ONE-STEP PYROLYSIS/ACTIVATION OF CORNELIAN CHERRY AND OLEASTER STONES

M. G. Ucak and S. Eser
Department of Materials Science & Engineering
209 Academic Projects Building
The Pennsylvania State University, University Park, PA 16802, USA

Introduction

Activated carbons prepared from lignocellulosic materials by physical or chemical activation methods have found applications as adsorbents especially in industrial waste water treatments [1,2]. Fruit stones, which are of lignocellulosic nature, have been studied for activated carbon production by many researchers [3-5].

In this study, we investigated the possibility of preparing activated carbon by one-step pyrolysis/ activation from whole cornelian cherry and oleaster stones for which no study has been reported. Unlike most fruit stones which have thick shells and require crushing to make activated carbons, the stones of cornelian cherry and oleaster have slim cylindrical shapes with pointed ends and thin porous shells. Therefore, they may be activated as whole stones to make strong granules of carbon.

Experimental

Cornelian cherry (from Pennsylvania) and oleaster stones (from Turkey) were separated from the flesh of the fruits, washed and dried for activation process. The fruit stones were kept in their original forms. Cornelian cherry stones are approximately 15 mm in length, 5 mm in diameter and 20 mm in length, while oleaster stones are 20 mm in length and 4 mm in diameter. A stainless steel tube reactor in a vertical tube furnace were used for activation experiments. Steam was introduced into the reactor at the beginning of the pyrolysis/ activation. The activation temperatures and time were selected as 700, 750 and 800°C and 4 hours based on a previous study [3].

The stones were characterized by elemental (LECO CHN 600 and LECO Sulfur Titrator) and proximate analyses, and the activated carbons were characterized by elemental analysis, iodine and methylene blue adsorption tests using standard methods. The surface area and porosity of the carbons were analyzed using N_2 adsorption at 77 K (Gemini II 2370, Micromeritics) and CO_2 adsorption at 273 K (ASAP 2010, Micromeritics).

Results and Discussion

Figure 1 shows the solid carbon yield from pyrolysis/ activation as a function of activation temperature. The solid yield values, calculated as the ratio of the weight of the resulting activated carbon to the initial weight of the sample. Increasing the temperature from 700 to 800°C, decreased the c. cherry stone solid yield from 24 to 14%. The high volatile matter content (76%) of the stones and possible oxidation of chars during activation could have caused the apparent linear change of the solid yield with temperature. The oleaster stones were more reactive than c. cherry stones; the pyrolysis/activation at 800°C for 4 h resulted in nearly complete burn out of the stones. For detailed characterization, we used carbons produced at 800°C for 4 h from c. cherry stones and at 750°C for 6 h from the oleaster stones with solid yield of 15%.

The elemental and proximate analyses of the fruit stones before and after activation are shown in Table 1. Both stones have low ash and sulfur contents. Their volatile matter contents are comparable, but oleaster stones have much higher oxygen and hydrogen contents, and lower carbon content than c. cherry stones. Higher reactivity of oleaster stones can be explained by their high oxygen and hydrogen contents. Upon pyrolysis/activation, both stones produced solids with a carbon content of approximately 93% on a dry-ash-free basis.

Table 2 shows the iodine and methylene blue uptakes of the same activated carbons prepared from the stones. Both carbons have moderate iodine uptakes; the oleaster stone carbon has a particularly high methylene blue uptake. Figure 2 and Figure 3 show the N_2 and CO_2 adsorption isotherms for each carbon, respectively. The surface areas and micropore volumes calculated from the isotherms are given in Table 3.

These results show that the measured iodine uptakes agree well with N_2 BET surface areas. The increase in N_2 adsorption in the relative pressure of 0.3 and 1.0 indicates both materials have some mesopore capacity. For both stones, the DR plot of CO_2 adsorption isotherms are linear at low relative pressures, and for higher relative pressures, the N_2 isotherms make an upward turn as saturation pressure is approached, indicating capillary condensation in mesopores. High methylene blue uptake of the carbon from c. cherry stones also shows that this material has a high mesopore capacity. There is a good agreement between micropore volumes calculated from N_2 and CO_2 adsorption.

Activated carbons prepared from crushed stones under the same conditions produced slightly lower solid yields (~10% lower) and lower (7% lower) BET surface areas.

Acknowledgments

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References

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Table 1. Elemental and Proximate Analyses.

	C. Cherry		Oleaster	
	Raw	Activated	Raw	Activated
Moisture	0.2	0.4	11.0	1.9
Ash	1.4	7.9	0.7	4.5
Volatile	76.2	6.4	77.2	5.8
C	53.8	94.1	48.7	94.6
H	5.8	1.0	7.3	1.5
N	1.3	1.1	0.8	1.6
S	0.1	0.02	0.06	0.02
O	39.0	3.8	43.0	2.3

Table 2. Iodine and Methylene Blue Uptakes

	I_2 uptake mg/g	Mb uptake mg/g
C. Cherry	799	416
Oleaster	652	145

Table 3. BET Surface Areas and Micropore Volumes

	N_2 adsorption		CO_2 adsorption	
	S. A. m^2/g	V_m cm^3/g	S. A. m^2/g	V_m cm^3/g
C. Cherry	766	0.29	692	0.28
Oleaster	662	0.25	622	0.25

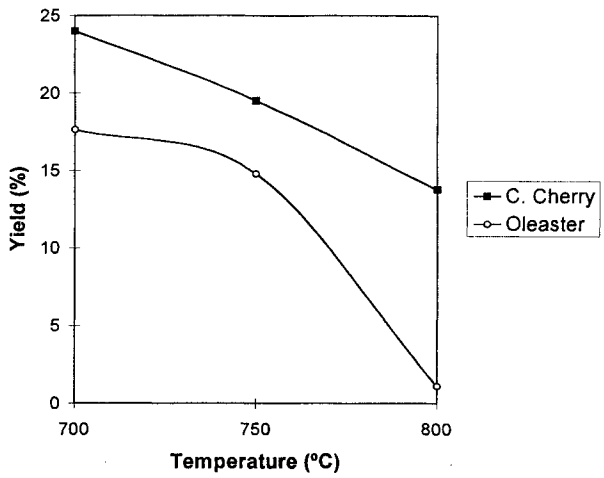

Figure 1. Solid yield of activated fruit stones at 4 hours.

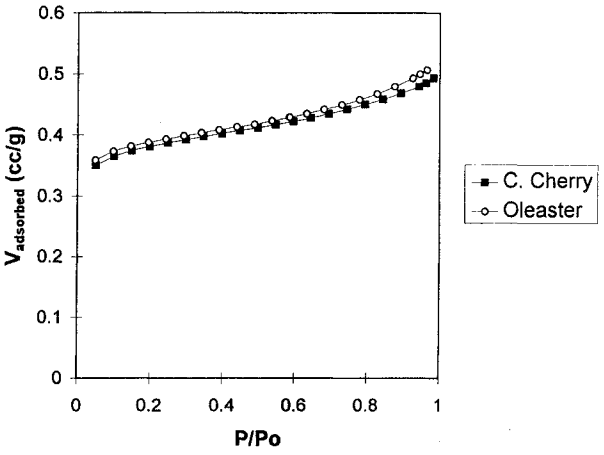

Figure 2. N_2 Adsorption Isotherms

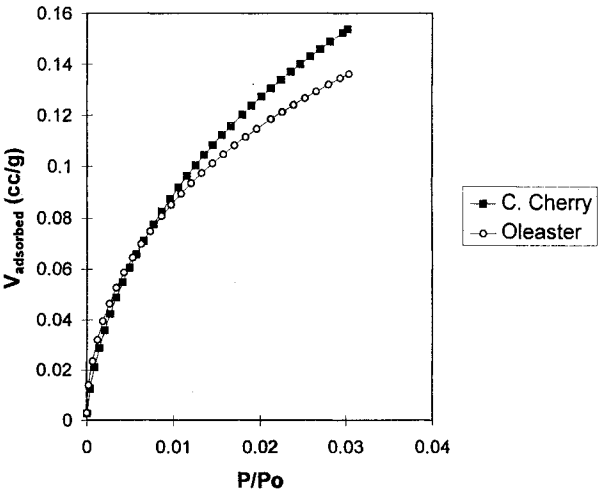

Figure 3. CO_2 Adsorption Isotherms