

HIGH YIELD ACTIVATED CARBON FROM BIOMASS BY AIR ACTIVATION

Xiangfeng Dai and Michael J. Antal, Jr.

Hawaii Natural Energy Institute and the Department of Mechanical Engineering
University of Hawaii at Manoa
Honolulu, HI 96822

INTRODUCTION

With its large internal surface area, activated carbon has extraordinary adsorptive capabilities. It is employed in a wide range of applications, mostly as a purifying agent to remove trace quantities of undesirable species from gas or liquid phase as well as an economical medium to recover precious materials. The demand for activated carbon has been continuously increasing in the past decade. In 1988, the consumption of activated carbon in industrialized countries was 300,000 tons (Roskill, 1990). The United States accounts for 43% of this amount - around 130,000 tons. Since then, the demand in the U.S. market is estimated to have increased at a rate of 5% per year to around 230,000 tons by the year 2000. Because of worldwide increasing environmental problems and stricter regulations set by governments in both industrialized and developing countries, the demand for activated carbon will continue to increase.

Commercial production of activated carbon employs high temperatures of above 800°C using steam or carbon dioxide as an activating agent from coal and limited amount of biomass by thermal activation process. On the other hand, yield of activated carbon from biomass is low, e.g., 5 - 8 % from coconut shell. Consequently, activated carbon produced by conventional method is expensive. The retail price of activated carbon ranges from \$2 - \$6 per kg depending on the type.

In this article, a novel thermal process of producing high-yield activated carbon from Macadamia shells by air or a mixture of air and inert gas at low temperature is discussed. Characteristics of the carbon are presented.

EXPERIMENTAL

Macadamia shells as agricultural by-products in Hawaii are employed as the original material in this work. Raw Macadamia shells are in hemispherical shape with about 25 mm diameter and 3 mm thickness. Macadamia shells undergo a series of pretreatments and post-treatments before forming the final products -- activated carbons. Pretreatments include pyrolysis in a pressurized lab reactor, in which high yield charcoal is obtained as described elsewhere [Dai, 1995; Antal, 1996], and then followed by high temperature carbonization process at atmospheric pressure without oxygen presence. Afterwards, carbonized charcoal is subjected to oxygenation process, in which various operating conditions are investigated to fine tune the final product. The major operating parameters include temperature, total pressure, oxygen partial pressure (P_{O_2}), oxygenation time and carbon burn-off, etc. Finally, oxygenated charcoal receives post-treatment at high temperature, namely, the activation process as termed in this work, degassing or desorption process as termed commonly, thereby forming activated carbon. The raw charcoal retains the shape of its raw shell. The hemispherical charcoal is employed only in the lab reactor. Granulated charcoal particles with 6×14 mesh are employed in both the lab reactor and the ceramic reactor which will be discussed next.

The key step is the oxygenation process. Part of the oxygenation process has been conducted in the lab reactor, with which a detailed arrangement and operating procedure similar to the ceramic reactor is described elsewhere [Dai, 1995]. However, most significant progress was made in the ceramic reactor. The ceramic reactor system is schematically shown in Fig. 1. Pretreated granulated charcoal is loaded in the upper portion of the reactor. Due to strong exothermic reaction in the oxygenation process, nitrogen or helium is mixed with air to serve as a thermal ballast. Air passing a regulator from the air tank is controlled by a micrometering valve and measured using a mass flow controller (Aalorg model GFM-1700) before reaching an on/off valve. Similarly, nitrogen or helium is controlled by a micrometering valve and measured using a rotameter (Brook model 1110-01F1B1A) before passing an on/off valve. Then air and nitrogen/helium are mixed and fed into the 50 mm diameter ceramic reactor. The product gas leaves the reactor to a 3-way valve, one way going to the sampling bag while the other going to a rotary flow meter (GCA/Precision Scientific wet test meter) after a cooling section. The desired temperature is obtained by controlling an external heater with a variable voltage transformer and an internal heater with a temperature controller. A thick bed of glass beads is packed upstream of the charcoal sample layer to improve heat transfer and uniformity of flow. Two type K thermocouples contact the charcoal sample to record the charcoal temperature. Flow meters are calibrated at room temperature before onset of the experiment using a soap film flow meter. Gas samples are taken in the sampling bag as well as in an in-line port with a septum downstream of the 3-way valve. Then, the sample gas is analyzed by a Gas Chromatograph (Hewlett Packard

Model 6890) equipped with a thermal conductivity detector and a column made of two concentric columns capable of separating nitrogen and oxygen (Alltech CTR). The adsorptive properties are reported in terms of iodine number, BET (N_2) surface area, and pore size distribution. Iodine number test follows ASTM D4607-86. BET surface area and pore characteristics are analyzed by a gas sorption analyzer (Quantachrome Autosorb-1).

RESULTS AND DISCUSSION

A series of experiments have been conducted under a range of operating conditions in oxygenation process using nitrogen/air mixture in the lab reactor. A set of typical results is shown in Table 1. As seen in the table, both large and small sized oxygenated charcoal have low iodine number, i.e., 121 mg/g and 282 mg/g, respectively. When surface oxides are removed after post-treatment, iodine number of both activated carbons increases dramatically -- 366 mg/g and 506 mg/g for large and small size. Higher iodine number of small particles is partly due to higher burn-off and probably mostly due to its small size, in which case, the effect of mass transport within charcoal pores is much less important than in large particles. From this result and the fact that granulated or powdered activated carbon is predominantly used in applications, granulated charcoal has been used in this study since then.

Another series of experiments were conducted in the ceramic reactor to reveal conditions for producing high yield, good quality activated carbon. A typical experimental result is shown in Table 2, in which a thick bed of charcoal samples is employed and post-treatment is followed. As seen in the table, yield and iodine number of activated carbon is quite different, depending upon the location in the packed bed. Activated carbon at the bottom layer has a higher iodine number of 652 mg/g with an overall mass yield of 12%, while the top layer has a lower iodine number of 260 mg/g but with a higher mass yield of 29%. This suggests that the overall reaction rate highly depend upon oxygen partial pressure. Activated carbon at the layer next to the bottom seems the best compromise in terms of yield and quality (iodine number). This sample would have an overall yield of around 20% with an iodine number over 700 mg/g if the oxygenation time were longer.

The result of one experiment with a thin layer of carbonized charcoal treated with pure air in the oxygenation process shows that activated carbon with an iodine number of 700 mg/g is obtained, compared to iodine number of 181 mg/g for carbonized charcoal as listed in Table 2. A fraction of this sample burned during oxygenation process as ash was collected from the reactor. Thus, it is crucial to control temperature and oxygen partial pressure in this process. This is one of the reasons why activated carbon is difficult to produce by air/oxygen activation.

The pore size distribution of a typical activated carbon with an iodine number of 625 mg/g is shown in Fig. 2. A double-peaked distribution is observed, one at around 0.8 nm in micropore regime while the other at around 36 nm in mesopore regime. From engineering point of view, this activated carbon has potential to be oxygenated for longer time by creating more pores and/or enlarging micropores so that higher surface area would be obtained. From application point of view, this kind of structure favors fast mass transport of adsorbates with a micropore size into the deep part of the pores compared to uniform micropore dominated pore structure, hence increasing process efficiency.

A TGA analysis on post-treatment of oxygenated charcoal by a colleague (Dr. G. Varhegyi) in Hungarian Academy of Science shows that desorption of surface oxides as CO_2 reaches its peak rate at around 500°C and as CO at around 700°C. Further increase in temperature will shorten the pre- and post-treatment time but may take a risk of having carbon annealed at above 800°C. This confirms our earlier results that a temperature of 750°C is best for pre- and post- treatment of charcoal among temperatures examined at 600°, 750° and 950°C.

CONCLUSION

Activated carbon with a high yield of above 20% from Macadamia shells is realized in a novel process including a series of pre- and post-treatments. This is compared to the 5 - 8% realized by conventional thermal activation method. The key process -- oxygenation is carried out at low temperatures using air or a mixture of air and inert gas as an activating agent. The pore structure and iodine number of 600 - 700 mg/g suggest that this activated carbon have potential of further increasing its surface area by finer tuning of the operating parameters.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation (Grant # CTS95-21423) and the Coral Industries Endowment of the University of Hawaii. The authors would like to thank Dr. Maria Burka (NSF) for her continuing interest of this work, Dr. Gabor Varhegyi with Hungarian Academy of Science for TGA analysis, Guilherme Bezzon, Dr. Angela Garcia and Dr. Makoto Sakurai for their assistance.

REFERENCES

- Antal, M. J., Croiset, E., Dai, X. et al. "High yield biomass charcoal". *Energy & Fuels*. Vol. 10, No. 3, 652-658, 1996.
- Dai, X., Norburg, N., and Antal, M. J. "Production of charcoal and activated carbon at elevated pressure". *Symposium on Materials and Chemicals Synthesis from Fossil Fuels and Biomass*. ACS, 285-287, 04/95.
- Roskill Information Service, Ltd. "The economics of activated carbon 1900". *PTS Research Studies*. 1-180, 08/90.

Table 1. Results of Macadamia shell activated carbon from the lab reactor

| size | burn-off | I.N. (ox) ^a | I.N. (ac) ^b | yield |
|-----------|----------|------------------------|------------------------|-------|
| φ25x3 mm | 0.194 | 121 mg/g | 366 mg/g | 24% |
| 6x12 mesh | 0.667 | 282 mg/g | 506 mg/g | 9.4% |

^a iodine number of oxygenated charcoal treated at 339°C, P_{O₂}=4.2 kPa in N₂ for 90 min;

^b iodine number of activated carbon.

Table 2. Results of Macadamia shell activated carbon from the ceramic reactor^a

| location | yield | iodine number |
|-----------------------|-------|---------------|
| (carbonized charcoal) | 0.30 | 181 |
| #1 (bottom) | 0.12 | 652 |
| #2 | 0.25 | 552 |
| #3 | 0.27 | 420 |
| #4 | 0.28 | --- |
| #5 (top) | 0.29 | 260 |

^a oxygenated at 250°C, P_{O₂}=12.7 kPa in N₂ for 62 min.

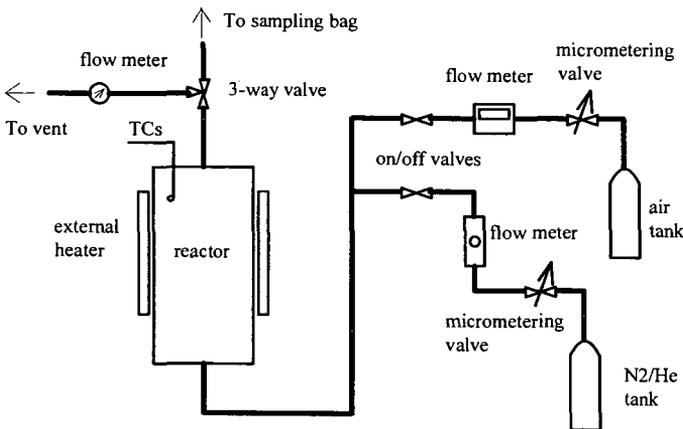


Fig. 1 Schematic of the ceramic reactor for activation

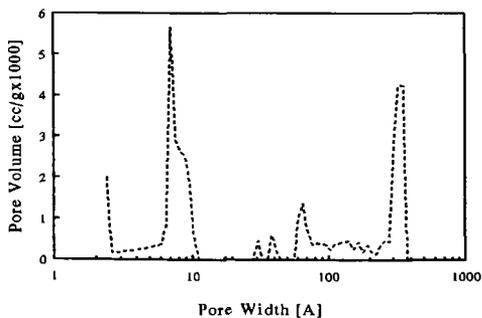


Fig. 2. Pore size distribution of Macadamia shell activated carbon