TIRE-DERIVED ACTIVATED CARBONS
FOR GAS SEPARATION, STORAGE AND CLEANUP

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Introduction

Each year, about 242 million tires are disposed of in the United States [1]. As of 1993, about one-fifth of these tires were recycled or burned as fuel, with the balance stockpiled or exported. About 2 to 3 billion tires were in stockpiles. These stockpiles have lead to environmental problems, including increased mosquito populations, tire fires, and illegal tire dumping [1].

This paper describes the development of sorbents from waste tire for gas storage, and the separation and removal of toxic materials such as volatile organic compounds (VOCs) from gas streams. Tire rubber consists primarily of styrene-butadiene rubber ($\approx 62\%$ by mass) and carbon black ($\approx 31\%$ by mass) [2]. When tire rubber is pyrolyzed, the rubber polymer matrix breaks down, yielding 33-38% solid char, 38-55% liquid oil, and 10-30% gasses by mass. The char can be used to produce carbon sorbents, and the oils and gasses can be burned as low-energy fuels, with an energy content similar to a No. 8 or No. 10 fuel oil [3]. Producing activated carbons from waste tire rubber enables recycling of this material and potentially provides a low cost adsorbent for air pollution control applications.

Experimental

Tire samples were obtained from Atlas of Los Angeles, CA and National Tire Service of Chicago, IL. Proximate and ultimate analyses of the tire samples and of Illinois IBC-106 coal [4] are provided for comparison in Table 1.

Sample Preparation

Raw tire samples were heated in ultra-high purity (UHP, 99.999%) nitrogen to activation temperatures in a stainless steel wire basket inside a horizontal 4.5 cm ID ceramic tubular reactor furnace (Lindberg model 54232), and subsequently activated. The activation gas was a mixture of 0.5 l/min steam and 0.5 l/min UHP N_2. Deionized water was delivered to the reactor using a peristaltic pump, and was heated to $>200°C$ before injection into the reactor. Samples were activated at temperatures between 700 and 900°C for 0.5 to 3.0 hr.

Sample Characterization

The BET surface area, t-plot micropore volume, and BJH-method pore size distribution were determined by the multipoint N_2 (77 K) adsorption isotherm (relative pressure $P/P_0 = 0.001 - 1.000$) measured with a volumetric adsorption apparatus (Micromeretics ASAP 2400).

The carbon molecular sieve (CMS) properties of the carbons were evaluated by O_2/N_2 selectivity and capacity. N_2 and O_2 were introduced individually into an evacuated cell containing the degassed sorbent. The uptake of gas was measured as a decrease in pressure of the cell.

The natural gas (methane) volume storage capacity (V_m/V_s) was estimated using an empirical equation by Parkyns and Quinn, based on the micropore volume and bulk density of the sorbent [5]; where V_m is the volume of CH_4 stored and V_s is the bulk volume of the sorbent. Previous work at ISGS/UIUC shows that this equation fits empirical data for tire-based sorbents reasonably well [3].

The trichloroethane (TCA) adsorption capacity of samples at 298 K and 1.0 atm was determined by measuring the mass uptake on the sorbent of 3000 ppmv TCA diluted in N_2 using a gravimetric balance (CAHN 2000). TCA was provided as a compressed gas from MG Industries, and gas flow rates were controlled using a mass flow controller (Tylan FC-280). Other VOCs (acetone, toluene, and methyl ethyl ketone) are being tested following a similar procedure.

Tire-Derived Sorbent Applications

A surface area and pore structure comparison is made between tire-derived carbon sorbents and those from Illinois coal (Fig. 1). Indicated are total mass losses in processing and BET surface areas. In general, the tire carbons have more meso- and macropores in comparison to carbons prepared from Illinois coal, and increased mass loss increases the BET surface area.

Carbon Molecular Sieve (CMS) Properties

One sorbent made from waste tire (T2-AC1) activated at 900°C for 2 hr (86% total mass burnoff from raw sample) exhibited O_2 and N_2 equilibrium adsorption capacities of 5.46 and 5.80 cm^3/g respectively, with an O_2/N_2 selectivity ratio of 0.94. While the selectivity of this sorbent is low, the storage capacity is comparable to CMS made from Illinois coals [6]. Carbon deposition may improve overall selectivity.

Methane Storage Capacity

The CH_4 storage capacity of selected tire-derived sorbents varied from 36 to 44 V_m/V_s with an average value

of 39 V_m/V_s. This is about half the measured capacity of Calgon BPL, a commercial activated carbon, or a carbon derived from Illinois IBC-106 coal [4].

VOC Adsorption

The TCA (trichloroethane) adsorption capacity was evaluated at 298 K for one sorbent made from scrap tire (T2-AC2) activated with steam at 900°C for 1.5 hr (92.4% mass loss) The equilibrium mass capacity at 3000 ppmv TCA in N_2 was 319 mg/g. This is about 45% the capacity of an activated carbon cloth (ACC) under the same conditions [7].

Conclusions and Future Work

Table 2 summaries the properties of select commercial sorbents, and those made from IBC-106 coal and waste tire. Sorbents made from scrap vehicle tires provide a two-fold environmental benefit: A recycling path is created for waste vehicle tires, and new sorbents are produced that may be more economical and beneficial to the air quality industry.

To compensate for the friability of tire carbons, sorbent pellets will be made. Work done at UIUC/ISGS is exploring alternative binders for the pellets, possibly incorporating other recycled materials.

Acknowledgments

References

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Table 1. Proximate and Ultimate Analysis of Raw Tire Samples and IBC-106 Coal

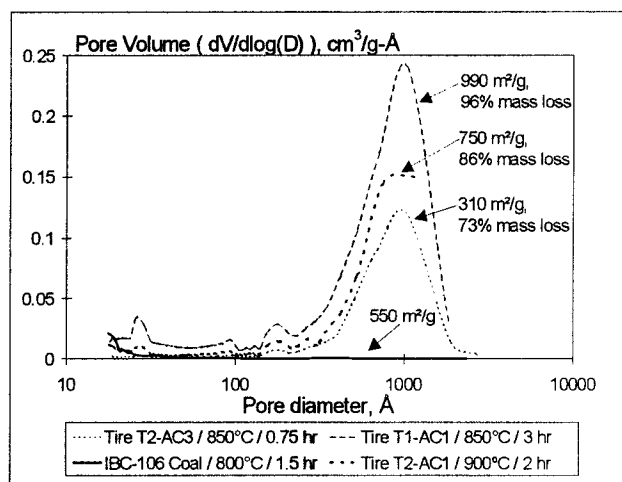|	Atlas (T1)	National (T2)	IBC-106
nominal size	2 - 3 mm	2.4 mm	---
proximate analysis (as received wt %)			
moisture	0.9	0.5	8.3
volatile matter	69.8	68.8	37.9
fixed carbon	26.2	27.7	45.9
ash	3.2	2.4	8.0
ultimate analysis (dry wt %)			
carbon	86.2	87.2	70.3
hydrogen	7.4	7.6	5.2
nitrogen	0.1	0.2	1.5
oxygen	1.5	0.9	10.6
total sulfur	1.7	1.6	3.7
energy content (dry, ash-free) [kJ/kg]			
	---	40,100	30,600

--- = not available

Figure 1. Pore size distributions (pore volume vs pore diameter) of select carbons made from scrap tire (Atlas and National) and Illinois IBC-106 coal with steam activation at different temperatures and processing times. Indicated are BET surface areas and total mass losses in processing.

Table 2. Properties of Select Carbon Sorbents

Sample	BET surface area [m²/g]	Est. CH_4 cap. (V_m/V_s)	TCA capacity [mg/g]	O_2 capacity [cm³/g]	N_2 capacity [cm³/g]	O_2/N_2 selectivity
TireT1-AC1	990	36	---	---	---	---
Tire T2-AC1	750	44	---	5.46	5.80	0.94
Tire T2-AC2	940	---	319	---	---	---
Tire T2-AC3	310	38	---	---	---	---
IBC-106 [4], [6]	1060	76	---	4.37	2.71	1.61
Calgon BPL [3]	1030	73	---	---	---	---
ACC-20 [7]	1460	---	715	---	---	---

--- = not available