LOW-SEVERITY EXTRACTION OF PITCH FROM COAL FOR CARBON FIBER PRODUCTION

A.J. Berkovich, R. Andrews, D. Jacques and T. Rantell

Center for Applied Energy Research, University of Kentucky
2540 Research Park Drive, Lexington, KY, 40511 USA

Introduction

The use of coal derived pitches as precursors for value added carbon products include binders and impregnators for carbon electrode manufacture as well as production of different types of carbon fiber. As the range of applications for new carbon based products increases the potential exists to tailor precursor properties for specific applications. This paper reports on the production of pitch feedstocks via mild solvent extraction of coal for producing general-purpose carbon fibers.

Crude anthracene oil, an inexpensive and readily available coal tar distillate was used to extract pitch from a suite of coals using low severity extraction conditions. Anthracene oil has been shown to be a good solvent for coal dissolution [1-10]. Pitch extraction yields ranged from 40 to 60 % without the use of catalysts or hydrogen gas over pressures. Pitch yield was found to increase with increasing coal aromaticity.

Carbon fibers were fabricated from the coal extracts and their physical properties measured. The influence of pitch precursor composition on the properties of the derived fibers was examined.

Experimental

Coal samples from Western Kentucky (W.Ky), Pittsburgh (Pitt.) and Northeast Wyoming's Black Thunder (B.T) mine were used for the extraction experiments. Proximate and ultimate analysis results for these coals are summarized in Table 1. Anthracene oil was supplied by Reilly Industries, Inc and was used as received. No hydrogenation of the solvent was performed. Analysis supplied by Reilly for anthracene oil was: 0.5 % maximum moisture; 1.12 gcm^{-3} minimum density; 104 ^{o}C minimum flash point; 91.5 % C; 6.0 % H; 1.0 % N; 1.0 % O; 0.5 % S.

Pitch extractions were performed in 500 mL stainless steel tubing bomb reactors that were heated by immersion in a fluidized sand bath. Coal samples were crushed to < 60 mesh and then slurried with anthracene oil in a coal to solvent ratio of 1:2 w/w and placed into the tubing bombs. Extractions were performed at 350 ^{o}C for 60 min.

After each extraction the tubing reactor was allowed to cool to room temperature and the off gas volume measured. The contents of the reactor and lines were washed with THF, and then soxhlet extracted with THF. The soxhlet thimble containing residual solids (THF insoluble fraction) was placed in a vacuum oven overnight to dry, cooled in a desiccator and then weighed to determine coal conversion. The THF soluble fraction was vacuum distilled to recover THF and to recover anthracene oil. The distillate recovered was weighed to determine solvent recovery. The pot residue (coal extract) was also weighed to calculate pitch yield. The softening point of the extracted pitches was measured using a Mettler Softening Point Apparatus (ASTM D3461-85, 1989). Typically, a softening point of 220 to 260 ^{o}C was desired for ease of fiber forming and processing.

Pitch samples were transferred to a Wayne bench scale extruder fitted with a 6.2mm diameter screw and 0.3mm dia x 1mm capillary die. Tests were conducted to determine the conditions under which the samples could be successfully extruded to produce a continuous thread. Feed size distribution and the temperature profile along the barrel and nozzle were crucial to this task. The extruded thread was attached to a wind-up drum rotating at speeds of up to 1700rpm (12m/s) to draw filament in the range 15 to 30μm.

Tows of fiber cut from the wind-up drum were stabilized by heating slowly in air to 310^{o}C. During stabilization the fibers undergo oxidative cross-linking reactions that progressively increase the softening point of the pitch until it becomes infusible. The fibers are then rapidly carbonized by heating to 1000^{o}C in nitrogen. During carbonization volatile components and impurities are lost and the fibers develop the crystalline structure that confers their strength and stiffness. The tensile properties of the fibers were measured using a MTS QTest instrument for single filament tests following ASTM D3379.

Results and Discussion

The results of anthracene oil extractions for the 3 coals in the sample suite are presented in Table 2. Replicate extractions were performed on each coal. The pitch yields were calculated from the mass of pitch (daf) recovered from vacuum distillations that were within the useful softening point range (200-260 ^{o}C) for fiber fabrication. Coal conversion was calculated on a dry ash-free basis from the difference in mass between the feed coal and the residual solids after extraction. The results of proximate and ultimate analyses on the extracted pitches are given in Table 3 and 4. Inspection of Table 2 shows that pitch yields were generally in the range of 40 to 65 % with coal conversions ranging from 25 to 50 %. Reasonable mass balances were also attained for all extractions performed.

The higher rank bituminous coals, W.Ky and Pitt, showed higher coal conversions compared to the lower rank BT coal. The majority of the extracted pitches softening points were within the desired range of 200 to 260 ^{o}C for carbon fiber fabrication. It can also be noted that in all extractions the pitch yield was higher than the coal conversion. Although this may seem to be an anomaly it is due to the way in which the softening point of the extracted pitch is controlled. To produce pitches with a softening point in the range of 200 to 260 ^{o}C required for fabrication into carbon fibers, a small variable amount of the high boiling solvent components are deliberately not removed during vacuum distillation of the coal extract solution. In practice, as more of the solvent is removed the softening point of the pitch increases and a concomitant decrease in pitch yield occurs. The data in Table 2 show that extractions with higher pitch yields had lower softening points and those with lower pitch yields had higher softening points.

Proximate analyses of the extracted pitches, Table 3, show all pitches had very low ash contents. This is an important property for fiber fabrication, since any residual particulate material present in the pitch can cause blockages in the fiber forming apparatus and/or cause defects and subsequent premature failure in the fabricated carbon fiber. The volatiles content of the extracted pitches is inversely proportional to the softening point, that is, pitches with higher softening points have lower volatiles content. A summary of ultimate analyses for the extracted pitches is shown in Table 4. Figure 1 shows the variation of H/C ratio with softening point. As may be expected H/C ratio decreases with increasing softening point.

Table 5 is a summary of fabrication data for the extracted pitches showing stabilization and carbonization, longitudinal fiber shrinkage, weight loss and final carbon yield data.

Table 6 shows that green fibers could be formed from all extracted pitches, with the exception of W.Ky 3, which had a very high softening point, 300 ^{o}C, which made melt spinning difficult. The green fibers formed from W.Ky and Pitt pitches were successfully processed to carbon fibers. Green fibers from the BT pitches could only be processed to fused clumps (stuck) of carbon fiber. Slower stabilization heating rates for the green BT fibers, down to 0.1 ^{o}C/min were attempted but where not successful. The reason for the BT green pitch fiber behavior is not clear. The BT pitch softening points are within a range consummate for fabricating carbon when compared to the other extracted pitches, further investigation and characterization of the BT pitch is warranted. For the fibers produced from bituminous coal pitch extracts, the percent shrinkage (longitudinal) decreased with increasing carbon content of the precursor pitch. The results also showed that high carbon yields were attained for all pitch derived fibers.

The physical properties of, tensile strength, modulus, strain and resistivity were measured for the fabricated carbon fibers. The results are presented in Table 7. The results show that carbon fibers produced from the bituminous coal extracts, W.Ky and Pitt showed higher strengths compared to the fibers produced from the lower rank BT coal extracts.

Acknowledgements

The authors wish to acknowledge the financial support of the U.S. Department of Energy under contract number DE-AC22-91PC91040.

References

[1] Davies GO, Derbyshire FJ, Price R. An investigation of coal solubility in anthracene oil. J. Inst. Fuel (1977);50(404);121-6.

[2] Banerjee S, Chowdhuri SB, Banerjee DK, Prasad M, Dutta AC, Majumdar S, Roy AK. Solvent extraction of coal at low pressure with a coal tar oil solvent – anthracene oil. Indian J. Technol. (1981);19(5):204-9.

[3] Franck HG, Stadelhofer JW, Biermann D. Solubilization of bituminous coal in aromatic and hydroaromatic solvents. Fuel (1983);62(1):78-80.

[4] Chiba K, Tagaya H, Kobayashi T, Shibuya Y. Solvent extract liquefaction of coal with fractionated anthracene oil and recycle solvent. Ind. Eng. Chem. Res. (1987);26(7):1329-35.

[5] Berkowitz N, Calderon J, Liron A. Some observations respecting reaction paths in coal liquefaction. Fuel (1988);67(7):1017-19.

[6] Cahill P, Harrison G, Lawson GJ. Extraction of intermediate and low-rank coal with hydrogenated anthracene oil (HAO). Fuel (1988);67(11):1521-8.
[7] Sharma DK, Mishra S. Successive sequential extractive disintegration of coal in coal-derived solvents under ambient pressure. Energy Fuels (1989);3:641-46.
[8] Mishra S, Sharma DK. Solvent extraction and extractive disintegration of coal in anthracene oil. Fuel (1990);69(11):1377-80.
[9] Rosal R, Diez FV, Sastre H. Hydrogen-transferring liquefaction of two different rank coals employing hydrogenated anthracene oil as a donor solvent. Ind. Eng. Chem. Res. (1992);31(10):2407-12.
[10] Cloke M, Wang C. Liquefaction behaviour of the maceral groups in Point of Ayr coal using hydrogenated anthracene oil in a tube bomb at varying temperatures. Energy Fuels (1995);9(3):560-5.

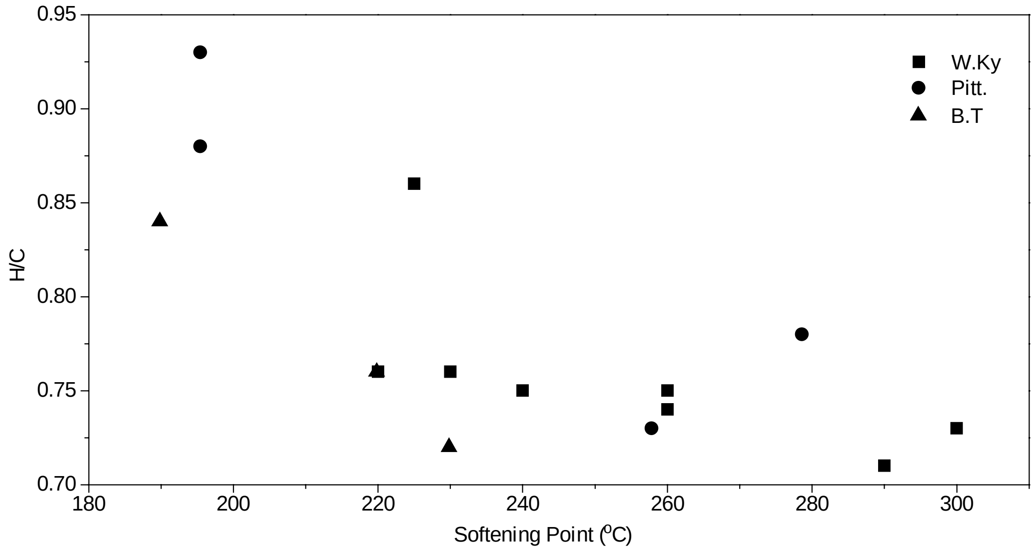

Figure 1. H/C versus softening point for extracted pitches.

Table 1. Proximate and ultimate coal analyses

Coal	Moisture (%)	Ash (%)	Volatiles (%)	Fixed C (%)	C (% daf)	H (% daf)	N (% daf)	S (% daf)	O_{diff} (% daf)
W.Ky	10.0	10.1	40.0	49.9	70.06	4.52	1.66	3.70	9.92
Pitt	2.2	7.8	39.5	52.7	76.22	4.95	1.53	2.48	6.95
BT	24.3	6.7	37.6	31.4	65.76	4.11	0.89	0.70	19.73

Table 2. Pitch extraction data summary.

Pitch	**Pitch Yield (% daf coal)**	**Coal Conversion (% daf coal)**	**Mass Balance (%)**	**Gas Yield (mL)**	**Soft Pt. (^{o}C)**
W. Ky 1	58.4	45.2	90.7	200	220
W. Ky 2	50.8	37.5	85.9	400	230
W. Ky 3	59.9	49.7	94.6	500	300
W. Ky 4	65.0	44.4	93.3	800	225
Pitt 1	37.5	25.0	84.8	<100	190
Pitt 2	40.4	30.3	84.9	<100	190
Pitt 3	40.7	35.9	91.8	100	270
BT 1	46.0	35.6	102.4	2200	220
BT 2	53.9	40.1	76.1	2500	230
BT 3	63.1	25.1	89.8	2000	190

Table 3. Proximate analysis summary coal extract pitches.

Pitch	**Moisture (%)**	**Ash (%)**	**Volatiles (%)**	**Fixed Carbon (%)**
W. Ky 1	0.06	0.07	68.1	31.8
W. Ky 2	0.11	0.07	53.5	46.3
W. Ky 3	0.06	0.16	46.9	52.9
W. Ky 4	0.14	0.05	58.8	41.0
Pitt 1	0.03	0.01	62.2	37.8
Pitt 2	0.02	0.01	61.7	38.3
Pitt 3	0.15	0.08	52.9	47.1
BT 1	0.07	0.23	63.8	35.9
BT 2	0.04	0.20	61.6	38.2
BT 3	0.03	0.26	61.5	38.2

Table 4. Ultimate analysis results for anthracene oil extracted pitches.

Pitch	**C (%)**	**H (%)**	**N (%)**	**O_{diff} (%)**	**Total S (%)**	**H/C**
W. Ky 1	83.7	5.4	1.4	8.5	0.88	0.76
W. Ky 2	85.0	5.4	1.7	6.3	1.53	0.76
W. Ky 3	85.8	5.2	1.7	5.5	1.61	0.73
W. Ky 4	83.4	6.0	1.6	7.6	1.47	0.86
Pitt 1	84.3	6.2	1.5	6.9	1.05	0.88
Pitt 2	82.7	6.4	1.6	8.2	1.13	0.93
Pitt 3	86.6	5.3	1.5	5.7	0.94	0.78
BT 1	86.9	5.5	1.3	5.7	0.47	0.76
BT 2	87.9	5.3	1.3	4.9	0.48	0.72
BT 3	85.4	6.0	1.4	6.8	0.42	0.84

Table 5. Carbon fiber fabrication data for extracted pitches.

Pitch	Spin Quality	Stabilization			Carbonization			Carbon Yield (%)
		Linear Shrink (%)	Weight Loss (%)	Status	Linear Shrink (%)	Weight Loss (%)	Status	
W.Ky 1	4	12	-5.8	3	13	41.9	3	54.7
W.Ky 2	3	8	0	3	12	41.8	3	58.2
W.Ky 3	0	n/a	n/a	n/a	n/a	n/a	n/a	n/a
W.Ky 4	3	12	1.9	3	15	33.0	3	67.0
Pitt 1	3	13	-7.7	3	14	41.0	3	47.7
Pitt 2	3	13	-2.8	3	14	32.6	3	65.5
Pitt 3	3	0	8	3	8	35.3	3	56.7
BT 1	3+	21	-13.1	1	14	38.7	1	46.7
BT 2	2	15	0.5	0	24	-35.8	0	64.0
BT 3	3	8	1.0	1	20	52.0	1	47.0

Spin Quality: 0 = unable to spin, 1 = strands, 2 = few s, 3 = >10 s, 4 = >1 min, 5 = >5 min..
Status: 0 = melted, 1 = stuck, 2 = slightly stuck, 3 = OK.
n/a = not applicable.

Table 6. Physical properties of extracted pitch derived carbon fibers.

Pitch	Diameter (μm)	Strength (MPa)	Modulus (GPa)	Strain (%)	Resistivity (m.Ω.cm
W.Ky 1	17.3	440	31	1.4	7.6
W.Ky 2	22.7	363	27	1.4	7.0
W.Ky 3	n/d	n/d	n/d	n/d	n/d
W.Ky 4	27.4	443	35	1.3	6.8
Pitt 1	23.9	435	28	1.5	7.2
Pitt 2	26.8	399	31	1.3	6.3
Pitt 3	22.2	426	36	1.2	6.2
BT 1	21.3	302	29	1.1	7.1
BT 2	n/d	n/d	n/d	n/d	n/d
BT 3	n/d	n/d	n/d	n/d	n/d

n/d = not determined