LOW SEVERITY EXTRACTION OF PITCH FROM COAL AS A PRECURSOR TO VALUE ADDED PRODUCTS - REVISITED.

A.J. Berkovich, C.J. Lafferty and F.J. Derbyshire
Center for Applied Energy Research
University of Kentucky
2540 Research Park Drive, Lexington, KY, USA, 40511.

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ABSRACT: This paper presents preliminary results from a detailed investigation into different methods of extraction of pitch from coal and their affect on the properties of the final pitch product. One such method is the use of cheap and readily available petroleum residues that act as solvents for pitch. Crude anthracene oil, a cheap petroleum residue was shown to extract a reasonable yield of high boiling point material from coal at low temperatures with no over pressure. A series of extractions at temperatures ranging from 200 to 450 °C were performed on coals differing in rank and heteroatom contents. The results indicate that maximum extraction yield occurs between 350 and 400 °C. The extraction capability of recycled anthracene oils recovered from prior extractions was also assessed. Carbon fibres from pitch extracts were produced and their physical properties assessed.

INTRODUCTION: The use of coal derived pitches as precursors for valued added carbon products is well known. As the range of applications for new carbon based products increases the potential exists to tailor precursor properties for specific applications, for example carbon fibres. This paper examines pitch extraction methods and how different extraction conditions effect the properties and performance of pitch derived carbon fibres as a lead into tailoring properties of extracted pitches.

Petroleum residues, such as anthracene oil and petroleum based solvents have been shown to be good solvents for high boiling point liquids from coal (coal derived pitches) [1-4]. However, previous work on coal solvent extraction using such solvents has usually involved pre-hydrogenation of the solvent as well as high gas over pressures during the extraction. Hydrogenation and high pressure extractions adversely affect the economic potential of a solvent extraction process. The aim of this paper was to prepare pitches using mild extraction conditions and assess the potential of these pitches as precursors to value added carbon products.

EXPERIMENTAL: Pitch extractions were performed in 50 mL stainless steel tubing bomb reactors which were heated in a fluidised sand bath while being shaken by a mechanical shaker. Coal samples were crushed to < 60 mesh and then slurried in different ratios with the solvent before being placed into the tubing bombs. Two different solvents were used, anthracene oil as well as panasol (a commercially available petroleum derived solvent). The solvents were not hydrogenated nor was any gas over pressure used during the extractions. Extraction temperatures ranged from 250 to 450 °C, with extraction between 10 minutes and 3 hours. After extraction, the reaction mixture was extracted in a Soxhlet apparatus using THF. The THF soluble fraction was then vacuum distilled to 300 °C at 1 mm Hg. The THF insoluble residue was dried in a vacuum oven and its mass used to calculate the yield of extracted material. The softening point of the extraction pitch material was measured. Typically a softening point of 200 to 240 °C was desired for ease of fiber forming and processing. The fiber forming and processing methods have been described elsewhere [5]. Coal samples from Northeast Wyoming's Black Thunder mine and Western Kentucky was used for the extraction experiments. Proximate analyses of the coals showed, Black Thunder contained: 8.89 % moisture; 5.76 % ash; 39.88 % volatile matter; 45.47 % fixed carbon, the Western Kentucky contained: 2.30 % moisture; 8.90 % ash; 34.42 % volatile matter; 53.45 % fixed carbon.

RESULTS and DISCUSSION: Mild condition solvent extractions were preformed on Black Thunder coal. The effect of temperature was examined first. Extractions with coal to solvent ratios of 1:2 with anthracene oil and panasol were performed at 200, 250, 300, 350, 400 and 450 °C for 1 hour. Figure 1 compares the effect of temperature on extraction yield for Black Thunder coal using anthracene oil and panasol. Figure 1 shows that anthracene oil produced a higher yield of pitch compared to panasol with the maximum extraction yield occurring at approximately 350 °C for anthracene oil and approximately 450 °C for panasol.
The effect of different extraction time was also examined. Again a coal to solvent ratio of 1:2 was used and extraction times of 10 minutes to 3 hours were examined. Figure 2 shows extraction yield versus extraction time. Inspection of Figure 2 shows that 80 % of the extraction yield is attained during the first 20 minutes.

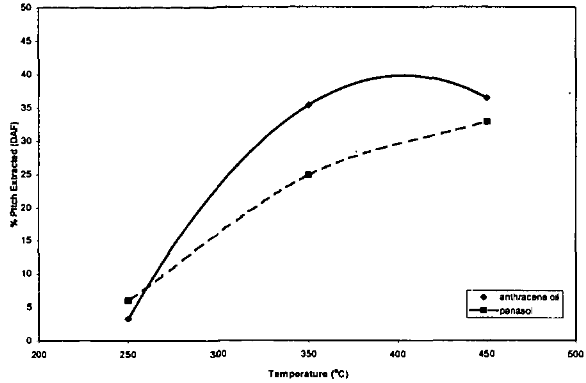

Figure 1 – Effect of temperature on extraction yield for Black Thunder coal.

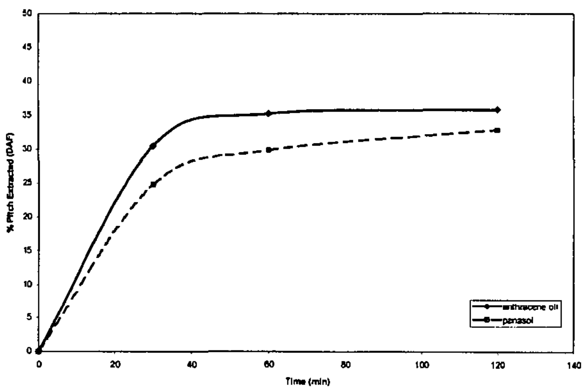

Figure 2 – Effect of time on extraction yield for Black Thunder coal.

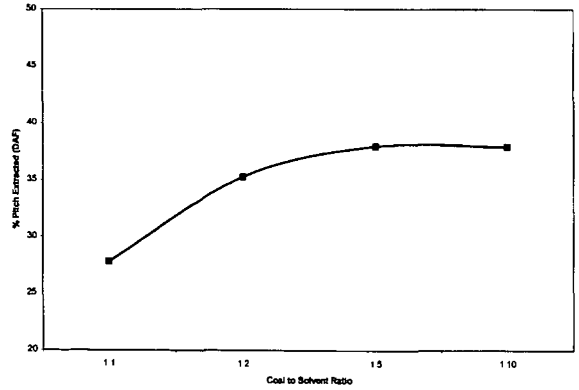

Figure 3 – Effect of increasing solvent concentration on extracted pitch yield

The effect of coal to solvent ratio was also examined, Figure 3 shows a plot of extracted pitch yield versus solvent to coal ratio where anthracene oil was used. Figure 3 shows that using coal to solvent ratios greater than 1:2 did significantly increase the pitch yield. From the results of these preliminary experiments the following extraction parameters were used for subsequent extractions: coal to solvent ratios of 1:2; extraction temperature, 350 °C; extraction time, 60 minutes. The re-use of solvent recovered from distillation was also investigated. Pitch extractions were preformed on Black Thunder coal using recycled solvent as well as mixtures of recycled and fresh solvent. Table 1 shows extracted pitch yields for these experiments. The results showed only a slight decrease in extraction yield for the recycled solvents compared to fresh solvent. The mixtures of fresh and recycled showed almost the same extraction capabilities as the fresh solvent.

Table 1 - Extracted pitch yields for recycled solvents, yields for fresh solvent shown in brackets.

Solvent	% Yield
recycled anthracene oil	28.3 (35.3)
recycled panasol	20.0 (24.82)
1:1 recycled anthracene oil and fresh anthracene oil	35.2
1:1 recycled panasol and fresh panasol	26.8

A summary of pitch extraction conditions and yields is shown on Table 2. The results show that extractions preformed on Black Thunder coal under mild conditions have lower extracted pitch yields compared to those using more severe conditions. Tables 2 and 3 contain characterisation data for the extracted pitches. The results show that pitches extracted under mild conditions have very similar characteristics to those extracted under severe conditions. More importantly however, are the characteristics of the fibres formed from the extracted pitches.

Table 2 – Summary of extraction yields and extraction methods.

Coal	Extraction Method	% Yield	Extracted Pitch
Black Thunder	a.oil; 350; 60	35.3	BT1
Western Kentucky	a.oil; 350; 60	90.6	WK1
Black Thunder	pan; 350; 60	24.8	BT2
Western Kentucky	pan; 350; 60	89.2	WK2
Black Thunder	a.oil; 370; 60; H_2	90.0	BT3

Extraction Method: solvent; temperature (°C); time (min)
a.oil = anthracene oil, pan = panasol

Table 3 – Summary of extracted pitch properties.

Pitch	Softening Point (°C)	Ultimate Analysis (% DAF) C	H	N	O	S
BT1	220	87.6	5.03	1.1	1.6	0.5
WK1	210	91.1	4.5	1.7	1.7	1.0
BT2	220	85.7	5.8	1.4	6.8	0.3
WK2	260	90.2	4.3	1.8	2.5	1.1
BT3	230	87.1	6.0	1.4	5.2	0.3

Carbon fibres formed from the extracted pitches were tested for strength, modulus and resistivity. A summary of these properties is shown in Table 3. Table 3 shows that the physical properties of the carbon fibres formed from pitches extracted under severe and mild conditions are similar.

Table 3 – Summary of properties of pitch derived carbon fibers.

Extracted Pitch	Strength (MPa)	Modulus (GPa)	Resistivity $m\Omega cm^{-1}$
BT1	400	82	8.0
WK1	576	86	47
BT2	319	63	16.7
WK2	347	69	16.3
BT3	380	n/a	27.3

The results show that although extraction yields are lower for the mild condition extractions compared to the severe condition extractions, the properties of the extracted pitches and pitch based fibres are similar. Therefore there is the potential to produce pitch from coal using a low temperature and low pressure method without sacrificing the performance of the final carbon product.

CONCLUSIONS: Low severity solvent extraction of coal using anthracene oil and panasol were performed to produce a high boiling point liquid, pitch. The pitch extraction yields of the mild condition techniques were compared to those performed under more severe conditions. Although the low severity extractions showed lower yields the chemical characteristics of the extracted pitches were similar to those extracted under more severe conditions. The physical characteristics of carbon fibres formed from pitches extracted under mild and severe conditions were similar.

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