SUPERCRITICAL FLUID EXTRACTION OF GOYNUK OIL SHALE AND AVGAMASYA ASPHALTITE DERIVED PITCHES USING CO_2

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Introduction

Supercritical fluid (SCF) extraction is a separation technique that uses the large changes in solvent strength a compressed liquid can exhibit near its critical point [1]. In comparison with liquid solvents, the supercritical fluid has high diffusivity and low density and viscosity, thus allowing rapid extraction and separation. The solvent power of the supercritical fluid can be varied over a wide range by varying pressure or temperature and by adding organic modifiers [2,3]. Reduction in the amount of lower molecular weight components is required to produce suitable precursor pitches for production of isotropic carbon fibers. A relatively high softening point, to limit stabilisation time, is needed in pitches for isotropic fibers [4]. It is possible to produce pitch fractions having both different average molecular weights and narrower molecular weight ranges than the parent pitch by SCF extraction [1]. In this study, SCF extraction using CO_2 with and without solvent modifier has been investigated as a potential fractionation technique for improving the properties of pitch precursors produced by air-blowing, N_2-blowing, and vacuum distillation of tar materials which were derived from the copyrolysis of Goynuk oil shale (GOS) and Avgamasya asphaltite(AA).

Experimental

SCF extraction was performed with a ISCO Model 260D syringe pump. An air-blown pitch (S-Air) derived from Goynuk oil shale (GOS) tar, a nitrogen-blown pitch (S5A5-N_2) derived from 50%GOS-50%AA tar, a vacuum distilled and extracted with hexane, respectively, pitch (S7A3-VH) derived from 70%GOS-30%AA tar were extracted using CO_2 and CO_2 modified with hexane at different temperatures and pressures. Extractions were carried out dynamically for 30 minutes. For each extraction process 1g of pitch precursor supported on 2g of diatomaceous earth hydromatrix directly in the 5 ml extraction cell. Modifier was spiked onto the sample matrix mixer in the extraction cell. The extracts were trapped in vials containing 5-10ml of DCM. These pitches were also compared to high a softening point pitch, Aerocab75. In order to determine the effectiveness of the extraction process, samples of the original pitches, extracts and residues were analysed by size exclusion chromatography (SEC), gas chromatograpy (GC), and mass spectroscopy (MS), as described elsewhere [5].

Results and Discussion

The general properties of the pitches studied are shown in Table1. Percentage of the extract recovered from the pitches for various temperatures and pressures using CO_2 and CO_2 modified with 0.3 ml hexane are presented in Table2. The results show that the extraction recoveries of pitches were increased when the temperature and pressure increased. However, the effect of the temperature and modifier is not as significant as the effect of pressure. The increase in pressure increased the density. Although the increase in temperature reduced the density, the solubility increased. As seen from the Table2 the solubility of light molecular weight fraction was increased with increasing pressure for the pitches in which hexane was used as a modifier.

Conclusions

The high recoveries of extracts from S-Air pitch (62.0%) are probably due to the greater content of low molecular weight hydrocarbons in this material.

References

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Table1. General properties of the pitches

Pitches	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O[a] (wt%)	H/C	CY (wt%)	SP (°C)
S-Air (1.5hrs,270°C)	87.55	9.60	1.05	1.70	0.10	1.32	ND	110
S5A5-N_2(1hr,300°C)	86.45	7.10	1.25	3.30	1.90	0.98	ND	160
S7A3-VH	81.95	7.35	2.40	3.85	4.45	1.08	62.20	180
Aerocab75	93.15	5.10	T/N	1.50	0.25	0.66	75.00	230

CY: carbon yield, SP: softening point, a: by difference, T/N:trace/nil, ND: not determined

Table2. Extraction recovery of pitches using CO_2 and CO_2 modified with 0.3 ml hexane

Conditions			Percent Recovery (wt%)			
Solvent	Temp. (°C)	Press. (atm)	S-Air Aerocab75	S5A5-N_2		S7A3-VH
CO_2	100	200	30.6	28.9	3.4	0.2
CO_2-hexane	100	200	35.9	8.9	5.6	0.3
CO_2	100	400	38.3	40.3	7.1	1.6
CO_2-hexane	100	400	39.6	9.4	13.2	-
CO_2	150	200	40.6	31.9	4.0	0.6
CO_2-hexane	150	200	43.9	33.3	6.7	1.1
CO_2	150	400	59.3	35.7	12.3	2.5
CO_2-hexane	150	400	62.0*	36.2	29.1	-