ACTIVATED CARBON FROM VACUUM PYROLYSIS CHARCOAL

N.-Z. Cao[1], F. Soutric[2], H. Darmstadt[1] and C. Roy[1,2]

[1] Institut Pyrovac Inc., Parc technologique du Québec métropolitain
333, rue Franquet, Ste-Foy (Qc) G1P 4C7 Canada

[2] Université Laval, Département de génie chimique, Québec (Qc) G1K 7P4 Canada

Introduction

Bark residue is an abundant waste material of the forest industry. In the province of Québec alone 2.5 Mt (dry basis) are produced every year. This material can be transformed by vacuum pyrolysis into useful products. The Pyrocycling® process is conducted at a temperature and total pressure of approximately 450 - 500 °C and 20 kPa, respectively. Pyrocycling® of bark residues @ 4 % moisture yields approximately 14 % gas, 21 % water, 31 % oil and 34 % charcoal [1]. The gas is used as a make up heat source to supply the energy required for the pyrolysis process. The oil is a source of valuable chemicals, such as phenols [2]. In this work the pyrolytic charcoal was tested as feedstock for the production of activated carbon.

An important difference between vacuum pyrolysis and traditional atmospheric pyrolysis conducted at temperatures up to 500 °C is that during the vacuum process the residence time of the gas and vapours evolved during the thermal decomposition process is short. Thus, secondary reactions, such as deposition of pyrolysis vapours in charcoal pores and formation of carbonaceous deposits are limited. The vacuum pyrolysis process was developed in this laboratory first at the bench scale, then with a process development unit (PDU) with a capacity of 100 kg/h and finally using an industrial scale reactor of industrial scale (3.5 t/h) which operation started in the Spring of 1999 in Jonquière (Qc) Canada.

Experimental Details

A mixture of softwood (spruce, fir and pine) bark, obtained from Daishowa Inc., Québec (Qc) Canada was pyrolyzed in a bench scale batch reactor and in the continuous PDU. In the batch experiments the bark feedstock was heated in a laboratory reactor under vacuum at a heating rate of 5 °C/min up to the final temperature selected. The sample was held at this temperature for a specified time and then allowed to cool down to room temperature under vacuum. In the continuous experiments the bark was fed under vacuum into the PDU heated to 450 °C, the residence time of the solids in the PDU was approximately 20 min. The pyrolysis total pressure was 4 and 20 kPa for the batch and continuous experiments, respectively. Charcoal activation was performed with steam alone. Prior to the activation the sample was heated

Table 1. Surface area, micropore volume and pore size of vacuum pyrolysis charcoals

| Charcoal			DR Micropore (from CO_2 data)	
Pyrolysis Conditions	Heat post-treatment	Reactor*	Surface Area	Vol.
T [°C] t [min]	T [°C]		[m²/g]	[cm³/g]
450 60	-	B	370	0.16
450 120	-	B	433	0.19
550 30	-	B	555	0.24
450 20	-	C	5	-
450 20	450	C	434	0.20
450 20	570	C	546	0.24
450 20	660	C	621	0.27
450 20	760	C	631	0.27

* B: Batch reactor, C: Continuous reactor

under nitrogen at a rate of approximately 5 °C/min to the activation temperature selected. Cooling after the activation also occurred under nitrogen.

The charcoal and activated carbon were characterised by nitrogen and carbon dioxide adsorption at 77 and 273 K, respectively, using a Autosorp 1 MP apparatus from Quantachrome, Boynton Beach, Fl. The micropore surface area and volume and pore size distribution were calculated with the DR and DFT [3] methods, respectively, using the software provided by Quantachrome. The combined micro and mesopore volume was calculated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$.

Results and Discussion

The charcoals obtained in the batch reactor had medium surface areas ranging from 350 to 550 m²/g (Table 1). The charcoal from the continuous PDU reactor had a considerably smaller surface area (5 m²/g). This lower surface area of the sample from the continuous reactor is likely due to the higher pyrolysis pressure and shorter residence time of the solids as compared to the batch experiments. It is reasonable to assume that the decomposition of the bark feedstock was not complete under the set of conditions used and that more severe pyrolysis conditions (e.g. higher temperature or longer residence time of the solids) would be necessary to achieve complete decomposition of the feedstock. The pyrolysis
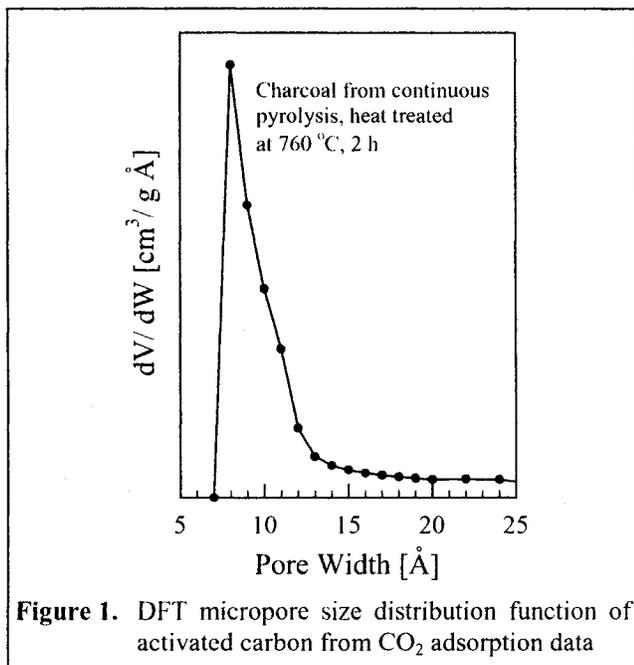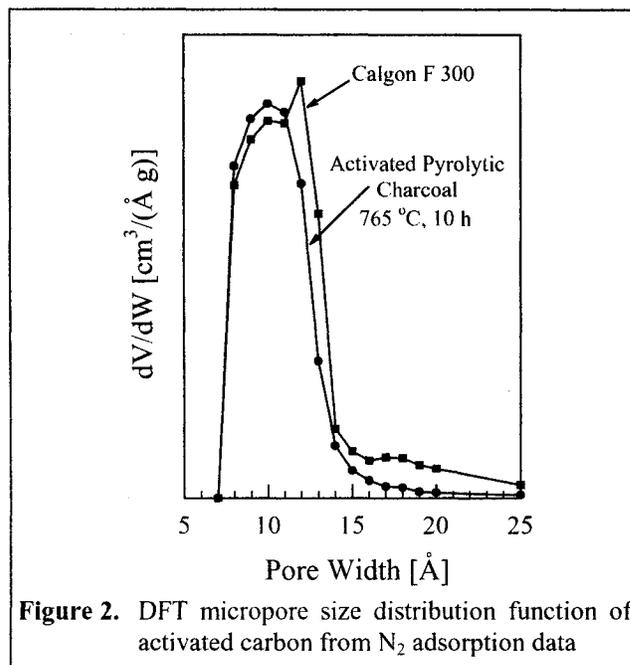
Figure 1. DFT micropore size distribution function of activated carbon from CO_2 adsorption data

Figure 2. DFT micropore size distribution function of activated carbon from N_2 adsorption data

conditions currently used in the PDU are optimised with respect to the quality and yields of the liquid products and the process economics. A solution to this is the post pyrolysis heat treatment of the charcoal under a nitrogen flow at atmospheric pressure during 2 h. The data in Table 1 show that the charcoals from the PDU after the nitrogen heat treatment and from the batch experiments at the same temperature had very similar surface areas and pore volumes. The maximum surface area was approximately 630 m²/g after a heat-treatment at 760 °C. The pore size distribution for all charcoals was similar, exhibiting a peak at a pore width of 8 Å. A typical example is shown in Figure 1. Adsorption in such narrow pores is too slow for practical applications.

An activation treatment of these charcoals is, therefore, necessary. The charcoal from the PDU was steam activated at a temperature of 765 °C. The highest surface area obtained was 850 m²/g. This value and the micropore volume are somewhat smaller when compared

Table 3. Surface area, pore volume and pore size of activated (765 °C) vacuum pyrolysis charcoals (continuous reactor).

| Residence time | DR Micropore (from N_2 data) | | Mesopore |
| | Surface Area | Volume | Volume |
[h]	[m²/g]	[cm³/g]	[cm³/g]
2	608	0.22	0.09
6	760	0.27	0.20
10	853	0.30	0.25
15	851	0.30	0.29
Calgon F 300	993	0.35	0.15

with the commercial grade Calgon F 300, whereas the mesopore volume is higher (Table 3). The pore size distribution of the activated charcoal and the commercial grade are comparable (Figure 2).

Conclusion

Activated carbon with properties close to commercial grades can be produced from vacuum pyrolysis charcoal.

Acknowledgement

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