

# DEVELOPMENT OF BINDER PITCHES FROM COAL EXTRACT AND COAL-TAR PITCH BLENDS

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## Abstract

There is concern among U. S. industrial pitch producers about domestic sourcing of quality binder pitches. Binder pitches are essential ingredients in the manufacture of carbon anodes. Although considerable work has focused on combining petroleum-derived materials with conventional coal-tar pitches, relatively little effort has been directed toward using solvent extracts from coal as feedstocks for blending. Researchers from West Virginia University and Koppers Industries, Inc. studied the effects of pitches developed by solvent extraction of coal. These coal-derived pitches were mixed with conventional coal-tar pitches in quantities sufficient to form laboratory-scale anodes. Formulations with a coal-tar pitch were used as controls. The binder pitches, green and baked anodes were then subjected to a battery of standard tests. The results of using solvent-extracted coal pitch on anode characteristics including thermal conductivity, electrical resistivity, compressive strength, air permeability, bulk density, etc., are presented herein.

## Introduction

West Virginia University and Koppers Industries have been involved with the Consortium for Premium Carbon Products from Coal, a Department of Energy sponsored program. A mission of the CPCPC is to find uses of coal for other than conventional combustion and metallurgical coke making purposes. However, a major impediment to a wider application of coal as a source for carbon products is the presence of inherent inorganic matter. This material is not simply a diluent and thus affects all practical aspects of coal utilization. In this regard, West Virginia University researchers have shown that coal can be converted into a wide variety of pitch precursors each one with a chosen slate of characteristics and properties [1-4]. One feature of the process involves prehydrogenation of coal followed by extraction using the dipolar, aprotic solvent N-methyl pyrrolidone (NMP). This solvent has been shown to be highly effective for substantially reducing the ash-forming matter in coal-derived materials [5].

Currently, there are adequate supplies of coal tar on a worldwide basis [6]. However, many recovery coke ovens in the United States have closed and new facilities are not expected to be built any time soon. Consequently, North America has become a net importer of coal tar and related feedstocks. To mitigate the sourcing shortfall, we have investigated the effects of using coal extracts as extenders or additives to conventional coal-tar pitch in anode fabrication.

## Binder Pitch Preparation

The Pennsylvania State University supplied a bituminous coal from Arch Coal, Incorporated. Some of the properties of the coal are provided in Table I.

Table I Characteristics of Bituminous Coal

Moisture		Ash Content		Volatile Matter
wt%		wt%		wt%
1.79		7.36		31.57
Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
wt%	wt%	wt%	wt%	By Diff.
80.3	4.56	1.41	0.71	5.65
Vitrinite	Liptinite	Inertinite	Minerals	
vol%	vol%	vol%	vol%	
57.2	8.3	30.3	4.2	

The coal was ground to pass through a Tyler 20-mesh sieve and dried in a vacuum oven to remove moisture. Coal-derived pitches were produced in batches by placing 600g of coal along with 1.5L of a liquid vehicle into a 3.8L stirred-bolted-closure autoclave. The reactor was purged of air with hydrogen gas and then pressurized to 2.8MPa with molecular hydrogen at room temperature. The coal was hydrogenated at 450°C for 1 hour. Following reaction, the reactor was cooled to room temperature and vented. The products were washed out with NMP and collected in a 10L flask. Three liters of NMP were added to the flask and the mixture agitated for about 2 hours at 110°C. Afterward, the mixture was transferred to a centrifuge to remove

unconverted coal and mineral matter by centrifugation at 2000G for one hour. The supernatant liquid was decanted and placed in a rotary evaporator device to remove and recover NMP. Finally, the coal-derived pitch was dried in a vacuum oven at 150°C overnight before weighing. This material is designated WVU pitch. The hydrogenation procedure was repeated until enough material was produced for blending with the Koppers standard coal-tar pitch (SCTP).

Blends were developed by placing the appropriate amount of WVU pitch with SCTP in a heated vessel at about 20-30°C above the softening point temperature of the SCTP. The blend was stirred constantly to ensure complete mixing and then cooled. The pitch blend was removed from the vessel as a thick paste and placed on metal pans to solidify. The solid pitch blend was ground and sealed in plastic bottles until ready for use. Two blends were produced, a 50:50 and a 85:15 wt:wt STCP:WVU Pitch. Table II provides characteristics of the binder pitches.

Table II Properties of Pitches and Their Blends

	WVU Pitch	SCTP	SCTP:WVU 50:50	SCTP:WVU 85:15
Mettler SP °C	116.0	109.4	111.1	107.8
Conradson Carbon, wt%	52.7	57.8	57.6	56.1
QI, wt%	nil	13.1	6.6*	11.1*
TI, wt%	19.8	30.3	25.1*	28.7*
β-Resin, wt%	19.8	14.4	18.5	17.6
Ash Content wt%	0.03	0.07	0.08	0.11
Density, g/cm <sup>3</sup>	1.24	1.34	1.28	1.33

\*Calculated

#### Pilot Anode Preparation

Pilot anodes were formed into 10.2cm diameter by 15.2cm height cylinders using a vibration technique, baked, and evaluated. Sized petroleum coke was premixed according to a standard anode coke formulation shown in Table III.

Table III Anode Coke Formulation, wt%

Coarse	Fines	Intermediate	Butts
31.5	37.0	14.6	16.9

The binder level for the anode formulations ranged from 14.0 up to 16.0 at 1.0wt% increments. The pitch and coke were added cold to a 155-165°C preheated mixer before transferring to a mold

set to a temperature of 150°C. Typical vibroforming conditions were conducted at about 50Hz through an amplitude of 0.6cm. Baking of the green anodes was accomplished in a three-zone, horizontal furnace under a blanket of nitrogen. The baking profile was 10°C/hr to 600°C; 25°C/hr from 600°C to 1160°C; hold at 1160°C for 14hr; cool to room temperature. The final internal bake temperature of the baking retort was approximately 1100°C. After baking, 5cm diameter cores were cut for testing and evaluation.

## Results

### Preliminary Studies

Before proceeding with the development of the pilot anodes, an initial study was conducted to determine the efficacy of coal extracts as a binder pitch [7]. Because only a limited amount of coal-derived material was available, a preliminary bench-scale anode forming was undertaken. Only a single anode was made at a particular binder level with the coal-extract material and its blend with the coal-tar pitch. Two anodes were formed at each binder level for the coal-tar and petroleum pitch. The pitches are designated WVU pitch, SCTP for a standard coal-tar pitch, and SPP for a standard petroleum pitch. A blend of 80 parts SCTP and 20 parts WVU pitch was also prepared. For this study, 5cm diameter anodes were made. Although slightly different coal and binder pitches were used in these preliminary studies, the coal extract and anode preparation steps were similar to those already described. Table IV shows the properties of the pitches.

Table IV Analyses of Pitches Evaluated in 5cm Diameter Molded Anodes

	WVU Pitch	SCTP	SPP	SCTP:WVU 80:20
Mettler SP °C	119.2	111.6	112.0	114.5
Conradson Carbon, wt%	50.7	57.8	46.9	57.3
QI, wt%	0.5	14.7	0.1	11.9
TI, wt%	11.5	30.3	3.2	26.5
β-Resin, wt%	11.0	15.6	3.1	14.6
Ash Content, wt%	0.07	0.24	0.03	0.20
Density, g/cm <sup>3</sup>	1.21	1.33	1.22	1.31

The baked anode test data for the preliminary work are summarized in Table V. In Table VI are listed the averages of the runs for the 10.2cm diameter baked anodes while Table VII provides data for the 5cm diameter cores obtained from them.

Table V Control and Preliminary Pitch Baked 5cm Anode Properties

Sample No.*	GAD <sup>1</sup> g/cm <sup>3</sup>	BAD <sup>2</sup> g/cm <sup>3</sup>	Electrical Resistivity $\mu\Omega\text{m}$	Air Permeability nPm	Crush Strength MPa	CTE Avg. $10^{-6}/^{\circ}\text{C}$ @ 300 $^{\circ}\text{C}$	Thermal Conductivity W/m-K	Insitu CV <sup>3</sup> wt%
WVU-14	1.553	1.480	89.3	8.38	12.94	3.616	2.02	59.9
WVU-15	1.581	1.498	85.2	9.05	14.22	3.938	1.96	57.2
SCTP-14	1.626	1.553	67.1	1.09	33.59	3.655	2.27	57.5
SCTP-15	1.613	1.538	74.2	2.22	26.31	3.976	2.20	61.8
SPP-14	1.621	1.527	71.0	1.45	26.32	3.830	2.15	51.9
SPP-15	1.643	1.540	65.7	0.89	28.87	3.816	2.33	53.6
SCTP:WVU-15 80:20	1.588	1.502	82.3	4.82	18.49	3.926	2.03	60.1
SCTP:WVU-16 80:20	1.625	1.538	69.6	1.31	27.69	4.189	2.25	60.7

\*Sample No. shows pitch type and binder level content in wt%.

<sup>1</sup>Block green apparent density, g/cm<sup>3</sup>; <sup>2</sup>Block baked apparent density, g/cm<sup>3</sup>; <sup>3</sup>Insitu coking value, wt%.

Table VI Characteristics of 10.2cm Diameter Green and Baked Pilot Anodes

	SCTP		SCTP:WVU 50:50			SCTP:WVU 85:15			SCTP:SPP 50:50		SCTP:SPP 85:15	
	15	16	14	15	16	14	15	16	15	16	15	16
Pitch, wt%	15	16	14	15	16	14	15	16	15	16	15	16
Block GAD <sup>1</sup>	1.526	1.563	1.531	1.567	1.597	1.521	1.554	1.598	1.537	1.589	1.543	1.593
Block BAD <sup>2</sup>	1.478	1.510	1.474	1.498	1.508	1.472	1.496	1.527	1.473	1.517	1.492	1.530
Insitu CV <sup>3</sup>	69.3	69.3	63.6	63.7	63.6	65.7	66.1	66.2	63.4	63.5	69.1	69.4
% Shrinkage	1.46	1.54	1.45	1.07	0.247	1.63	1.41	0.98	1.41	1.34	1.37	0.99

<sup>1</sup>Block green apparent density, g/cm<sup>3</sup>; <sup>2</sup>Block baked apparent density, g/cm<sup>3</sup>; <sup>3</sup>Insitu coking value, wt%.

Table VII Core Properties Developed from 10.2cm Pilot Anodes

	SCTP		SCTP:WVU 50:50			SCTP:WVU 85:15			SCTP:SPP 50:50		SCTP:SPP 85:15	
	15	16	14	15	16	14	15	16	15	16	15	16
Pitch, wt%	15	16	14	15	16	14	15	16	15	16	15	16
CAD <sup>1</sup> , g/cm <sup>3</sup>	1.49	1.52	1.49	1.51	1.52	1.48	1.51	1.53	1.48	1.52	1.52	1.55
Electrical Resistivity $\mu\Omega\text{m}$	75.6	62.3	77.3	66.5	63.9	86.1	71.1	63.5	69.3	60.9	71.9	61.9
Air Permeability nPm	5.73	1.70	2.34	1.07	0.73	3.59	2.17	1.00	4.97	1.16	2.13	0.83
Crush Strength MPa	34.30	41.16	30.38	31.48	34.56	29.44	32.47	39.54	36.27	36.5	37.84	46.98
CTE Avg. $10^{-6}/^{\circ}\text{C}$ @ 300 $^{\circ}\text{C}$	4.022	4.027	3.726	3.763	3.774	3.804	3.830	3.787	4.032	3.852	4.081	4.062
Thermal Conductivity W/m-K	2.25	2.43	2.22	2.43	2.43	2.20	2.39	2.44	2.05	2.44	2.29	2.45

<sup>1</sup>Core apparent density

## Discussion

The measurements depicted in Table IV indicate that the softening point temperature and coking value for the coal-extract, coal-extract/coal-tar blend, and petroleum pitch are within the range found for conventional coal-tar binder pitch. Quinoline insoluble matter is naturally low for WVU pitch and SPP because of their origin, though the amount of toluene insolubles in the former is significantly greater than the latter. However, both the green and baked apparent densities for the WVU pitch indicate that the binder level was not optimal, as well as most of the other property values show. For example, as shown in Table V, the anodes made with the WVU pitch were electrically more resistive and considerably weaker.

The results of the analyses for the 10.2cm diameter pilot anodes are summarized in Tables VI and VII. These results prove to be more favorable than for the preliminary work with the 5cm diameter test anodes. For example, a comparison at the 15 and 16wt% binder level for baked apparent density and core apparent density is shown in Figures 1 and 2, respectively.

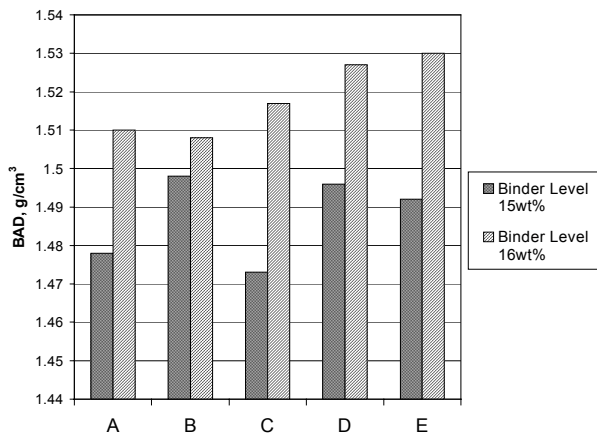


Figure 1: Baked apparent density vs. binder composition. A, SCTP; B, SCTP:WVU 50:50; C, SCTP:SPP 50:50; D, SCTP:WVU 85:15; E, SCTP:SPP 85:15.

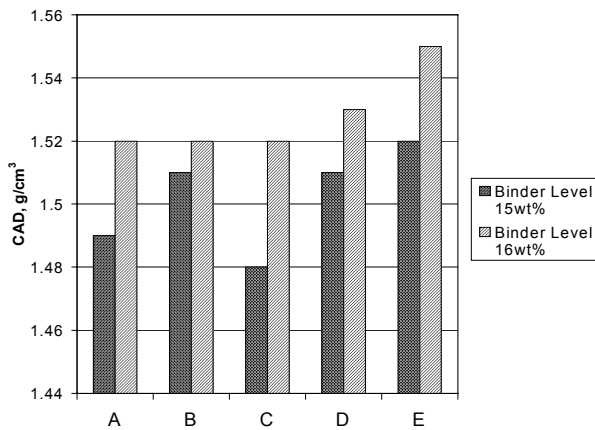


Figure 2: Baked core apparent density vs. binder composition. A, SCTP; B, SCTP:WVU 50:50; C, SCTP:SPP 50:50; D, SCTP:WVU 85:15; E, SCTP:SPP 85:15.

For similar binder formulations, the overall trend in density changes for the baked apparent density tracks that for the core materials, with the core densities being somewhat higher. Whether with the coal extract or petroleum pitch, the 50:50 blends resulted in an essentially identical core density at the 16wt% binder content. Nevertheless, a synergism may be present when using either the WVU or petroleum pitch at the 85:15 blend composition since the core densities are significantly greater than the coal-tar pitch control alone.

The electrical resistivity values at the 15wt% binder level remained relatively constant between about 67 and 72 $\mu\Omega\text{m}$ , except for the coal-tar pitch control with a value over 75 $\mu\Omega\text{m}$ , Figure 3. Increasing the binder content to 16wt% decreased resistivity for all anode cores to approximately 60 $\mu\Omega\text{m}$ . Crush strength is displayed in Figure 4 where it can be seen that the SCTP:SPP 85:15 at the 16wt% binder level produced the highest strength.

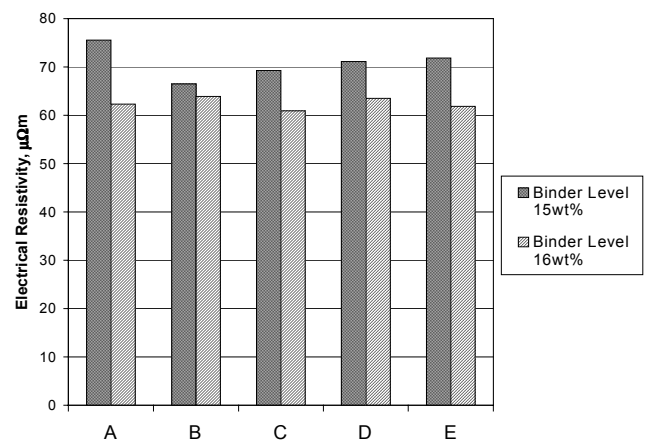


Figure 3: Electrical resistivity vs. binder composition. A, SCTP; B, SCTP:WVU 50:50; C, SCTP:SPP 50:50; D, SCTP:WVU 85:15; E, SCTP:SPP 85:15.

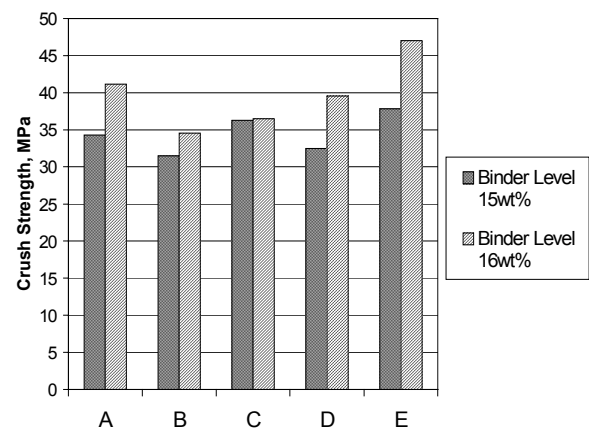


Figure 4: Crush strength vs. binder composition. A, SCTP; B, SCTP:WVU 50:50; C, SCTP:SPP 50:50; D, SCTP:WVU 85:15; E, SCTP:SPP 85:15.

The most dramatic effects on anode properties were observed for changes in the coefficient of thermal expansion, Figure 5. The addition of coal extracts to the standard coal-tar pitch at the 85:15 composition was more successful in reducing dimensional changes than the coal-tar pitch/petroleum 50:50 composition.

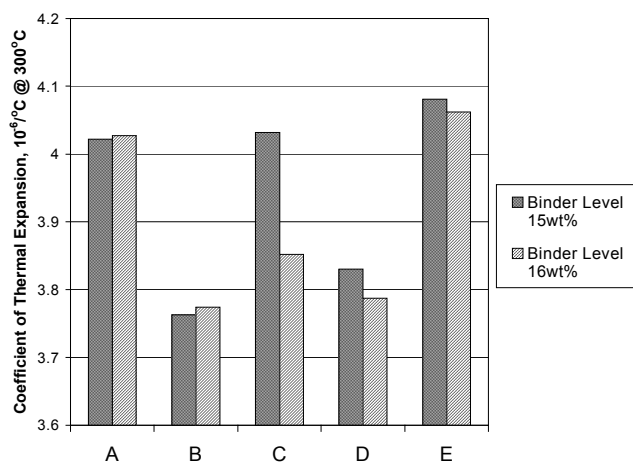


Figure 5: Coefficient of thermal expansion vs. binder composition. A, SCTP; B, SCTP:WVU 50:50; C, SCTP:SPP 50:50; D, SCTP:WVU 85:15; E, SCTP:SPP 85:15.

### Recommendations

The results indicate that coal extracts offer the potential to be used as additives to conventional coal-tar pitches for use as binders in anode fabrication. Additional work should be conducted to extend the range of binder content in order to determine the optimal binder level for the pitch blends.

### Acknowledgement

The authors thank Matthew Plants and Tom Baron for providing their assistance and technical expertise.

### References

1. P. G. Stansberry, J. W. Zondlo, R. Andrews, T. Rantell, and J. C. Withers, "Development of Coal-Based Pitches for Carbon-Carbon Composites" (Paper presented at the Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, 12 September, 2000).
2. M. S. Seehra, A. S. Pavlovic, V. S. Babu, J. W. Zondlo, P. G. Stansberry, and A. H. Stiller, "Measurement and Control of Anisotropy in Ten Coal-Based Graphites," *Carbon*, 32 (1994), 431-435.
3. P. G. Stansberry, J. W. Zondlo, A. H. Stiller, and P. Khandari, "The Production of Coal-Derived Mesophase Pitch" (Paper presented at the Twenty Second Biennial Conference on Carbon, San Diego, California, July 1995), 244.
4. P. G. Stansberry, J. W. Zondlo, and A. H. Stiller, *Carbon Materials for Advanced Technologies* (New York, NY: Elsevier Science, 1997), 205.
5. K. Reneganathan, J. W. Zondlo, E. A. Mintz, P. Kneisl, and A. H. Stiller, "Preparation of an Ultra-Low Ash Coal Extract Under Mild Conditions," *Fuel Processing Technology*, 18 (1988), 273-278.
6. K. Fitzgerald et al., "Pitch Quality and Supply Trends" (Sixth Annual Carbon Conference, Great Lakes Carbon Corporation, The Woodlands, Texas, 27 September 2000).
7. E. R. McHenry, "Evaluation of Pitches and Cokes From Solvent-Extracted Coal Material" (Final Report DE-AC05-96OR22464, Department of Energy, 1996).