Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil

Vol. 21, No. 04, pp. 585 - 591, October - December 2004

USE OF GRAPE MUST AS A BINDER TO OBTAIN ACTIVATED CARBON BRIQUETTES

A. C. Deiana*, D. L. Granados, L. M. Petkovic, M. F. Sardella and H. S. Silva

Instituto de Ingeniería Química - Facultad de Ingeniería,
Universidad Nacional de San Juan,
Av. Libertador 1109, Oeste, 5400, San Juan - Argentina
Phone: (54) (264) 421-1700 Ext: 308/228,
Fax (54) (264) 420-0289
Email: cdeiana@unsj.edu.ar

(Received: January 15, 2002 ; Accepted: May 12, 2004)

Abstract - The results of studies on briquetting activated-carbon-based adsorbent materials, prepared from raw materials from the region of Cuyo, Argentina, are reported in this article. Several steps were carried out to obtain activated-carbon briquettes from *Eucalyptus camaldulensis Dehn* wood. These steps included carbonization of wood to obtain char; blending of char and a novel binder, i.e., grape must; formation of cylinder-like briquettes by pressure; and activation of the resulting material. The material was activated with steam under different temperatures, activation times, and activating agent flow rates. Impact resistance index, axial compressive strength, tensile strength by diametrical compression, BET area, and pore volume were measured for product characterization. Satisfactory surface areas and mechanical strengths were found in the final products.

Keywords: Activated carbon briquettes, mechanical properties, surface properties.

INTRODUCTION

Activated carbons are unique and versatile adsorbents because of their extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity. They are used in a variety of fields, such as food and chemical industries, wastewater treatment, solvent recovery, air pollution control, and hydrometallurgy (Bansal et al., 1988). For some of these uses, a high mechanical strength and good adsorption characteristics are required. Briquetting processes, which involve mixing and pressing of char particles with adhesive materials, usually increase the mechanical strength of the final products. Briquette quality is generally determined by the type of raw material and binder utilized and the precise way in which the operations related to briquetting and activation are carried out.

Different methods to obtain briquettes from activated carbons can be found in the literature (MacDowall, 1989; Yan et al., 1996; Yamada and Tsumuki, 1997). Briquetting processes applied to coals were reviewed by Rhys-Jones (1963) and Schinzel (1981). A theoretical picture that represents both the principal facets of char briquetting and conversion of raw briquettes into formed coke was presented by Taylor (1988). Clarke and Marsh (1989) assessed the factors that generally affect the properties of coal briquettes.

The work presented here is part of a more extensive study conducted to develop appropriate processes to prepare activated carbon from regional lignocellulosic materials, e.g., wood, grape stalks, and fruit stones (Deiana et al., 1998). The results from the studies of activated carbon briquettes, prepared from eucalyptus wood char and molded with concentrated grape must, are reported here.

---

*To whom correspondence should be addressed

Tests on the use of more traditional binders, i.e., petroleum-derived commercial materials, were also carried out for the purpose of comparison.

Concentrated grape must was thought to be an interesting and novel binder for the preparation of briquettes. This hypothesis was formulated based on previous studies (Schinzel, 1981) on the use of binders that have a high concentration of carbohydrates. Concentrated grape must is obtained by partial dehydration of grape must. Although its composition is complex, its main components are glucose and fructose (around 860 g sugar/L). Small amounts of organic acids (tartaric, malic and citric), phenolic compounds, metals, and vitamins are also present (Cenzano and Cenzano, 1994).

EXPERIMENTAL

Materials

The lignocellulosic material used for preparing char was wood from *Eucalyptus camaldulensis Dehn* trees, a common variety in the region of Cuyo, Argentina. The proximate and ultimate analyses are shown in Table 1.

Concentrated grape must provided by Arenas Winery (Caucete-San Juan) and petroleum-derived commercial materials, i.e., Asfalt Paper® asphaltic paint and Inertol Tech Sika asphaltic emulsion, were utilized as binder materials. The analyses are given in Tables 2 and 3.

Table 1: Analysis of *Eucalyptus camaldulensis Dehn* wood

Proximate analysis (% wt)	
Ash	1.00
Moisture	10.51
Volatile matter	69.14
Fixed carbon	19.35
Ultimate analysis (% wt)	
C	45.34
H	6.77
N	0.20
O	47.69

Table 2: Analysis of concentrated grape must

Refractive index (293 K)	1.4654
Density (293 K)	1.345 kg/L
Sugar (fructose + glucose)	860 g/L
Sucrose	below detection limit
Total acidity	0.4 meq/kg
Total cations	0.6 meq/kg
Chlorides	0.3 meq/kg
Sulfates	0.3 meq/kg

Table 3: Analysis of the petroleum-derived materials

ASTM standard test	Asphaltic paint	Asphaltic emulsion
Conradson carbon (wt %) D 189-88	39.03	35.48
Water content (wt %) D 4007-81/87	below detection	49
Quinoline insolubles (wt %) D 2318-86	below detection	6.24

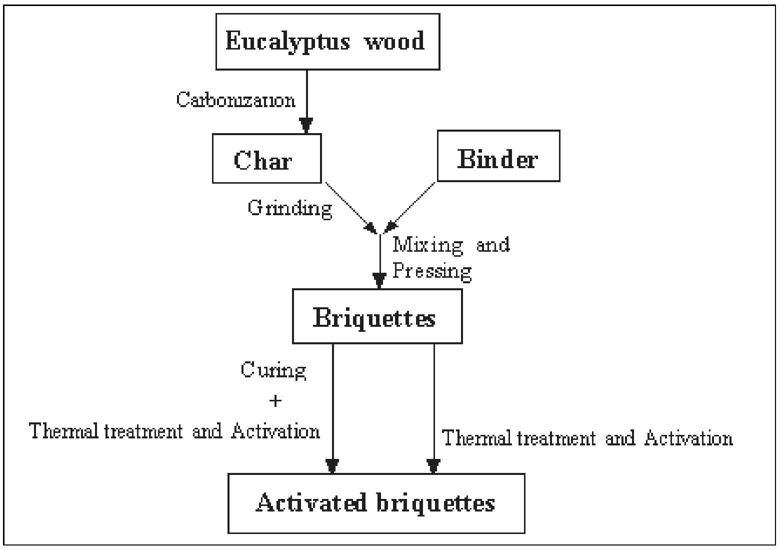

Figure 1: Diagram of the process for preparing activated carbon briquettes

Methods

The methods selected to prepare activated carbon briquettes involved several steps (see Fig. 1). These steps, which were selected after analysis of several alternatives described in the literature (e.g., Rubio et al., 1999), are summarized below.

a) Char Preparation

Batches of 2000 grams of eucalyptus wood were carbonized in a retort-like stainless steel reactor. This carbonization consisted of heating up the sample from room temperature to 773 K at a rate of 1.4 K/min and maintaining the final temperature for 2 hours. A K-type thermocouple and a digital temperature controller were used to set and control the retort temperature. The product obtained, i.e., char, was crushed and sieved. Two fractions were collected and stored: the one that passed through the 80 mesh ASTM (0.18 mm) sieve and the other that was retained between the 80 and 20 mesh ASTM (0.18 to 0.85 mm) sieves.

b) Conformation of Briquettes

The briquettes were made by mixing in a mortar measured amounts of char and binder and pressing 1 g of the resulting mixture into a 10 mm I.D. stainless steel mold held in a homemade hydraulic press. Briquette length was around 14 mm. Binder:char ratios were 1:3 and 1:4. Pressures applied were 140 and 280 MPa for 6 min. The resulting made briquettes were measured, weighed, and stored.

c) Thermal Treatment and Activation

The briquettes were submitted to a thermal treatment and activation in a 300 mm long stainless steel reactor with an internal diameter of 30 mm heated by an electric oven. A K-type thermocouple and a digital temperature controller were used to set and control the reactor temperature. The thermal treatment consisted in heating up the briquettes at either 5 or 15 K/min from room temperature to the selected activation temperature in flowing nitrogen gas. The activation step was performed using flowing steam as the activating agent at either 1123 or 1153 K. Tests in 1 and 1.7 g of steam/(g char h) and activation times of 105 and 150 minutes were conducted. Once the activation step had taken place, the reactor was cooled down to room temperature in flowing nitrogen gas. The activated briquettes were measured, weighed, and stored.

d) Curing

Some samples were also submitted to a curing process prior to the thermal treatment and activation. This curing process consisted in a thermal treatment at 473 K in 400 mL/min flowing oxygen gas for 2 h.

e) Characterization of Activated Carbon Briquettes

Impact resistance and compressive strength were determined as a measure of the briquette’s mechanical properties. BET areas and pore volumes were measured to evaluate the surface properties.

Impact resistance was determined by means of the so-called impact resistance index (IRI) (Richards, 1990), which considers the number of drops and the number of pieces into which each briquette breaks when it is repeatedly dropped from a stationary point at 2 m height onto a concrete floor until it fractures. Axial compressive strength and tensile strength by diametrical compression were determined in rigid-frame controlled load equipment at a load rate of approximately 1 Kgf $(cm^2\ s)^{-1}$.

The BET area and pore volume were determined in a NOVA 2200 apparatus by means of N_2 adsorption measurements at 77 K.

Experimental Design

The experimental design was developed adopting a “base experiment” as the starting point and generating the remaining experiments by changing the experimental conditions.

The base experiment included the processing of a mixture of eucalyptus wood char and concentrated grape must under the following conditions: a particle size below 0.18 mm, a binder:char ratio of 1:4 wt., a briquetting pressure of 140 MPa, thermal treatment at a heating rate of 5 K/min up to 1123 K in 1.7 g flowing steam/(g char h), an activation time of 105 min, and without curing.

Samples consisting of 15 briquettes were submitted to the thermal treatment and activation, which was duplicated for each set of experimental conditions. BET areas and pore volumes were measured on two briquettes randomly chosen from each sample and mechanical strength indexes, on three briquettes from each sample. It is worth mentioning that data reproducibility was within 10 % for all experiments, and overall averages are reported herein.

RESULTS AND DISCUSSION

A summary of the experimental conditions is presented in Table 4. Each row shows the conditions for a particular experiment. Test 1 corresponds to the base experiment. In tests 2 to 9, one condition was changed each time, but grape must was kept as the binder agent. For test 10, three things were different: conformation pressure and binder:char ratio were changed and a curing step was included. Tests 11 and 12 included asphaltic paint and tests 13 and 14, asphaltic emulsion. The last two tests were blank experiments. BET areas and pore volumes were the only tests carried out on the blanks. Mechanical strength indexes were not measured because the eucalyptus char turned into powder easily and the structure of the grape must was fragile after activation.

Table 4: Experimental conditions

Test	Conformation				Thermal Treatment	Curing	Activation		
	Char particle size (mm)	Binder*	Binder: char ratio	Pressure (MPa)	Heating rate (K/min)		Temp. (K)	Time (min)	Water vapor rate (g/g h)
1	< 0.18	Mu	1:4	140	5	No	1123	105	1.7
2	0.18-0.85	Mu	1:4	140	5	No	1123	105	1.7
3	< 0.18	Mu	1:3	140	5	No	1123	105	1.7
4	< 0.18	Mu	1:4	280	5	No	1123	105	1.7
5	< 0.18	Mu	1:4	140	15	No	1123	105	1.7
6	< 0.18	Mu	1:4	140	5	Yes	1123	105	1.7
7	< 0.18	Mu	1:4	140	5	No	1153	105	1.7
8	< 0.18	Mu	1:4	140	5	No	1123	150	1.7
9	< 0.18	Mu	1:4	140	5	No	1123	105	1.0
10	< 0.18	Mu	1:3	280	5	Yes	1123	105	1.7
11	< 0.18	Pa	1:4	140	5	No	1123	105	1.7
12	< 0.18	Pa	1:4	140	5	Yes	1123	105	1.7
13	< 0.18	Em	1:3	140	5	No	1123	105	1.7
14	< 0.18	Em	1:3	140	5	Yes	1123	105	1.7
15	0.84 - 3.36	-	No binder	-	5	No	1123	105	1.7
16	-	Mu	-	-	5	No	1123	105	1.7

*Mu: concentrated grape must; Pa: asphaltic paint; Em: asphaltic emulsion

Table 5 shows the surface and mechanical properties of the briquettes obtained under the corresponding experimental conditions given in Table 4. BET areas and pore volumes are presented in columns 2 and 3. Averages (M) and standard deviations (SD) for impact resistance indexes (IRI), axial compressive strengths (ACS), and tensile strengths by diametrical compression (DCS) are detailed in columns 4 to 9.

From these results it is apparent that the different variables had an effect on the mechanical and surface properties of the final briquette. The BET area for granular activated carbon was 825 m^2/g (see blank experiment reported as test 15 in Table 4) and for the rest (i.e., tests 1 to 14) was within the range of 576-849 m^2/g. Thus, it is apparent that a decrease in surface area occurred in an important number of samples when a briquetting process was applied. However, under some treatment conditions such as a binder:char ratio of 1:3 (test 3) or when the curing step was included (test 6), surface areas above 800 m^2/g were obtained.

Table 5: Surface and mechanical properties of activated carbon briquettes

Test	Surface properties		Mechanical properties *					
	BET area m^2/g	Pore volume cm^3/g	IRI		ACS kg/cm^2		DCS kg/cm^2	
			M	SD	M	SD	M	SD
1	689	0.322	50	1	8.59	0.19	1.25	0.05
2	820	0.382	37	1	6.58	0.27	0.93	0.03
3	811	0.379	150	3	12.33	0.54	2.78	0.07
4	699	0.326	80	2	10.07	0.41	1.84	0.04
5	593	0.278	25	1	6.44	0.20	0.99	0.04
6	849	0.396	67	1	6.73	0.16	1.01	0.01
7	746	0.350	N/A**	-	N/A	-	N/A	-
8	806	0.375	75	1	7.62	0.20	1.31	0.05
9	680	0.320	25	1	5.78	0.03	0.71	0.01
10	611	0.288	350	4	25.25	1.27	6.59	0.04
11	720	0.337	25	1	2.19	0.09	0.38	0.01
12	781	0.364	N/A	-	N/A	-	N/A	-
13	576	0.268	37	1	2.14	0.04	0.50	0.01
14	584	0.274	70	1	6.78	0.33	1.50	0.01
15	825	0.388	-	-	-	-	-	-
16	854	0.403	-	-	-	-	-	-

*IRI: impact resistance index; ACS: axial compressive strength;
DCS: tensile strength by diametrical compression; M: average
SD: standard deviation

**N/A: not analyzed, see text

A blank test performed on pure concentrated grape must showed that this type of material can develop a large surface area and pore volume (see test 16 in Table 5). This might explain the increase in surface area as the grape must:char ratio increased (see tests 1 and 3). This behavior has also been seen for other carbonaceous material such as grape stalks briquetted with grape must (Deiana, et al., 2002).

In comparing tests 1 and 2, a larger surface area was found for the latter, in which larger char particles were used. It might be hypothesized that a larger void fraction favored interparticle, instead of intraparticle, must accumulation, and consequently development of a larger surface area was fostered by the must itself.

In the process of briquetting with concentrated grape must, the larger the amount of binder, the higher the briquetting pressure, and the longer the activation time, the better the IRI values obtained (compare test 1 with 3, 4, and 8). In addition, the introduction of a curing step in the process also increased the IRI result (test 6). Larger char particles, higher heating rates, and lower steam flow rates affected the IRIs negatively (tests 2, 5, and 9). From Table 5 it is also apparent that the ACS and DCS indexes varied in the same way as the IRIs. IRI values of at least 50 were considered satisfactory after applying a criterion reported by Rubio and coworkers (1999), who found IRI indexes above 50 for briquettes obtained from a low-quality coal blended with at least 15% commercial binder pitch. Note that test 1, i.e., the base experiment, gave this value. Even though most variables influenced the product properties, only a larger amount of binder and a higher conformation pressure improved the mechanical properties markedly. It is worth mentioning that, because some samples appeared deteriorated after activation, their mechanical properties could not be measured.

The highest briquetting pressure, the highest binder:char ratio and a curing step were adopted for test 10 in order to evaluate the combined effect of these variables, which were the ones that improved the surface and mechanical properties considerably. Although the mechanical properties of the activated briquettes were notably increased as expected, one of the lowest values for the BET area is seen. This behavior might be understood as a micro-intrusion of liquid binder into cracks and voids of the char structure due to the higher pressure, according to the compaction and cementing model proposed by Taylor (1988). As the sample is thermally treated and activated, the binder is cemented and might block some of the surface, which would no longer be available to the activating agent.

Because petroleum-derived binders are widely used in briquetting processes (Rhys-Jones, 1963), briquettes obtained with concentrated grape must (tests 1 and 3) were compared to those prepared with asphaltic paint (tests 11 and 12) and asphaltic emulsion (tests 13 and 14). For the two experiments with asphaltic paint, the briquettes had acceptable BET areas and the inclusion of the curing step in the process improved this property. The mechanical properties of these briquettes were not satisfactory. Tests 13 and 14 were carried out with a binder:char ratio of 1:3 because the blend with the lower ratio did not compact adequately under pressure. The briquettes obtained had the lowest BET areas, while the mechanical properties improved slightly in respect to those displayed by briquettes prepared with asphaltic paint.

It can be concluded that concentrated grape must showed better results than the petroleum-derived binders studied here, when activated-carbon briquettes were prepared from Eucalyptus wood. The high content of carbohydrates in the concentrated grape must is likely the cause of its adhesive properties. Furthermore, an interesting feature is that, in the range of ratios studied, higher grape must contents resulted in larger surface areas of the briquetted final product.

CONCLUSIONS

The results of studies on the conformation of activated-carbon-based adsorbent materials, prepared from *Eucalyptus camaldulensis Dehn* wood and concentrated grape must, have been presented. These results indicate that concentrated grape must can be used as binder to prepare activated carbon briquettes because the surface properties and mechanical strength obtained were satisfactory, compared with other briquetting studies mentioned in previous work.

The surface properties, such as BET area, were improved by an increase in temperature and time during activation, a lower heating rate during thermal treatment, the inclusion of curing, a larger amount of binder, and a larger particle size. Better mechanical properties, determined by impact resistance index, axial compressive strength and tensile strength by diametrical compression, were found in products obtained with higher binder:char ratios and at higher conformation pressures.

The advantage of using grape must is that no important decrease in surface area is found when comparing briquetted with nonbriquetted products. For comparison purposes some experiments were also carried out with petroleum-derived commercial products. The products obtained in these cases did not have good mechanical properties.

As a final conclusion from these studies, the best strategy for producing activated carbon briquettes from Eucalyptus camaldulensis Dehn wood and grape must as binder would include pressing a blend of char and grape must at 140 MPa and a must:char ratio of 1:3, curing it in oxygen at 473 K, heating it up to 1123 K at 5 K/min in flowing nitrogen, and steam activation at 1123 K for 150 minutes at a rate of 1.7 g/(g h).

ACKNOWLEDGMENTS

The UNSJ grant received for research is acknowledged. The authors are also grateful to Instituto de Investigaciones Mineras – UNSJ – for lending their NOVA equipment, to Instituto de Materiales y Suelos – UNSJ – for running the strength tests, and Arenas Winery (Caucete-San Juan) for providing the concentrated grape must.

REFERENCES

Bansal, R.C., Donnet, J., and Stoeckli, F., Active Carbon. Marcel Dekker, Inc. New York, (1988).

Cenzano, J.M. and Cenzano, A.M., Tecnología y legislación del vino y bebidas derivadas. AMV Ediciones - Mundi Prensa, Madrid (1994).

Clarke, D.E., and Marsh, H., Factors Influencing Properties of Coal Briquettes. Fuel, 68, p. 1031 (1989).

Deiana, A.C., Petkovic, L.M., and Noriega, S.E., Carbón activado a partir de materias primas regionales. Información Tecnológica - Chile, 9 (5), p. 89 (1998).

Deiana, C., Petkovic, L., Silva, H., Aguilar, E., Sardella, F., and Venturini, R., Residuos y subproductos para la obtención de briquetas de Carbón Activado, VI Curso-Taller Iberoamericano de Adsorbentes y Catalizadores para la Protección Ambiental. Redes Temáticas VC y VC – CYTED, p. 9, Caracas, Venezuela (2002).

MacDowall, J., Method of Producing Granular Activated Carbon. US Patent 5,162,286 (1992).

Rhys Jones, D.C., Briquetting. In: Lowry HH Editor, Chemistry of Coal Utilization, 2nd supplementary volume. John Wiley & Son, New York (1963).

Richards, S. R., Physical Testing of Fuel Briquettes. Fuel. Proc. Technol., 25, p. 89 (1990).

Rubio, B., Izquierdo, M. T., and Segura, E., Effect of Binder Addition on the Mechanical and Physicochemical Properties of Low Rank Coal Char Briquettes. Carbon, 37, p. 1833 (1999).

Schinzel, W., Briquetting. In: Lowry HH Editor, Chemistry of Coal Utilization, supplementary volume. John Wiley & Son, New York (1981).

Taylor, J.W., Compaction and Cementing of Char Particles with a Tar-derived Binder. Fuel, 67, 1945 (1988).

Yamada, T. and Tsumuki, K., Adsorbent Body Including Activated Carbon and Inorganic Binder for Bonding Together Activated Carbon Grains, and Method of Producing the Adsorbent Body. US Patent 5,685,986 (1997).

Yan, Z.Q., McCue, J., and Tolles, E., Preparation of High Activity, High Density Activated Carbon with Activatable Binder. US Patent 5,538,932 (1996).