

PRODUCTION OF ADSORBENT CARBONS
FROM ILLINOIS COAL AND SCRAP TIRE FOR NATURAL GAS STORAGE

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Adsorbed natural gas storage is being considered as an on-board storage technology for natural gas vehicles because it costs less to build and to refuel than does compressed natural gas storage.¹ Carbon-based adsorbents have been found to have the most favorable gas storage density compared to other adsorbents.^{2,3} The objective of this study is to develop a technology for producing adsorbent carbons from Illinois coal and scrap tire and evaluate the potential application of these materials for use in low pressure natural gas vehicles.

EXPERIMENTAL

The sample coal, IBC-106 (-8 mesh), was provided by the Illinois Basin Coal Sample Program.⁴ Shredded tire (8 mesh) was obtained from three vendors: Atlas (Los Angeles, CA), National Tire Services (Chicago, IL) and Baker Rubber (South Bend, IN). A tubular reactor system was used for carbon production experiments. In a typical run, 1-3 gm of coal (-20+100 mesh) or tire sample was used. A three-step process was applied to produce adsorbent carbon from Illinois coal: coal oxidation in air at 225°C for 0.5-9 h, devolatilization of oxidized coal in N₂ at 400-500°C for 1 h and char activation in 50% H₂O in N₂ at 825-850°C for 0.5-3 h.⁵ The production of carbon from tire included only two steps: devolatilization of tire in N₂ at 600°C for 1 h and char activation in 50% H₂O in N₂ at 850°C for 0.5-3 h. Single-point BET surface areas of the carbons were determined from N₂ (77 K) adsorption data obtained with a Monosorb flow apparatus (Quantachrome Corp.). Micropore volumes were calculated using t-plot based on the N₂ adsorption isotherm (p/p_0 0.0011-1) measured with a volumetric adsorption apparatus (Micromeritics). Screening tests were made with a pressurized TGA (Spectrum Research and Engineering) to measure the relative CH₄ adsorption capacities (g/g) of the carbon products at pressures up to 500 psig. A 4.6 cm³ pressurized vessel was constructed to measure the volume of CH₄ adsorbed per volume of the carbon bed (V/V, cm³/cm³).

RESULTS AND DISCUSSION

Table 1 lists a number of carbons produced from Illinois coal and scrap tire under various conditions. A commercial activated carbon, BPL (Calgon Carbon Co.), was available as the reference adsorbent. The V/V CH₄ adsorption capacities of carbons from Illinois coal were measured and ranged from 51 to 73 cm³/cm³. These values are comparable to that of BPL. The V/V adsorption capacities of carbons from scrap tire were found to be lower than that of coal carbon due to their low surface areas. Figure 1 shows the CH₄ adsorption isotherms (0 to 500 psig) for BPL and three selected carbon products. It has been recognized that pre-oxidation is a necessary step in production of activated carbon

from a caking coal and that devolatilization at intermediate temperatures is favored to efficiently create new cross links within coal's network, hence to preserve its microporosity.⁵ Carbon #1 produced without the pre-oxidation step showed lower surface area and adsorption capacity (Table 1), as caking destroys microporosity by structural realignment. Figure 2 shows the effect of devolatilization temperature on surface area and adsorption capacity of two carbon sets produced with devolatilization at 400 and 500°C, respectively. Both carbon sets had the same oxidation and activation conditions. It seems that a lower devolatilization temperature leads to slightly higher surface area and CH₄ adsorption capacity. It is noticed as well that during char activation the maximum CH₄ adsorption capacities correspond well with the maximum surface area. Based on an earlier study,⁵ the effect of coal oxidation on coal's caking behavior was investigated. It was found that the coal's agglomeration or caking behavior is a function of its oxidation time and devolatilization temperature. Figure 3 shows that a coal oxidized for a certain time period has different caking behaviors at different heat treatment temperatures (HTT), e.g., the coal oxidized for 3 h is a noncaking coal at 700°C HTT, but is caking at 850°C. It is also interesting to note that the coal oxidized for only 0.5 h and then devolatilized at 400°C for 1 h had no agglomeration during 850°C steam activation. In other words, IBC-106's caking can be eliminated by either 0.5 h oxidation at 225°C followed by 400°C devolatilization, or 4-5 h oxidation at 225°C followed by 850°C devolatilization. The effect of coal oxidation on carbon surface area and CH₄ adsorption was investigated further by extending the oxidation time to 9 h. Figure 4 illustrates a correlation between surface area of Carbons #1-6 and time of coal oxidation at 225°C. The optimum oxidation time appears to be 4 h. Again, CH₄ adsorption capacities correspond well with surface area as the oxidation time changes. Carbon #7 with the highest V/V CH₄ adsorption capacity produced in this study was activated at 825°C. Table 1 shows that it also has the highest surface area and micropore volume.

CONCLUSIONS AND RECOMMENDATION

Carbon adsorbents were produced from Illinois coal and scrap tire for natural gas storage. Some carbons produced from coal showed comparable CH₄ adsorption capacities to that of BPL. These initial results are encouraging when considering the possibility of pelletizing the treated samples. Carbon densification is expected to increase the V/V CH₄ adsorption by 20 to 40%.⁶ It was concluded that surface area and micropore volume are important factors for natural gas storage. Controlling the pre-oxidation time and devolatilization temperature are critical in eliminating the coal's caking behavior.

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Table 1. Properties of activated carbons produced from Illinois coal and scrap tire

Carbon # *	Production conditions†	Coal or tire weight loss (daf), wt%	Carbon surface area (dry), m ² /g	CH ₄ adsorption at 500 psig g/g	Bulk density g/cm ³	CH ₄ adsorption at 500 psig cm ³ /cm ³ ‡	Micropore volume cm ³ /g
1	n400(1)850(1.5)	75.8	897	0.0424	0.33	50.6	-
2	225(2)400(1)850(2)	78.3	970	0.0497	0.38	62.7	-
3	225(3)400(1)850(2)	77.7	978	0.0479	0.39	57.2	-
4	225(4)400(1)850(2)	76.9	1037	0.0541	0.44	67.3	0.374
5	225(6)400(1)850(2)	77.3	932	0.0474	0.45	62.8	-
6	225(9)400(1)850(2)	79.9	961	0.0478	0.43	64.4	-
7	225(3)400(1)825(3)	76.9	1056	0.0509	0.44	73.3	0.408
BPL	Commercial carbon	-	883	0.0505	0.46	67.3	0.429
A	n600(1)850(1.5)	77.0	330	0.0310	0.24	43.1	-
B	n600(1)850(2)	80.0	510	0.0400	0.21	43.0	-
C	n600(1)850(2.5)	82.0	570	0.0520	0.20	43.5	0.235
D	n600(1)850(3)	85.0	737	0.0540	0.15	43.6	0.254

* #1-7: Carbons from coal; A-D: Carbons from tire; ‡ Corrected to the standard conditions (1 atm, 25°C)

† Oxidation °C (h) devolatilization °C (h) activation °C (h); "n": non-oxidation

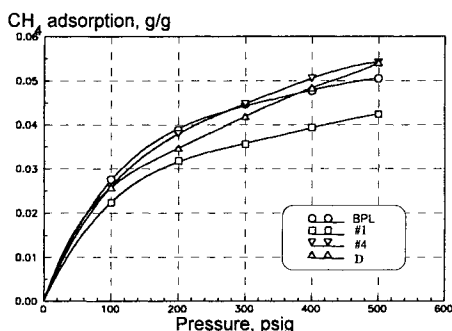


Figure 1. Methane adsorption isotherms for BPL and selected carbons from Illinois coal and scrap tire (Carbons #1, #4 and D)

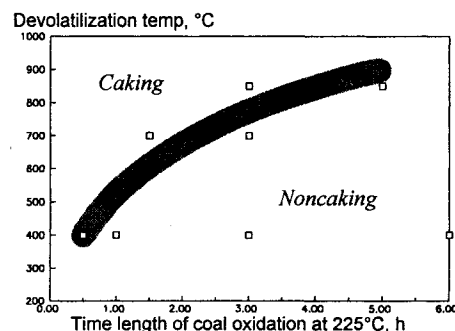


Figure 3. Effect of coal oxidation time and devolatilization temperature on caking property of IBC-106 coal

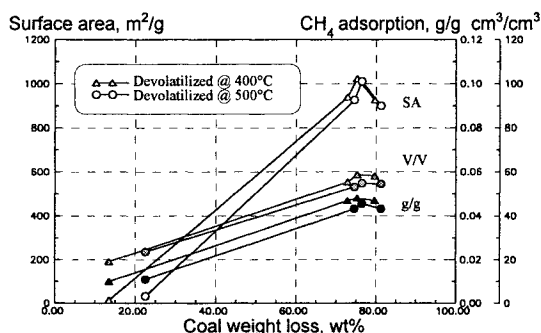


Figure 2. Effect of devolatilization temperature on surface area and methane adsorption of coal carbons

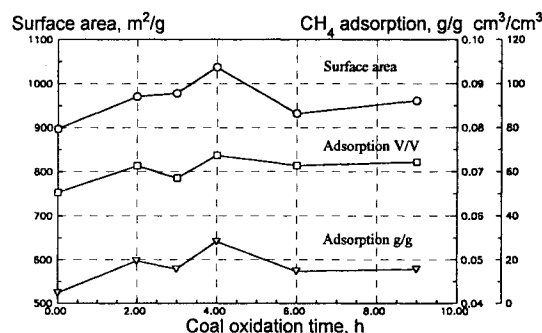


Figure 4. Effect of pre-oxidation time on surface area and methane adsorption of coal carbons (#1-6)