EARLY RESULTS OF A NOVEL METHOD FOR MANUFACTURING HIGH YIELD MACADAMIA SHELL ACTIVATED CARBON

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Introduction

Activated carbons find many applications as adsorbents, support materials of catalyst, and so on[1]. Usually, activated carbon is produced by treating carbon at high temperature (around 800 °C) with steam or CO_2. In these methods, the yield of activated carbon from the raw feedstock is around 10%. Because feedstock costs are significant, it is important to produce the activated carbon with higher yields. Of course, it is also important to improve its surface area. Recently, we described a process for producing High-Yield (HY) charcoal[2] from biomass. The focus of this paper is the activation of HY-charcoal by treatment with oxygen in compressed liquid water at low temperature. There are some advantages for this treatment in compressed liquid water. The oxygenation step can be conducted at high oxygen concentration so that the treatment time can be decreased. The reaction between carbon and oxygen is strongly exothermic, but by using water as a thermal ballast, the temperature is controllable easily during the reaction.

Experimental

Activation experiments in hot compressed water were conducted by using a packed bed, tubular reactor. The reactor tube is made of Hastelloy alloy, C-276 with 0.815" i.d. and 31" length. High-yield Macadamia nut shell charcoal was ground and sieved between No.30 sieve and No.14 sieve. It was pretreated and subsequently packed in the center of reactor. Glass beads, whose diameter was 3 mm, were also packed both upstream and downstream of the carbon. These beads improve heat transfer within the reactor. At the beginning of the experiment, the reactor was pressurized and heated by use of an electric furnace and an entrance heater with a flow of deionized, degassed water. When the temperature and pressure became stable at the experimental condition, the solution was switched from water to hydrogen peroxide. The reaction temperature and pressure were 200 °C and 10 MPa, respectively. Experiments were conducted with 0.8 M and 0.2 M H_2O_2. Treatment time taken in these experiments was a few hours. Table 1 shows the conditions of oxygenation. During the experiment, gas samples were taken at the outlet of the reactor and the gas generation rate was also measured. The composition of gas samples was analyzed by use of a HEWLETT PACKARD model 6890 Gas Chromatograph. For the solid sample, the mass change during oxygenation was measured and conversion was calculated. Then the oxygenated charcoal was subject to a post-treatment and the yield of activated carbon was calculated. Iodine number was measured for oxygenated charcoal and activated carbon by following the ASTM method D4607-86. BET surface area was also measured for oxygenated charcoal and activated carbon by use of a Quantachrome AUTOSORB-1 gas sorption analyzer. Table 2 shows the properties of pretreated charcoal feedstock used in these experiments.

Table 1 Oxygenation conditions

No.	T [°C]	P [MPa]	H_2O_2 conc. [M]	Treatment time [h]
1	200	10	0.8	5.25
2	200	10	0.8	2.67
3	200	10	0.8	6.83
4	200	10	0.8	1.67
5	200	10	0.8	0.77
6	200	10	0.2	5.1
7	200	10	0.2	7.52

Table 2 Properties of pretreated charcoal feedstock

Charcoal	Iodine Number [mg/g]	BET-S.A. [m^2/g]
Macadamia Shell Charcoal	169	164.2

Results and Discussion

H_2O_2 decomposition

By use of experimental data available in the literature[3], the required time for complete decomposition of H_2O_2 in the aqueous solution was estimated and it was much less than the residence time of the liquid in our experimental conditions. Complete decomposition of H_2O_2 was also suggested from the result of good oxygen balance shown later.

Oxygenation step

Figure 1 shows an example of the time history of output

gas flow rate for experiment #7. Output gas was mainly CO_2 and includes a small amount of CO, especially in the latter part of experiment. Some CO probably reacts with excess O_2 and is converted to CO_2.

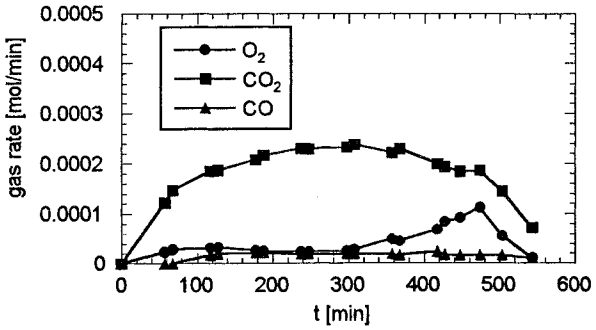

Fig.1. Time history of output gas flow rate (No.7).

Activated carbon

Table 3 shows the yield, iodine number and BET surface area for activated carbon. Yield of Macadamianut shell charcoal from initial material is around 40 wt%[2]. Therefore, the yield of these activated carbons from the initial material is more than 20 wt%. This value is almost twice as large as that of conventional methods (around 10 wt%). In the best case, an iodine number of more than 800 mg/g of was attained. Figure 2 shows a comparison of pore size distribution between pretreated charcoal and activated carbon for the highest surface area result (No.1). For activated carbon, an increase of pore volume whose diameter is between 2 and 30 Å was found. It is supposed to cause the increase of surface area.

Table 3 Results of activation

No.	Yield[1)] [-]	Iodine No. [mg/g]	BET-S.A. [m^2/g]
1	0.490	841	845.3
2	0.579	815	-
3	0.489	751	-
4	0.561	708	781.0
5	0.609	601	591.7
6	0.568	598	-
7	0.513	625	631.2

1): Yield from raw charcoal.

Mass balance

Table 4 shows the typical result of carbon and oxygen balance during the oxygenation and post-treatment (No.7). The input carbon was the amount of carbon packed as the pretreated charcoal and the output carbon was that of carbon acquired as the activated carbon and the carbon included in output gas product. The input oxygen was the amount of oxygen pumped into the reactor as H_2O_2 and the output oxygen is that of unreacted oxygen and oxygen included in output gas products. In this calculation, all the output gas product was assumed to be CO_2. As shown in this table, good mass balance was obtained. Results for other experiments were similar to this result.

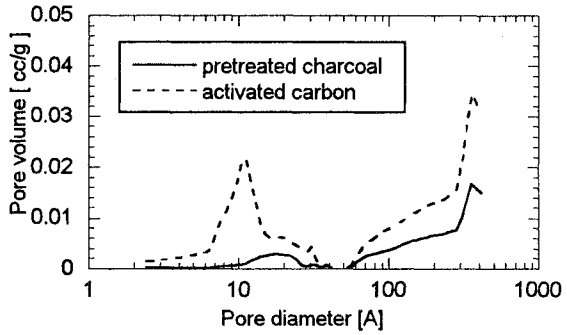

Fig.2. Comparison of pore size distribution between pretreated charcoal and activated carbon (No.1).

Table 4 Results of carbon and oxygen balance

	C [mol]	O [mol]
Input	0.489	0.136
Output	0.460	0.143

Conclusions

High yield macadamianut shell charcoal was oxygenated in compressed hot liquid water with oxygen for a few hours and activated. The yield from the initial macadamia shell was around 20 wt%, which is almost twice as large as that of conventional methods. During activation, significant increase of micro pore volume was found and the Iodine number of activated carbon was around 600 to 800 mg/g. Good mass balance for carbon and oxygen was obtained.

Acknowledgments

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