

## ADSORBED NATURAL GAS STORAGE WITH ACTIVATED CARBON

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### INTRODUCTION

Despite technical advances to reduce air pollution emissions, motor vehicles still account for 30 to 70% emissions of all urban air pollutants.<sup>1</sup> The Clean Air Act Amendments of 1990 require 100 cities in the United States to reduce the amount of their smog within 5 to 15 years. Hence, auto emissions, the major cause of smog, must be reduced 30 to 60% by 1998.<sup>2</sup> Some states like California have set stringent laws to clean up severe air pollution. Beginning in 1997, 25% of all cars sold in California must qualify as low emissions vehicles (LEVs). By 2005, 75% of the cars sold in California must be LEVs.<sup>3</sup> This situation has spurred interest in research and development of alternative fuels.

#### Alternative fuels

*Electricity:* Although electric vehicles (EV) do not produce tailpipe emissions, pollution is produced at power plants that generate electricity to charge the vehicles' batteries. If 50% of the electricity is produced from coal, 20% from natural gas, and the remaining 30% from nuclear or hydro power, then EVs will produce 99% less hydrocarbons, 99% less CO and 60% less NO<sub>x</sub>, compared with conventional gasoline fueled vehicles. However, SO<sub>x</sub> and particulate emissions could increase by a factor of five.<sup>4</sup> Other pollutants can also result from the use of batteries in vehicles. Water quality and solid waste disposal could be additional environmental problems. EV can be used to reduce local air pollution in specific markets such as vehicles for public services or urban use where speed and range are not limitations. EVs are also recommended for those regions where fossil fuels are not the primary fuel used to produce electricity.

*Methanol, liquefied petroleum gas and hydrogen:* Vehicles operating with M85 (85% methanol/15% gasoline) or M100 (pure methanol) have similar CO and NO<sub>x</sub> emissions to conventional gasoline fueled vehicles.<sup>5</sup> The largest emission benefit from methanol (M100) fueled vehicles is their reduced ozone-producing potential (Table 1).<sup>6</sup> Emissions from liquefied petroleum gas (LPG) fueled vehicles are comparable to gasoline fueled vehicles except for ozone formation. Hydrogen fueled vehicles theoretically produce no pollutants except NO<sub>x</sub>, which can be further reduced by lowering combustion temperature.<sup>7</sup> However, it is important to consider that hydrogen is made by coal gasification or water electrolysis, and these processes generate air pollutants directly or indirectly.

*Natural gas:* Natural gas can be used as a fuel for vehicles and offers many environmental benefits. A natural gas vehicle (NGV) uses a conventional spark ignition engine with only minor modifications. Natural gas burns more completely and produces less air pollutants than gasoline. There are three technologies for on-board natural gas storage: liquefied natural gas (LNG), compressed natural gas (CNG) and adsorbed natural gas (ANG). CNG has been commercialized worldwide. ANG uses adsorbents and operates at a much lower storage pressure (500 psig) than CNG (3,000 psig), thus has relatively lower capital and maintenance costs.

There are about 40,000 NGVs in the US and about one million worldwide.<sup>5</sup> Emission data (Table 2) show that NGVs, compared with conventional vehicles, have significantly lower CO emissions due to better mixing of the gaseous fuel, lean fuel to air ratio and lack of fuel enrichment to start.<sup>5,6</sup> Carcinogenic pollutant (e.g., benzene and 1,3-butadiene) emissions are effectively eliminated.<sup>6</sup> Because the hydrocarbon constituent in NGV exhaust is dominantly methane, which has insignificant photochemical reactivity, emissions from NGV are expected to contribute the least to ozone formation (Table 1).<sup>6,8</sup>

Natural gas, as an automobile fuel, has emerged as a leading alternative to conventional fuels. In the short term, depot-based commercial fleets (e.g., buses and taxis) will be the first beneficiaries of NGV because of limited range and lack of fuel-service infrastructure.

Improvement in the technologies for adsorbed natural gas (ANG) storage will offer significant opportunities for reducing capital and operating costs.<sup>7,9,10</sup>

#### **Adsorbed natural gas**

The key ingredient for successful commercialization of ANG is the adsorbent. The natural gas storage capacity of an adsorbent is usually evaluated in terms of its volumetric methane storage capacity ( $V_m/V_s$ ), where  $V_m$  is the volume of stored methane at standard temperature and pressure, and  $V_s$  is the volume of the storage container. Commercial development of ANG requires adsorbents with low costs (< \$2.00/lb) and high gas storage capacities (> 150  $V_m/V_s$ ).<sup>9</sup> Activated carbons have the most favorable gas storage density.<sup>7,11</sup> This paper describes some methods for producing adsorbent carbon from an Illinois bituminous coal and scrap tires. The potential application of these low cost adsorbents in low pressure ANG vehicles is also evaluated.

#### **Coal and scrap tire as parent materials**

Because combustion of Illinois coals is increasingly restricted due to their higher sulfur contents, they are being studied as potential precursors for commercial activated carbon production.<sup>14</sup> The US has large stockpiles of waste tires, growing at a rate of approximately 280 million tires per year.<sup>12</sup> Currently over 80% are landfilled, constituting a loss of significant resources and creating environmental problems. If some of these tires are converted into activated carbons, millions of tires would be diverted from the nation's landfills. Carbons from these sources may meet the cost and adsorption capacity requirements for ANG adsorbents.

### **EXPERIMENTAL**

#### **Sample preparation**

Adsorbent carbons were produced from an Illinois coal, IBC-106 (Free Swelling Index: 4.5<sup>13</sup>). The raw coal, provided by the Illinois Basin Coal Sample Program<sup>13</sup>, was ground and sieved from -8 mesh to -20+100 mesh and to -100 mesh. The -20+100 mesh portion was used as feedstock for physical activation and the -100 mesh portion was used for chemical activation. Shredded automotive tires used in this study were obtained from three vendors: Atlas (Los Angeles, CA), National Tire Services (Chicago, IL), and Baker Rubber (South Bend, IN). Their nominal particle diameters were 3, 1 and 0.4 mm, respectively. Results from proximate and ultimate analyses of the IBC-106 coal and a typical tire sample are listed in Table 3.

#### **Adsorbent production**

Carbon adsorbent production by both physical and chemical activation techniques was carried out in a bench scale tubular reactor with a horizontal tube furnace (Lindberg, Type 54232). For physical activation, a three-step process was applied: coal oxidation in air at 225°C for 2 or 4 h; devolatilization of oxidized coal in nitrogen at 400°C for 1 h; and steam activation of the resulting char in 50% steam in nitrogen at 800-850°C for 0.5-5.5 h. The air oxidation step was performed in an auto-programmable ashing furnace (Fisher Scientific, Model 495A) with unlimited air supply. About 12 g of sample was used during oxidation and devolatilization while 1 to 2 g of sample was used during steam activation. The gas flow rate during devolatilization and steam activation was 1 L/min. For chemical activation, about 2 g of the coal (-100 mesh) was mixed with granular KOH (coal/KOH mass ratio 1:1) and ground into a gel-like solid using a mortar and pestle. This mixture was then activated at 800°C in 100% nitrogen for 0.5 and 1.25 h. After chemical activation, the sample was immediately submerged in deionized water, filtered, crushed, and then washed again in deionized water to remove KOH derivatives which may have been on the surface of the particles.

Physical activation of the tires was carried out by a two-step process: devolatilization of about 5 g sample tire in nitrogen at 600°C for 45 min; and then steam activation of the resulting char in 50% steam in nitrogen at 850-900°C for 0.5-3 h. Chemical activation of the tires with KOH was performed in a similar manner to that of coal, except tires were chemically activated at 900°C for 0.5 to 1.5 h.

#### **Adsorbent characterization**

BET surface areas and t-plot micropore volumes (micropore volume is defined as the volume of pores < 17 Å) were calculated based on the nitrogen adsorption isotherms (relative pressure  $P/P_0$ : 0.001-1) measured with a volumetric adsorption apparatus (Micromeritics ASAP2400). Methane adsorption capacity, on a mass basis (g/g), at pressures up to 500 psig was determined with a pressurized thermogravimetric analyzer (Spectrum Research and Engineering Model TL-TGA

1900/600 PTGA). Buoyancy correction was performed for coal-derived carbon when calculating the methane adsorption capacity (g/g). The true density of activated carbons produced from Illinois coal was taken as 2.2 g/cm<sup>3</sup>.<sup>14</sup> Vm/Vs values (cm<sup>3</sup>/cm<sup>3</sup>) were determined from the experimental data obtained with a custom built 4.92 cm<sup>3</sup> pressurized vessel at 500 psig.

#### **Pelletization**

Select tire-derived carbons were made into pellets using a 1/4 in. (6.35 mm) diameter cylindrical die and manual press. Samples of 100-200 mg were prepared by mixing the carbon with a liquid 1-step phenolic resin (Durez 7347A, Occidental Chemical) binder. The resin was used at a mass ratio of 5-20%. The mixture was then placed in the die and compressed. The die and pellet were subsequently heated at 165°C in an oven (Precision Scientific, Model 17) for 5 min to insure proper setting of the binder. The die was then removed from the oven and allowed to cool to room temperature before removing the pellet.

## **RESULTS AND DISCUSSION**

#### **Physical activation**

Properties of several carbon samples produced by physical activation of the IBC-106 coal are presented in Table 4. Properties of a commercial activated carbon, BPL manufactured by Calgon Carbon Corp., are included in the table for comparative purposes. Vm/Vs values of coal-derived carbons range from 54 to 76 cm<sup>3</sup>/cm<sup>3</sup>. These values are comparable to that of BPL. The measured Vm/Vs value for BPL is consistent with values reported by other researchers.<sup>15-17</sup> Select sample products were then ground to minimize their inter-particle space and increase their bulk density. Bulk densities of select carbons with initial Vm/Vs values of 70 cm<sup>3</sup>/cm<sup>3</sup> increased by 35% when the -20+100 mesh granular products were ground to -325 mesh. Using this revised bulk density and a Vm/Vs value of 76 cm<sup>3</sup>/cm<sup>3</sup> provides a Vm/Vs value of 103 cm<sup>3</sup>/cm<sup>3</sup>.

Tire-derived carbons were produced from each of the parent tire samples. The tire samples from Atlas and National Tire Services were activated with steam. Production conditions and properties of tire-derived carbons are also listed in Table 4. Tire-derived carbons have lower micropore volumes and methane storage capacities than coal-derived carbons, possibly due to their lower bulk densities. For the highly activated samples (TA2), 10% by mass of the original tire sample remains. Steam activation probably leads to broadening of pores in the tire-derived carbons. Theoretical models have predicted an optimum pore width of 11.4 Å for methane storage. Even deviations of 2-3 Å from this optimal pore size significantly reduces the ability of the pore to adsorb methane.<sup>18</sup> Therefore, it is possible that the highly activated tire carbons have micropores which have broadened so that many pores are larger than ideal. Pore size distributions of sample products have yet to be determined.

#### **Chemical activation with KOH**

BET surface areas and micropore volumes of the chemically activated carbons from coal (0.5 h activation) are significantly higher than those of physically activated carbons. However, the Vm/Vs value for the KOH-activated carbon is lower (Table 4). This is attributed to the resulting lower bulk density. Chemical activation of the coal appears to be an effective method for producing carbon adsorbents for gas storage, provided that the carbon's bulk density can be increased. The methane adsorption capacity (g/g) for KOH-activated carbon is 50% higher than that of BPL at 500 psig (Table 4). Carbon sample C1 was prepared from the coal without pre-oxidation. Its methane adsorption capacity (g/g) is 15% lower than that of BPL at 500 psig. This is most likely due to its lower micropore volume. Carbon sample C2 was prepared by pre-oxidation for 4 h resulting in a surface area of 1037 m<sup>2</sup>/g. Pre-oxidation of the coal causes increased methane adsorption capacity at 500 psig when compared to BPL or the activated carbons prepared without pre-oxidation.

Tire samples from Baker Rubber were chemically activated since it was closest in size (0.4 mm) to the crushed KOH. It is desirable to have as much direct contact as possible between the KOH and the tire since the reaction involves two solid materials. KOH-activated tire-derived carbons have much higher bulk densities than the steam-activated tire-derived carbons, most likely due to the chemical reaction between the two solids resulting in the realignment of carbon structure. As a result of their increased bulk density, methane storage capacities of the KOH-activated carbons are 40-50% higher than the physically activated carbons.

#### **Pelletization**

Pellets were formed from select tire-derived carbons and chars. In all cases, the bulk density of the material increased over 100%. The changes of adsorbent bulk density, micropore volume and

Vm/Vs values are summarized in Table 5. Efforts to make pellets with < 10% binder were unsuccessful. The unactivated char was mixed with binder at a mass ratio of 5% (of the char). Although pelletization of the TA3 carbon increased bulk density by about 160%, the micropore volume was reduced by 50%, resulting in no effective change in Vm/Vs values (Table 5). The loss of micropore volume is most likely due to the large amount of binder (11%) required to make the pellet. The binder may block access to the micropores by covering or filling the pores. A micropore volume reduction of about 20% has been reported.<sup>19</sup> Micropore volume did not seem to be impeded when making a pellet from the TA4 char prior to activation. This result cannot be attributed to the amount of binder used with the char. Since significant mass loss occurs during activation, the amount of binder in the final activated pellet is roughly the same as the TA3 pellet. Instead, the binder does not limit micropore development during activation and may actually contribute to the total micropore volume by developing micropores during activation. Similar results were observed for the KOH-activated tire-derived carbons.

## CONCLUSIONS

Activated carbons for natural gas storage were produced by physical and chemical activation of an Illinois coal and scrap tires. Volumetric methane storage capacities (Vm/Vs) were measured at pressures up to 500 psig. Vm/Vs values of 76 cm<sup>3</sup>/cm<sup>3</sup> are achievable when physically activating the coal. This value is comparable to that of 70 cm<sup>3</sup>/cm<sup>3</sup> for BPL, a commercial granular activated carbon. Vm/Vs values exceeding 100 cm<sup>3</sup>/cm<sup>3</sup> were achieved by grinding the granular coal-derived products. The increase in Vm/Vs is due to the increase in bulk density. KOH-activated coal-derived carbons have higher surface area, micropore volume, and methane adsorption capacity (g/g), but lower volumetric methane storage capacity, than the physically activated carbons. The lower volumetric methane storage capacity is due to the lower bulk density of KOH activated carbon. Tire-derived carbons have lower methane storage capacity due to their lower bulk density, when compared to the coal-derived carbons. Forming pellets from tire-derived carbons increases bulk density by as much as 160%. However, this increase was offset by a decrease in the micropore volume of the pelletized materials due to the amount of binder required in the process. As a result, Vm/Vs values were about the same for granular and pelletized tire-derived carbons. Carbon obtained by activating a pelletized tire-derived char increased storage capacity by about 20 %.

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## REFERENCES

1. DeLuchi, M.A. and Ogden, J.M. *Transpn. Res.* 27 255 (1989)
2. *USA Today* Oct. 23 (1990)
3. Keller, M.N. *Cars* pp.59 March (1992)
4. Johannson, L. *ENVIRO* 13 11 (1992)
5. Alson, J.A., Adler, J.M. and Baines, T.M. in *Alternative Transportation Fuels* Quorum Books, New York (1989)
6. Carslaw, D.C. and Fricker, N. *Chemistry & Industry* August 7 (1995)
7. Golovoy, A. *Proceedings: Compressed Natural Gas Soc. Auto. Eng.*, Pittsburgh PA (1983)
8. Seinfeld, J.H. *Air Pollution: Physical and Chemical Fundamentals* McGraw Hill (1975)
9. Nelson, C.R. "Physical Sciences NGV Gas Storage Research," Gas Research Institute, Chicago IL (1993)
10. Wegrzyn, J., Weismann, H. and Lee, T. *Proceedings: Annual Automotive Tech. Develop.* Dearborn MI (1992)
11. Quinn, D.F., McDonald, J.A. and Sosin, K. 207th ACS National Mtg, San Diego CA (1994)
12. *New York Times* p. D1 May 9 (1990)
13. Harvey, R.D. and Kruse, C.W. *Journal of Coal Quality* 7 109 (1988)
14. Sun, J. MS thesis, Southern Illinois University, Carbondale IL (1993)
15. Innes, R.A., Lutinski, F.E., Ocelli, M.L. and Kennedy, J.V. *Report AC 01-84CE50071* Washington, DC: US DOE (1984)
16. Parkyns, N.D. and Quinn, D.F. in *Porosity in Carbons* John Wiley & Sons, Inc. (1995)
17. Quinn, D.F. and McDonald, J.A. *Carbon* 30 1097 (1992)

18. Matranga, K., Stella, A., Myers, A., and Glandt, E. *Sep. Sci. and Tech.* 27 1825 (1992)

19. Kimber, G. Workshop on Adsorbent Carbon, Lexington KY, July 12-14 (1995)

Table 1. Equivalent ozone-producing potential for select vehicular fuels

Fuels	g of O <sub>3</sub> /mile
Gasoline	3.8
M85 (85% methanol in gasoline)	4.7
M100 (100% methanol)	1.8
CNG	0.2
LPG (Liquefied petroleum gas)	0.7

Table 2. Reduction of emissions from NGV when compared to gasoline fueled vehicle

Pollutants	% Reduction
CO	76
NOx	75
HCs (Non-methane)	88
Benzene	99
1,3-butadiene	100

Table 3. Proximate and ultimate analyses of IBC-106 coal (-20+100 mesh) and Atlas scrap tire

	Coal [wt%]	Tire [wt%]
Proximate analysis (as received)		
Moisture	8.3	0.9
Volatile matter	37.9	3.2
Fixed carbon	45.9	69.8
Ash	8.0	26.2
Ultimate analysis (dry)		
Carbon	70.3	86.2
Hydrogen	5.2	7.4
Nitrogen	1.5	0.1
Sulfur	3.7	1.5
Oxygen	11.3	1.7

Table 4. Type of treatment and properties of resulting activated carbons that are produced from Illinois coal, scrap tires and BPL

Sample ID	Pre-oxidation [°C, h]	Activation conditions [°C, h]	Surface area BET (dry) [m <sup>2</sup> /g]	Micropore volume [cm <sup>3</sup> /g]	CH <sub>4</sub> adsorption at 500 psig [g/g] <sup>d</sup>	Bulk density [g/cm <sup>3</sup> ]	Vm/Vs [cm <sup>3</sup> /cm <sup>3</sup> ]
C1 <sup>a</sup>	None	850, 1.5	897	0.330	0.0525	0.33	54
C2 <sup>a</sup>	225, 4	850, 2	1037	0.370	0.0643	0.44	73
C3 <sup>a</sup>	225, 4	825, 3	1056	0.410	0.0610	0.44	76
C4 <sup>a,c</sup>	None	800, 0.5	1478	0.620	0.0903	0.27	68
TA1 <sup>b</sup>	None	850, 3	888	0.254	0.0540	0.15	44
TA2 <sup>b</sup>	None	900, 1	1031	0.278	0.0530	0.13	41
TB <sup>b</sup>	None	850, 2.5	420	0.131	-	0.24	38
TC <sup>b,c</sup>	None	850, 1.5	820	0.274	-	0.33	53
BPL	unknown	unknown	1000	0.430	0.0606	0.46	72

<sup>a</sup> produced from Illinois coal (IBC-106)

<sup>b</sup> produced from tire samples from Atlas, National Tire Services and Baker Rubber, respectively

<sup>c</sup> activated with KOH

<sup>d</sup> Sample weight at 1 atm CH<sub>4</sub> used as starting weight for calculation; Data for tire-derived carbon obtained without buoyancy correction

Table 5. Effect of pelletization on bulk density, micropore volume and Vm/Vs of select tire-derived carbons

Sample ID	Bulk density [g/cm <sup>3</sup> ]	Micropore volume [cm <sup>3</sup> /g]	Methane storage Vm/Vs, [cm <sup>3</sup> /cm <sup>3</sup> ]
TA3	0.16	0.25	43
TA3 pellet	0.42	0.13	44
TA4 activated pellet	0.37	0.23	51

Carbon TA3 and TA4 produced from Atlas scrap tire samples