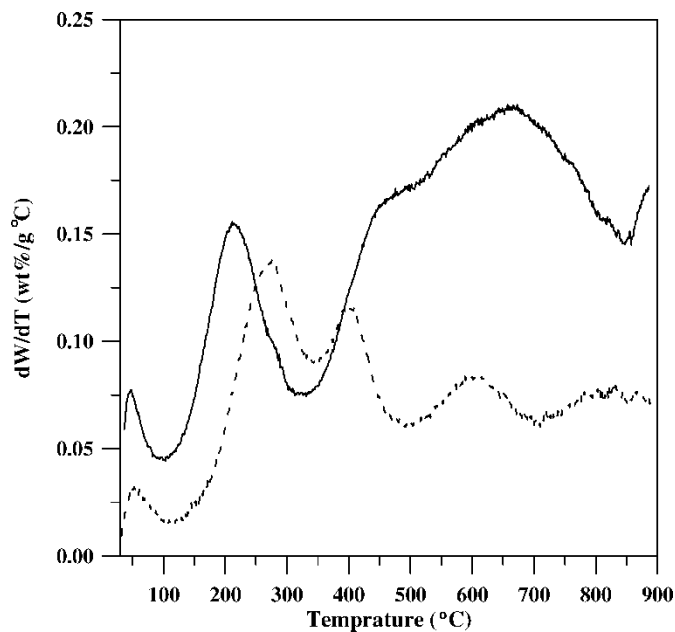


Figure 1. DTG evolution rates of spent carbons varied with temperature under a helium flow: (—) = ACB, and (---) = ACC.

As analyzed from Table 1, this can be ascribed to a higher proportion of microporosity in ACC than in ACB, which may result in a stronger affinity between the inner pore wall and phenol molecules, i.e., an overlapping effect. Therefore, the removal of physisorbed phenol is more favored in the case of ACB carbon at a lower temperature.

The chemisorbed fraction, together with some oxygen surface groups, were gradually released from the spent carbon at temperatures of 300–900°C. Meanwhile, different thermal degradations were in progress, producing several light byproducts such as CO, CO₂, and CH₄. Previous studies have reported the same result for desorption of phenolic compounds from spent carbons by using thermal regeneration in an inert atmosphere (21, 22). Otherwise, also shown in Fig. 1, ACC-P carbon has several peaks at 300–900°C. This is presumably due to different types of chemical bonding on the ACC surface.

It is of interest that the total evolution of ACB has a larger amount than that of ACC during the entire temperature range of 300–900°C. It can be inferred that these oxygen groups would interact with the adsorbate molecule on the carbon surface. For a donor-acceptor complex mechanism, carbonyl oxygen on carbon acts as the electron donor and the aromatic ring of adsorbate acting as the acceptor (18). Thus, the existence of acidic groups on activated carbon would participate in the phenol degradation process in thermal

regeneration (21). This observation can be supported by the fact that a larger amount of surface groups in ACB may generate more degradation reactions during thermal regeneration, thus causing a more serious carbon loss.

Pyrolysis of Spent Carbons

Pyrolysis of the spent carbons at different temperatures was performed under a He atmosphere, and porous structures and weight loss (W_L) of the regenerated carbons are shown in Table 3. It reflects that for both the carbons, their surface areas, pore volumes, and weight losses generally increase with the regeneration temperature. In comparison with the spent carbons, surface recovery is higher for ACC-P than for ACB-P at a fixed temperature. This can probably be attributed to the fact that the large number of oxygen groups existing on the carbon surface, leading to a greater fraction of phenol chemisorbed. These chemisorptions would elevate the difficulty of phenol desorption and the carbon weight loss. According to the analysis, the existence of oxygen groups onto carbons becomes one of the important criteria in selecting activated carbon based on promoting regeneration performance.

Strictly speaking, the pyrolysis treatment cannot totally recover the phenol-exhausted porosity in carbons; that is, the method only recovers $\sim 42\%$ for ACB and $\sim 69\%$ for ACC at 900°C in a specific surface area. As for the chemisorbed fraction for adsorbing phenol, the $-\text{OH}$ group would specifically interact with carbon surface groups, thus leading to a chemical bonding with high energy (11). During the thermal regeneration, these surface groups can be served as cracking centers with phenol molecules. These reactions may not only produce some light gases (22), but also leave some pyrolyzed remains of phenols that cause serious blockage of porosity in carbons. In other words, the more surface groups that exist, the higher the possibility of pore blockage.

Previous study has pointed out that completely removal of phenol in carbon requires a fairly high temperature at approximately 1200°C under a vacuum environment (2). In comparison, our study operated at 900°C indicates that it would be difficult to entirely remove phenol from the spent carbon surface. However, we do not suggest that the regeneration temperature is higher than 1000°C due to operating cost and reactor design. Additionally, there is a slight difference in the pore size distributions of regenerated carbons, indicating that almost no gasification occurs in pore structure. The reaction only allows slight enlargement and widening of the existing micropore.

Steam Regeneration of Spent Carbons

According to the above result, the pyrolysis procedure may leave an amount of carbonized phenolic residues, which must be gasified by the introduction of oxidizing gases at a high temperature. To promote a better regeneration efficiency, thermal regeneration with oxidizing gases, such as steam, was

performed in this study. This technique resembles steam activation of carbon precursor. Of course, activated carbon probably itself reacts with steam if operating conditions are not carefully monitored.

To investigate the carbon loss in steam regeneration, the gasification rates of carbons in steam are firstly analyzed. A global gasification rate of steam-carbon can be expressed as

$$R = -\frac{1}{m} \left(\frac{dm}{dt} \right) = k_0 \exp \left[-\frac{E_A}{RT} \right] \cdot P_{steam} \quad (2)$$

where R is the global gasification rate per unit mass of carbon, k_0 is the frequency factor, E_A is the apparent activation energy, and P_{steam} is the pressure of steam. The temperature dependence upon the gasification rates of carbons in steam is depicted in Fig. 2. It reveals that the gasification rate increases with temperature for both of carbons, indicating an apparently endothermic process. Compared with the carbons, the apparent E_A value has the following order: ACB (31.2 kJ/mol) > ACC (24.7 kJ/mol). Theoretically, a larger E_A value reflects that the reactivity is more sensitive to the increase of R along with the rise in temperature. This difference is likely attributed to two reasons:

1. the carbon produced from bituminous coal is considered to be more reactive with steam than coconut-based carbon;

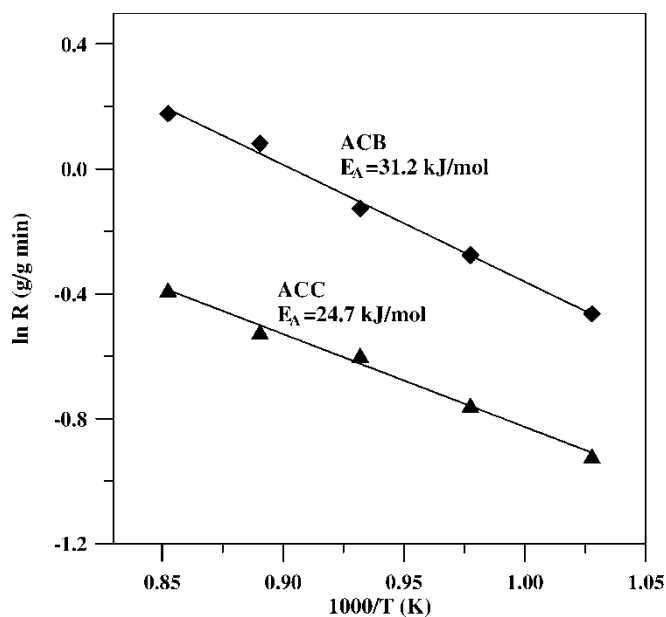


Figure 2. Variation of gasification rates with temperatures for both fresh carbons in a steam atmosphere: (◆) = ACB, and (▲) = ACC.

- the greater population of oxygen groups may facilitate the gasification in steam.

After steam treatment, surface characteristics and weight loss of final carbons varied with temperatures are also shown in Table 4. Again, it is clearly found that surface area and pore volume increase unanimously with temperature for the two carbons. As indicated from Table 3, the spent carbons treated by steam regeneration offers a more significant raise in the surface recovery of carbon, compared to pyrolysis. To clarify this influence, Fig. 3 displays that surface recovery, R_S , is an increasing function of the regeneration temperature. As expected, it is clear that ACC has a higher R_S value than ACB within temperatures ranging from 700°C to 900°C, whereas the carbon loss of ACC is smaller than that of ACB.

Generally, carbon residues from the adsorbed organic are presumed to be more amorphous than the carbon-based structure, and thus more easily gasified (10). Within the temperature range of 700–900°C, there is an obvious increasing trend of the mesopore fraction and the average pore diameter with the regeneration temperature. This can be ascribed to a fact that the development of porosity, including the surface area, pore volume, pore size distribution, and mean pore diameter, is a function of the

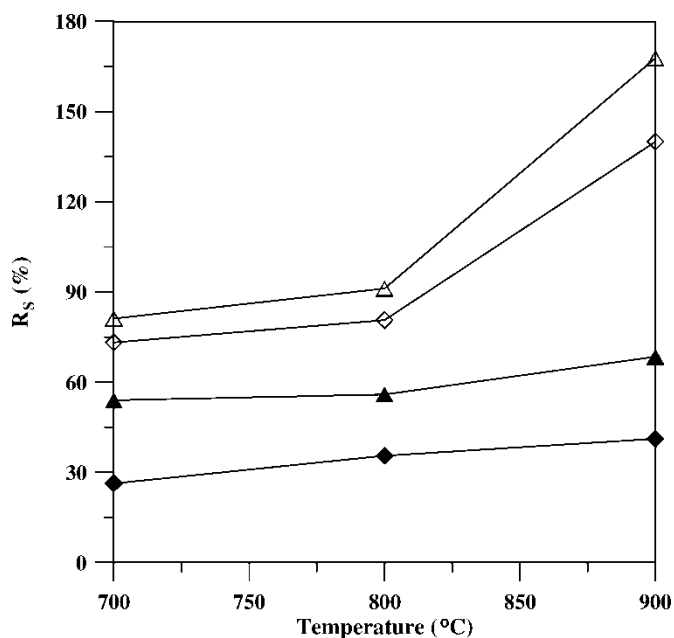


Figure 3. Surface area recoveries of spent carbons treated at different temperatures: (◆) = ACB, (■) = ACC for pyrolysis, and (◇) = ACB, (△) = ACC for steam regeneration.

Table 4. Surface characteristics of the treated carbons by pyrolysis and thermal regeneration at various temperatures

Regeneration temp. (°C)	S _{BET} (m ² /g)	Pore vol. (cm ³ /g)	Pore size distribution		D _p (Å)	W _L (wt%)
			Micro (%)	Meso (%)		
ACB-P by pyrolysis						
700	677	0.40	80	20	24	7.7
800	712	0.43	79	21	24	9.3
900	733	0.44	78	22	24	9.5
ACC-P by pyrolysis						
700	822	0.40	98	2	19	5.1
800	831	0.40	98	2	19	6.6
900	886	0.43	97	3	19	7.0
ACB-P by steam regeneration						
700	854	0.54	75	25	25	11.1
800	882	0.56	74	26	26	13.2
900	1106	0.85	61	39	31	20.4
ACC-P by steam regeneration						
700	942	0.45	97	3	19	9.1
800	986	0.49	96	4	20	10.2
900	1323	0.76	84	12	23	15.3

regeneration temperature. This means that the regeneration not only removes the carbonized residues, but also enlarges the micropores in carbon.

One can observe from Table 3 that the final ACC carbon treated at 900°C has the greatest porosity (1323 m²/g in surface area and pore volume in 0.88 cm³/g), which is much more than the fresh carbon. At this temperature, the gasification of carbon in steam is dominated by two mechanisms: widening of the original pores, and opening of the closed micropores. In other words, the steam regeneration seems like an activation process, capable of producing more excess surface area. However, it is noted that a large amount of carbon loss for both carbons, about 15–20%, occurs in this condition, i.e., temperature: 900°C; operating period: 10 min. To resolve this drawback, it can be improved by lowering the temperature, shortening the operating period, or reducing steam pressure.

CONCLUSIONS

This present study employed two methods, pyrolysis and steam regeneration, to recover surface porosity of exhausted carbons. Two types of activated carbons, made of bituminous coal and coconut, were found to have different porous characteristics and surface chemistry, determined by nitrogen

physisorption and TPD analysis, respectively. The DTG analysis indicates that the peak of physisorbed removal at different temperatures depend on the porosity of carbon. At chemisorbed removal at high temperature, the carbon with the higher population of oxygen content induces a more serious weight loss.

Pyrolysis at 700–900°C cannot completely remove all phenol molecules, and the surface recovery of spent carbons gradually increased with the regeneration temperature. This can be attributed to a greater amount of surface groups raises the accessibility to phenol chemisorption. The residues would block and fill with pores, decreasing the surface area and porosity. Thus, the oxygen surface complexes on the carbon surface can be served as cracking sites in determining removal efficiency. Comparing the two methods, the steam regeneration is a promising method in efficiently recovering the porosity of exhausted carbons, even enlarging and deepening the pore structure. However, it should be noticed that a larger amount of carbon loss occurs at 900°C. A key to successful thermal regeneration is to limit the regeneration temperature to below 900°C and to control the operating time and steam pressure, thereby minimizing the gasification of carbons. However, a deep research on optimal parameters' combination needs to be examined in the future.

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