

Activation of Charcoal from Waste Wood in Subcritical Water

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ABSTRACT

The green and low energy input process for activated charcoal production from waste wood was being developed by combination of gas phase carbonization and subcritical water activation. Waste wood is firstly carbonized in a pyrolyzer at different temperature and different treatment time. The carbonized waste wood, namely charcoal, is secondly activated to use waste water management. A charcoal pyrolyzed from waste wood at 400°C was treated under hydrothermal condition, at 200°C for 5 h in the absence and in the presence of additives (sulfuric acid, potassium hydroxide, citric acid and hydrogen peroxide). Hydrogen peroxide was effective for activated agent. The optimum condition for gas phase carbonization and activation in subcritical water was investigated. To judge the optimum condition, burn-off values (BO), which are the weight loss of charcoal after the reaction, were evaluated and absorption of methylene blue dye (MB) was used as index. As a result, it was found that low temperature carbonization and low temperature subcritical water treatment was effective for increase of adsorption of MB (~60 mg-MB/g-charcoal). By measurement of specific surface area and pore distribution, the activated charcoal at the low temperature process had meso pores on the surface regardless of small surface area (~50 m²/g). It was suggested that the charcoal made from low temperature gas phase pyrolysis contained high molecular weight tar and the tar was removed from the surface by decomposition in subcritical water.

INTRODUCTION

Activated carbon is important for wastewater management. Activated carbon used in wastewater management is typically made from imported coal or coconut shell. For establishment of robust supply systems for activated carbon, local materials such as waste wood can be advantageously used. For sustainable management of water, activated carbon produced at a local area, waste wood is a candidate as a starting material for making activated carbon. Conventionally, charcoal made from wood is activated at high temperatures (600~800 °C) after treatment in alkaline solutions. To reduce input energy and develop an effective method for the activation, hydrothermal treatment could be an alternative method because energy required for drying can be reduced and hydrolysis of condensation bonds in charcoal can occur along with functional group attachment. Activation of carbon by hydrothermal treatment could be a low temperature method because hydrolysis of

condensation bonds in charcoal can occur along with the process of ionic reactions that promote surface area expansion, functional group attachment.

Hazel nut shells hydrothermally carbonized at 250 °C have been activated at 600 °C and the activated charcoal has 250 m²/g surface area and 0.17 cm³/g micro pore volume. In this case, the peak top of micropore distribution on the hydrothermal char from hazel nut shells activated at 600 °C was at 1.5 nm [1]. Activation of a char (from olive stones) was investigated with supercritical water. For the comparison, classical steam activation was also performed for the same starting material. As a result, the reaction rate in supercritical water was enhanced and larger porosity at low degrees of burnoff was developed. The differences might result in the carbon-water reaction [2]. One of the main factors related in the reaction mechanism is probably concentration water. The density (concentration) of water at supercritical condition is hundreds times higher than that at atmospheric steam.

In this study, a waste wood charcoal produced by pyrolysis at 400 °C was hydrothermally treated at 200 or 300 °C for 1~5 h. Also in this study, a charcoal pyrolyzed from waste wood at 400°C was treated under hydrothermal condition, at 200°C for 5 h in the absence and in the presence of additives (sulfuric acid, potassium hydroxide, citric acid and hydrogen peroxide). The burn-off values (BO), which are the weight loss of charcoal after the reaction, were evaluated and absorption of methylene blue dye (MB) was used as index.

MATERIALS AND METHODS

Starting material was a charcoal of house waste wood pyrolyzed at 400 °C. Sulfuric acid, potassium hydroxide, hydrogen peroxide and methylene blue dye (MB) were all first grade obtained from a distributor. Pure water was obtained by water deionization and distillation apparatus.

For 200°C experiments, a hydrothermal reactor having Teflon inner (100mL) was employed. Amount of sample is about 1.5 g. To increase the amount of sample and temperature up to 300 °C, a stainless steel autoclave was used. The schematic diagram of the autoclave

used in this study was shown in **Figure 1**. In the case of the Teflon inner reactor, temperature and pressure profile were unknown because there was no sensor. For the autoclave, temperature and pressure profiles inside were measured. It took 30 min to reach temperature.

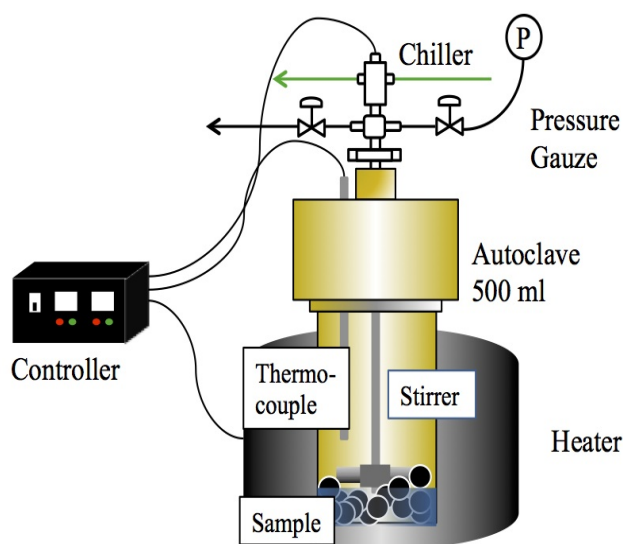


Figure 1 Schematic diagram of autoclave

The yield of the treated charcoal was evaluated on a weight basis and analyzed. Burn-off (BO) is equal to 100 minus the yield. Absorption of methylene blue dye (MB) was used as index and the procedures of the evaluation was based on JIS K 1474.

RESULTS

Table 1 shows the results. The specific surface area became higher after treatment in pure water (**Table 1**) and in the presence of citric acid. The yield shown in Table 1 was the amount of recovered solid material. That is, BO is quite small or minus. From the yield and ultimate analyses, H₂SO₄ and KOH became attached on the surface of the treated charcoal. However, functionalization may have prevented hydrothermal (or thermal) reactions from occurring on the charcoal surface.

Table 2 shows that BO was as high as 10 %, the surface area was 265 m²/g, and the micro pore volume was 0.14 cm³/g at 300 °C treatment. As stated in the introduction, hazel nut shells hydrothermally carbonized at 250 °C have been activated at 600 °C and the activated charcoal has 250 m²/g surface area and 0.17 cm³/g micro pore volume [1]. It was suggested that hydrothermal treatment of charcoal has a similar effect of 600 °C heat treatment.

Figure 2 shows the micro pore volume distribution of the raw and the treated charcoals of this work. As shown in Fig. 2, the charcoal treated at 300 °C had larger pore size distributions compared with that at 200 °C. The peak top of the micro pore distribution of the charcoal hydrothermally treated at 300 °C was 0.7 nm as shown in Fig. 1. On the other hand, the peak top of the hydrothermal char from hazel nut shells activated at 600 °C was at 1.5 nm. The

Table 1 Results of charcoals treated at hydrothermal condition at 200 °C for 5h.

Treatment	Yield [%]	Surface area [m ² /g]	O [%]	S [%]
Raw charcoal	-	3	23.5	0.41
Water	98.8	121	13.7	0.42
0.5 mol/kg H ₂ SO ₄	104.2	24	15.8	1.54
4.0 mol/kg H ₂ SO ₄	112.4	4	27.2	5.97
0.5 mol/kg KOH	107.0	17	19.3	0.42
1.0 wt% Citric acid	97.3	112	16.3	0.54

Table 2 Textural characteristics of the charcoal.

Treatment	BO [%]	Surface area [m ² /g]	Micro pore volume [cm ³ /g]
Raw charcoal	-	3	-
Water_200 °C_5 h	1.24	121	0.055
Water_300 °C_5 h	10.2	265	0.14

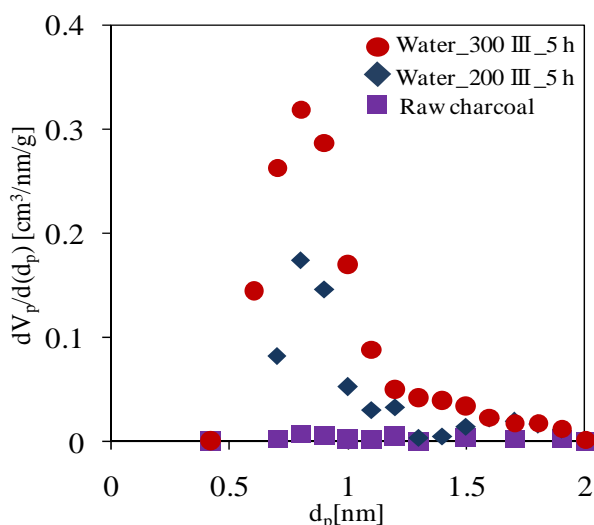


Figure 2 Pore size distributions of the charcoal.

smaller pore size distribution for charcoal produced in this work compared with the literature [1] was probably related to the reaction between water and charcoal.

To increase BO and MB adsorption capability, hydrogen peroxide was employed. By compared with the results with sulfuric acid and potassium hydroxide, hydrogen peroxide was effective for activated agent from the BO and MB point of view. In addition, by adjusting the conditions, it was found that low temperature carbonization and low temperature subcritical water treatment was effective for increase of adsorption of MB (~60 mg-MB/g-charcoal). **Figure 3** shows the relationship between methylene blue absorption (MB) and burn-off (BO) at hydrothermal treatment. With increasing burn-off (BO), MB increased linearly.

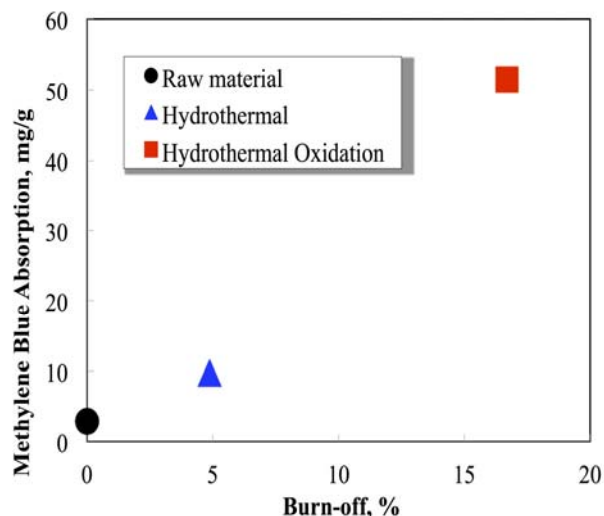


Figure 3 Relationship between methylene blue adsorption and burn-off

By measurement of specific surface area and pore distribution, the activated charcoal at the low temperature process had meso-pores on the surface regardless of small surface area (~50 m²/g). We now considered that the charcoal made from low temperature gas phase pyrolysis contained high molecular weight tar and the tar was removed from the surface by decomposition by partial oxidation with hydrogen peroxide in subcritical water. The details reaction mechanism is now investigated and the activated carbon having as good adsorption ability as commercial product will be produced.

CONCLUSION

Hydrothermal activation was investigated. In the presence of acid (sulfuric acid and citric acid) and base (potassium hydroxide), surface modification with the acid and base occurred. To enhance the BO and MB adsorption capability, hydrogen peroxide was effective. By adjusting reaction condition, high MB adsorption (60 mg-MB/g-carbon) was achieved. Specific surface area of the activated carbon produced at hydrothermal activation was still so low and the reaction condition for producing large specific surface area by keeping high adsorption ability must be investigated.

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