

Formed Activated Carbons from Bituminous Coals by KOH Activation

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INTRODUCTION

Coals of various ranks are important precursors for the synthesis of activated carbons in powder, granular or extrudate forms. The commercial manufacture of carbons from bituminous coals generally involves carbonization followed by steam activation of the char to generate the required pore structure and surface area. Pitch binders can be used to produce hard pelletized products. Large size carbons have higher market value than powders, as they can be used in fixed bed adsorbers, allowing cyclic operation, and regeneration.

Low rank brown coals can be processed into pelletized highly microporous carbons using a different approach to that described above (1, 2). This involves alkaline digestion of the humic acid rich coal with potassium hydroxide to form an extrudable paste which can be carbonized and activated in a single heat treatment step, although a subsequent leaching step is required to recover the reagent. The KOH promotes both binding and chemical activation, and no further activation with steam or CO₂ is required. Even though KOH has been shown to be an effective chemical activant for producing powdered activated carbons from petroleum cokes and bituminous coals (3, 4), these precursors do not contain humic acids or sufficient acidic functional groups to enable their colloidal dissolution in aqueous KOH. Therefore the successful pelletization of bituminous coal/KOH mixtures is not normally possible without added binder.

To attempt to circumvent this difficulty, an approach has been taken in which bituminous coals are subjected to an oxidative pretreatment in order to modify the coal structure, remove mineral matter, enhance digestion in KOH, and induce strong binding properties. This paper describes an investigation of the effects of pre-oxidation with HNO₃ on the production and properties of pelletized activated carbons from bituminous coals using KOH. Nitric acid was chosen because of its known ability to oxidize coals (5, 6), and because it has the advantage over other strong oxidants such as Cr₂O₇ in being able to generate humic acids in high yield (7,8). The research is germane to the diversification of use of coal resources, many of which face increasing environmental constraints on their direct utilization as fuels.

EXPERIMENTAL

Western Kentucky No.9 seam (high vol.C) coal was dried, ground to minus 100 mesh, and oxidized by reaction with an aqueous solution of HNO₃ at concentrations from 0.25 to 2N. The reaction was conducted with vigorous stirring at 373K for 8 hours, or until visible signs of reaction had ceased. The oxidation product was filtered and washed with distilled water prior to drying.

Extrudable pastes were prepared by slowly blending the appropriate dry feedstock in a paddle mixer with a concentrated KOH solution. A KOH/fixed carbon ratio of 1:1 was maintained for all feedstocks. Sufficient water was added to prepare a paste of suitable consistency for extrusion. A low-pressure screw extruder, equipped with a multi-hole die, was used to prepare the spaghetti-like product. The extrudate was dried overnight at 353K to form hard brittle strands which were then roller crushed and sealed in moisture proof bags.

Both HNO₃ and HNO₃/KOH treated feedstocks were carbonized in a N₂ purged tube furnace which was temperature programmed from ambient to 1173K at 15K/min., with a 60 min. dwell at the maximum temperature. After cooling, the product was water washed, boiled with a 5% HCl soln. to remove excess potassium, and dried. Proximate analyses were obtained using a LECO-MAC 400.

Information on the carbon pore structure was derived from nitrogen adsorption isotherms obtained at 77K on a Coulter Omnisorb 100CX apparatus; the micropore volume W₀ was determined using the Dubinin-Raduskevich equation (9). The average width of slit shaped pores was determined using the expression suggested by Stoekli et al. (10), which is valid for pores of diameter 0.45-2.5 nm;

$$L(\text{nm})=30/E_0+5705/E_0^3+0.028E_0-1.49$$

Specific surface areas, S_{BET}, were obtained from the adsorption isotherms using the BET equation.

Non-microporous surface areas, S'_{BET}, and micropore volumes were obtained using the α_s method (11); standard isotherm data were taken from Rodriguez-Reinoso et al. (12).

Relative carbon hardness was estimated using the Takeda microstrength hardness test method (13). Fourier transform infrared (FTIR) spectra of the HNO₃ treated coals were obtained from 0.4% loaded KBr discs using a Nicolet 20SX spectrophotometer.

RESULTS AND DISCUSSION

Nitric acid oxidation of the coal produced an expected decrease in ash content, due to leaching the acid-soluble minerals, Table 1(a). However, treatment with 0.25N and 0.5N HNO₃ did not remove all of the pyrite present in the coal, as the remaining pyrite separated from the lower density oxidation products during water washing. At low HNO₃/coal ratios the fixed carbon content of the oxidation products increased above that reported for the coal. This may indicate that, under conditions of moderate oxidation, products are generated that participate in thermally induced condensation reactions, resulting in a net increase in fixed carbon content. The test to determine the fixed carbon content provides conditions under which such reactions can take place. With more severe oxidation, there was a reduction in fixed carbon as, presumably, the increased oxygen content of the coal contributed to the loss of carbon as volatile products.

The FTIR spectra presented in Figure 1 reveal a progressive increase in the intensity of acidic hydroxyl (broad 3700-2400 cm⁻¹), carbonyl/carboxyl (~1700 cm⁻¹) and NO₂ (1547cm⁻¹) absorption bands with increasing severity of HNO₃ treatment. Interestingly, the spectra of the 1N and 2N HNO₃ oxidation products are comparable to those of untreated lignites or brown coals, such as Beulah (North Dakota, USA) and Loy Yang (Victoria, Australia), indicating that the acid treatment may have the desired result of effectively lowering the coal rank. The absorption bands associated with clays/silicates are unaffected by the HNO₃ treatment, while the intensities of the bands associated with aliphatic absorbance (~2900cm⁻¹ and 1450cm⁻¹) decrease with increasing oxidation severity. However, the loss of aliphatic structure may be exaggerated by changes in the infrared extinction coefficients.

Thermal treatment of the HNO_3 oxidized coals produced yields of char, Table 1(b), that were somewhat higher than the fixed carbon contents of the starting materials. Due to the loss of volatile matter on heat treatment, there was a general increase in ash content with oxidation severity.

The presence of KOH during heat treatment produced carbons with consistently lower yields than the corresponding thermal products, and these decreased with increasing oxidation severity, Table 1(c). Despite the lower carbon yields, the ash contents are reduced, rather than being further concentrated by the loss of carbonaceous material. Obviously, reaction with KOH converts some of the coal mineral constituents to soluble products that are removed upon product washing. Similar effects have been found in studies of the KOH activation of powdered bituminous coal (4).

Calculations based on the fixed carbon content, Table 1(b) and (c), show that fixed carbon is lost during KOH activation of the coals subjected to mild oxidation. In contrast, KOH activation of the more severely oxidized feedstocks results in negligible loss of fixed carbon during thermal treatment. Unpublished research has shown that no significant fixed carbon burnoff occurs on the activation of brown coal/KOH pellets (14). These observations suggest that the loss of fixed carbon during chemical activation by KOH exhibits an inverse rank dependence, with the more severely oxidized bituminous coals behaving similarly to low rank coals.

The nitrogen adsorption isotherm data presented in Table 2 reveal that HNO_3 oxidation decreases the already low surface area and pore volume of the bituminous coal feedstock. Thermal treatment also produces solid products with negligible porosity. These results contrast with the well established ability of HNO_3 to regenerate spent activated carbons (15).

On the other hand, the activated carbons produced with KOH reveal that even low levels of HNO_3 oxidative pretreatment have a marked effect on the generation of microporosity, Table 2. At the lowest level of oxidation, the BET surface area increases by over 30% and the micropore volume by about 75%. Increasing the severity of oxidation further enhances the development of surface area and micropore volume, which are increased by over 50% and 100% respectively, after treatment with 2.0N HNO_3 . The increase in surface area and pore volume of these carbons may help to explain their lower ash yields, since the high porosity will allow greater access during acid washing, leading to the more effective removal of soluble ash constituents.

The relative microstrength hardness of the active carbons is presented in Figure 2 along with some commercial carbons for comparison. The feedstocks and chars produced from the parent coal and after 0.25N HNO_3 oxidation did not form extrudable mixtures with KOH. At higher oxidation levels, the extent of reaction and dissolution in the KOH solution was found to increase with severity of treatment. The reaction between the 1N and 2N HNO_3 oxidation products and KOH was strongly exothermic with some NH_3 evolution. These mixtures behaved like colloidal gels and were readily extruded. A dramatic increase in product carbon hardness was found on going from 0.5N to 1N HNO_3 oxidation. Oxidation with 2N HNO_3 improved the carbon hardness above that determined for commercial bituminous coal-derived activated carbons.

SUMMARY

The pretreatment of bituminous coals by nitric acid oxidation produces a feedstock that, in the presence of KOH, is suitable for extrusion and for the synthesis of hard, high surface area activated carbons. Nitric acid serves several roles in the formation of pelletized carbons from bituminous coal:

- (1) it reduces the ash content,
- (2) it introduces sufficient acidic functionalities, including regenerated humic acids, to the

coal to enable dissolution in KOH solution, conferring binding properties for the formation of hard, shaped carbon precursors: the strength is retained during heat treatment, and

(3) it increases the ability of the KOH to generate microporosity.

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Table 1: Analysis of HNO₃ treated coals and heat treated products.

(a) oxidized coal

HNO ₃ Normality (W/W)	HNO ₃ /Coal Ratio	Ash	Volatiles	Fixed Carbon
		dry basis		
0	-	14.48	36.00	49.52
0.25	0.22	7.60	36.05	56.35
0.5	0.44	6.87	37.07	56.06
1.0	0.88	5.66	44.89	49.46
2.0	1.76	5.93	56.06	38.01

(b) Thermally treated coals(1173K)

HNO ₃ Normality	Yield (%w/w)	Fixed C Yield (%w/w)	Ash	Volatiles	Fixed Carbon
			dry basis		
0.0	66	110	11.17	2.33	86.50
0.25	69	107	8.73	2.29	88.97
0.5	59	95	8.77	<.1	91.18
1.0	55	98	7.98	2.41	89.61
2.0	52	117	9.94	3.29	86.77

(c) KOH activated coals (1173K; 1:1 KOH:Fixed Carbon)

HNO ₃ Normality	Yield (%w/w)	Fixed C Yield (%w/w)	Ash	Volatiles	Fixed Carbon
			dry basis		
0.0	54	83	5.02	7.91	87.07
0.25	53	84	3.73	8.60	87.67
0.5	52	81	5.83	7.18	86.98
1.0	49	95	4.65	5.84	89.51
2.0	45	108	4.01	3.26	92.73

Table 2: Nitrogen Adsorption Isotherm Data

(a): BET surface area of feedstocks and thermally treated coals (1173K)

HNO ₃ Normality	BET Surface Area (m ² /g ⁻¹)	
	Feedstocks	Thermally treated
0	21	2
0.25	6	1
0.5	2	1
1.0	6	4
2.0	1	11

(b): Activated Carbons

HNO ₃ Normality	Micropore Volume (cm ³ g ⁻¹)	BET Surface Area (m ² g ⁻¹)	Mean Pore Width Angstrom	Mesopore Surface Area (m ² g ⁻¹)
0	0.37	1035	-	36.6
0.25	0.65	1374	7.08	69.6
0.5	0.72	1473	7.63	38.1
1.0	0.71	1517	6.08	34.8
2.0	0.74	1602	7.13	52.2

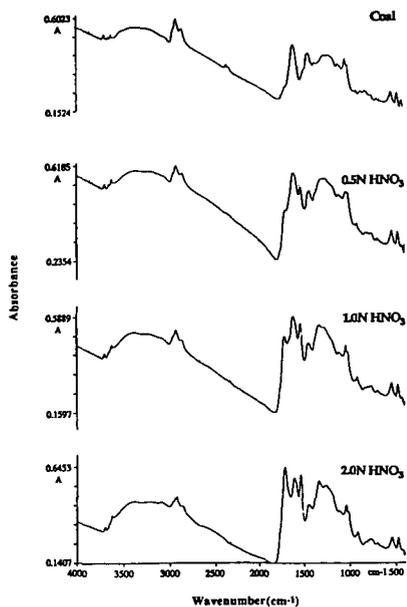


Figure 1: FTIR spectra of Western Kentucky No.9 bituminous coal and its solid HNO₃ oxidation products

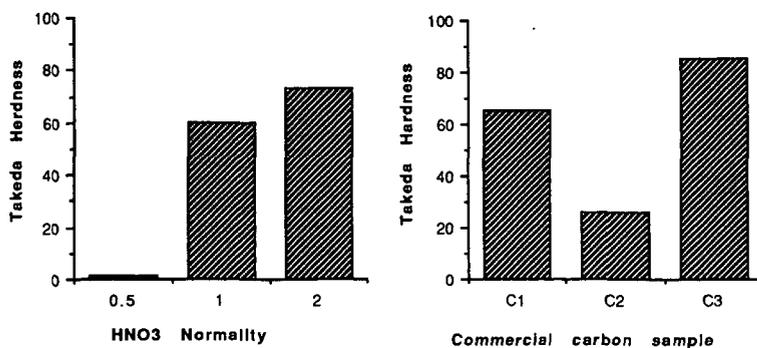


Figure 2: Takeda hardness of activated carbons and commercial samples. (C1 and C2: bituminous coal derived, C3: coconut shell derived)