

# Production of Mesophase Pitch from Coal Tar and Petroleum Pitches using Supercritical Fluid Extraction

**Mustafa Z. ÖZEL**

*Department of Chemistry, University of Pamukkale, Denizli-TURKEY*

**Keith D. BARTLE**

*School of Chemistry, University of Leeds, Leeds, LS2 9JT, U.K.*

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Supercritical fluid extraction (SFE) is currently being investigated as a possible technique in the production of high quality mesophase pitch from coal tar and petroleum pitches. Mesophase pitch is used to make high technology products, such as carbon fibre. The conventional production of mesophase pitch initially involves the removal of low molecular weight species from coal tar and petroleum pitches. The remaining residue is then transformed into a mesophase pitch through a polymerisation process. The aim of this study involves the extraction of light molecular weight species using SFE. Both petroleum and coal tar pitch contain complex aromatic molecules with an average molecular weight of 200 to 800, whereas mesophase pitch has a molecular weight range of about 1200 to 1300. Toluene, heptane, pentane and methanol were added to CO<sub>2</sub> as modifiers at temperatures between 80 and 200°C and at pressures of 200 to 400 atm. The effect of the temperature and pressure on extraction yield was found to be less than that of modifier addition and the results showed that the extraction yields were 19% and 33% from the petroleum and coal tar pitches respectively.

## Introduction

When an isotropic pitch is pyrolysed between 300°C and 500°C in an inert gas atmosphere, an anisotropic liquid crystalline phase, which is known as carbonaceous mesophase, emerges. Supercritical fluid extraction (SFE) has been investigated for the production of the mesophase pitch used to make high performance carbon fibre<sup>1</sup>. Previous works<sup>1,2,3</sup> have focused on the extraction of petroleum pitch using supercritical toluene in a vapour-liquid equilibrium at temperatures from 306°C to 400°C and pressures from 70 atm to 140 atm.

Carbon fibre has been prepared from a synthetic polyvinyl chloride<sup>4</sup>, polyacrylonitriles<sup>5</sup>, naphthene<sup>6</sup>, coal tar pitch<sup>7</sup> and petroleum pitch<sup>1,2,3</sup>. Economically, isotropic pitches, such as coal tar or petroleum pitches appear to be the more promising group of carbon fibre precursors since they are the cheapest starting materials.

The first step of producing carbon fibre involves the removal of low molecular weight species (extraction) followed by heat treatment at temperatures between 300 and 500°C. This affects the condensation of smaller aromatics into multi-ring systems with molecular weights of ca. 1200-1400. The transformation of

isotropic pitch to mesophase pitch is presumed to involve some kind of polymerisation reaction with the resultant mesophase quantity being normally 60-90% mesophase. An ideal mesophase pitch for spinning is one with a high mesophase content, a high percentage of fixed carbon and a high fluidity temperature (<450°C). SFE is becoming an increasingly important tool in analytical science and processing. It has several distinct advantages over classical solvent extraction techniques, including speed, low toxicity and cost.

## Natures of isotropic and mesophase pitches

Isotropic pitch has considerable potential as an inexpensive material for the economical production of high performance carbon fibre. Both coal tar and petroleum pitches contain high molecular weight carbonaceous materials and are residues from coal tar and crude oil distillation, respectively. Petroleum pitch is preferable to coal tar pitch as a starting material as it has a lower proportion of undesirable lighter components. Both pitches have wide molecular weight distribution with their average ranging between 180 and 600<sup>8,9</sup>. These complex molecules are basically classified into four groups: saturates, naphthene aromatics, polar aromatics and asphaltenes. Saturates are low molecular weight aliphatic compounds. Naphthene aromatics are made up of low molecular weight aromatics. Polar aromatics contain higher molecular weights and more heterocyclic rings. The asphaltene fraction has the highest average molecular weight.

## Mesophase formation

The first step in mesophase production involves the removal of light molecular weight species. This happens in conjunction with the free radical reaction of small aromatics to form polyaromatic molecules with molecular weights of about 1200, suitable for the formation of mesophase. The evaporation of the volatiles is important since they interfere with the formation of mesophase. When the isotropic phase has passed, the mesophase will react. All the existing methods of purification merely depend on the extraction. Successive extraction with solvents such as toluene, quinoline and hexane remove the soluble fraction, and ultimately the insoluble fraction is used to form mesophase.

Riggs<sup>10</sup> used solvent extraction on the isotropic pitch, which is said to produce mesophase pitches spinable below 400°C. It is thought that the low molecular weight species can be removed using a suitable solvent (e.g. toluene) prior to conventional heat treatment. Hutchenson<sup>2</sup> described a flow apparatus for measuring phase equilibrium data in mixtures of solvent and pitch at temperatures up to 400°C and pressures up to 76 atm using supercritical toluene. Isotropic pitch was successfully separated into narrow molecular weight bands in this region with no more than 20% of the pitch being extracted in the vapour phase<sup>2</sup>. Bolanos<sup>3</sup> has used a similar system to extract petroleum pitch at near critical conditions; 50-80% of the pitch was extracted from the solvent-rich liquid phase.

Greinke<sup>11</sup> used Size Exclusion Chromatography (SEC) to follow the molecular weight change of the isotropic and anisotropic phases during mesophase formation. Two pitches with different mesophase contents were prepared. The isotropic and anisotropic phases in each of them were separated by centrifugation into toluene soluble (TS) and insoluble (TI) fractions. These were obtained from the separated phases using Soxhlet extraction. The TI fraction was reductively ethylated to solubilize the insoluble fractions prior to injection into the SEC column. They found that the average molecular weight of the mesophase remained approximately constant at around 910, but that of the isotropic phase increased linearly with heat treatment time. The longer the treatment, the nearer was the molecular weight to that of the mesophase. This is

thought to be due to polyaromatic molecules in the mesophase being initially relatively unreactive and to there being a preferential movement of the polymerised molecules from the isotropic to the carbonaceous mesophase<sup>11</sup>. The reductive alkylation step solubilises the mesophase for SEC by introducing alkyl side groups into the polyaromatic molecules; it is believed that the introduction of a steric effect greatly affects the  $\pi - \pi$  interaction between adjacent molecules<sup>11</sup>.

## Heat treatment and mesophase pitch characterisation

During the heat treatment of pitch in the temperature range of 300-500°C, the polyaromatic mesophase was formed<sup>8</sup>. The processes are the volatilisation of low molecular mass constituents of the pitch and polymerisation and condensation reactions of the hydrocarbons. Hydrogenation, fragmentation, alkylation or dehydrogenative polymerisation can take the place of this heat treatment. Thermal cracking of the aliphatic side group at the alpha position in the aromatic molecules leads to the formation of free radicals. These aromatic free radicals react together to give aryl-aryl linkages, building up the polyaromatic molecules to form a carbonaceous mesophase. Higher carbon yield and lower mass loss after heat treatment is preferable.

Isotropic and mesophase pitches are characterised by standard procedures, which include elemental analysis, softening point and solubility tests. Since the pitch is a supercooled liquid, the transition from solid to liquid is not very distinct and the pitch does not have a true melting point but it gradually softens and becomes less viscous with increasing temperature<sup>9</sup>. Softer pitch is preferable for producing the mesophase pitch. Thus, it is important to determine the softening point. Hot stage microscopy can be used to obtain this.

In this study, we produced high quality mesophase pitch from coal tar and petroleum pitches using supercritical CO<sub>2</sub> with added modifiers. This method yielded similar results to traditional methods but has some advantages over them, as will be outlined later.

## Experimental

### Materials

Ashland 240 petroleum pitch was obtained from the Institute National del Carbon (Oviedo, Spain). Coal tar pitch was provided by the Institute for the Processing of Coal (Zabze, Poland). Both pitches were ground using an electrical grinder, and then sieved to 52 mesh. HPLC grade toluene, dichlorometane (DCM), chloroform, tetrahydrofuran (THF), methanol, pentane and heptane were used as modifiers or collection solvents. All other chemicals used were analytical grade reagents. This work was carried out in Leeds University's Chemistry Department.

### Laboratory-built extraction system

For extraction involving supercritical fluids, the instrumentation demands a number of components. Requirements are firstly a fluid source, usually a syringe pump that can deliver high pressures (above the critical pressures of the fluid), a temperature controlled oven to maintain extraction cell at a constant temperature (above the critical temperature of the fluid) and a collection device.

The extraction system was used for the extraction of coal tar and Ashland-240 petroleum pitches. The supercritical fluid apparatus consisted of a Varian 8500 syringe pump delivering pressurised CO<sub>2</sub> (BOC

Ltd, London, UK), to an extraction cell. The cell is made from a stainless steel tube (5 ml volume), fitted with two HPLC column end fittings (Manchester Valve Co., UK) which have a 2  $\mu\text{m}$  frit at both ends. The cell was placed inside a PYE Series 104 gas chromatography oven. A needle valve was fitted between the cell and restrictor (10-15 cm of 50-100  $\mu\text{m}$  i.d.  $\times$  375  $\mu\text{m}$  o.d. fused silica capillary), which was used to maintain the pressure in the extraction cell. The end of the restrictor was immersed in collection solvent (DCM). The flow rate of the fluid ( $\text{CO}_2$ ) was measured by a bubble flow meter connected to the collecting vial vent. Flow rates between 1.5 and 2.5 ml/min were obtained. Dynamic extraction was carried out for 30 minutes in each experiment.

### **Size Exclusion Chromatography**

The size exclusion chromatography (SEC) system consists of a Kontron 422 HPLC pump, a Rheodyne 7125 injector with a 20  $\mu\text{l}$  sample loop, two SEC columns (Alltech Jordi Gel DVB 500 A° and 100 A°, 5 $\mu\text{m}$  (polydivinylbenzene) packing, length 250 mm, i.d. 10 mm), a UV detector (Applied Chromatography Systems ltd model ACS-750/11 with detector cell volume 10  $\mu\text{l}$  and wavelength 254 nm). Tetrahydrofuran (THF) was used as a mobile phase with a flow rate of 1 ml/min. The signals from the detectors were sent to a PC with a data capture unit and a custom-made data capture program, and to a chart recorder. Ashland-240 petroleum pitch, coal tar pitch and their SFE extracts and residues were dissolved in THF before analysis.

### **Extraction from Ashland-240 petroleum pitch and coal tar pitch**

For each extraction process, 1 g of either the Ashland-240 petroleum pitch or coal tar pitch, supported on 2 g of pelletised diatomaceous earth hydromatrix (Varian, Harbor City, CA, USA), was placed directly into the 5 ml extraction cell. Modifier was spiked onto the sample-matrix mixer in the extraction cell. Extractions were performed at various temperatures (80-200°C) and pressures (200, 300, 400 atm). The sample was extracted for 30 minutes dynamically through a 15 cm, 75  $\mu\text{m}$  i.d. silica capillary restrictor and the extracts were trapped and collected in 21 ml vials containing 5-10 ml of DCM. DCM was the chosen solvent as it is suitable for trapping analytes of interest and for use in gas chromatography. The amounts of extracted material were determined by evaporating DCM under a  $\text{N}_2$  stream on a hot plate and weighing the residue to determine recovery.

## **Results and Discussion**

Ashland-240 petroleum pitch and coal tar pitch were extracted by  $\text{CO}_2$  and  $\text{CO}_2$  modified with co-solvents (toluene, heptane, pentane and methanol) at temperatures of 80, 140 and 200°C and pressures of 200, 300 and 400 atm. Extracts (light fractions) and residues (heavy fractions) were analysed by size exclusion chromatography (SEC).

### **Extraction from Ashland-240 petroleum pitch using pure $\text{CO}_2$**

Extractions were carried out dynamically for 30 minutes. Extracts were trapped into 10 ml of dichloromethane (DCM). The amount of non-volatile extracted material was determined by evaporating the DCM under a  $\text{N}_2$  stream on a hot plate and weighing the residue. Table 1 shows the percentage of the extract recovered from

the Ashland-240 petroleum pitch at various temperatures and pressures using CO<sub>2</sub>. The density of CO<sub>2</sub> increases when the pressure is increased at constant temperature, which enhances the solubility of various solutes. The results show that the extraction recoveries of Ashland-240 petroleum pitch increased when the temperature and pressure were increased. However, the effect of temperature is not as significant as the effect of pressure.

**Table 1.** Extraction recovery from Ashland-240 petroleum pitch at various temperatures and pressures using pure CO<sub>2</sub> (30 minutes dynamic extraction).

Pressure (atm)	Percent Recovery (wt%)		
	80°C	140°C	200°C
200	2.6	2.0	3.3
300	4.1	4.3	4.6
400	5.2	5.0	6.4

### Extraction from A-240 petroleum pitch using CO<sub>2</sub> modified with co-solvents

The addition of a small amount of solvent to the supercritical fluid can result in an increase in the solubility of solutes<sup>12</sup>. Polar solvents usually cannot be used as pure supercritical solvents because their critical temperatures are too high. Instead, CO<sub>2</sub> is used as a main solvent and a small amount of modifier including polar, acidic or basic groups is added in order to increase the polarity and density of the solvent. The selection of the modifier is determined by the volatility of the compounds involved and the solute-modifier interactions in the supercritical phase<sup>12</sup>. Modifier can be added to the system either on-line or off-line. Toluene is a major solvent which has been used often in the petroleum and coal industry. Toluene has also been used as a supercritical fluid to extract petroleum pitch at 76 atm and 400°C<sup>2</sup>; under these conditions, no more than 20% of the light fraction was extracted. In this study, toluene (1 ml for each extraction) was used as a modifier and Table 2 shows that 18.8% of the light fraction of Ashland-240 petroleum pitch was successfully removed under high temperature (200°C) and high pressure (400 atm) during 30 minutes of dynamic extraction. The solubility of the light molecular weight fraction increased sharply with increasing pressure (Table 2). Aliphatic (pentane, hexane) and alcoholic (methanol) solvents were also used as alternative modifiers. Table 3 shows how the modifiers and temperatures affect the extraction efficiency from Ashland-240 petroleum pitch. We have lower recovery at 80°C because at this temperature the volatility of the fractions is low. When we increase the temperature to 140°C, the volatility sharply increases, which in turn increases the solubility of the fractions and thus the recovery rates. It can be noted that a further increase in temperature to 200°C gave the best results in the experiment for this same reason. The results show that 15-19% of the light fraction of Ashland-240 petroleum pitch were extracted using CO<sub>2</sub> modified with co-solvents (200°C, 400 atm). Similar results have been obtained in ref. 1 with supercritical toluene. However, modified CO<sub>2</sub> is preferable as a supercritical fluid over supercritical toluene since CO<sub>2</sub> is a clean, environmentally friendly and non-toxic solvent.

### Extraction from coal tar pitch

Methanol and heptane were chosen as modifiers of CO<sub>2</sub>. Toluene was not chosen as a modifier in the extraction from coal tar pitch due to its toxic effects and also because of the desire to try something new, as toluene is very commonly used. Pentane, was not used because of its great similarity to heptane and heptane

was used to represent both. Table 4 shows the effects of the modifiers on the extraction recovery from coal tar pitch using CO<sub>2</sub>. Extraction was carried out for 30 minutes dynamically at 400 atm. A comparison of the Ashland-240 and coal tar pitch extracts shows that the removal of the light fraction from coal tar pitch is significantly more than from the Ashland-240 petroleum pitch under the same conditions. The recovery from the extraction from coal tar pitch using pure CO<sub>2</sub> is slightly higher than that from the Ashland-240 petroleum pitch using toluene-modified CO<sub>2</sub>. The high recoveries of extracts from coal tar pitch (33%) are probably due to the greater content of low molecular weight hydrocarbons in this material.

**Table 2.** Extraction recovery from Ashland-240 petroleum pitch at various temperatures and pressures using CO<sub>2</sub> modified with toluene (1 ml toluene, 30 minutes dynamic extraction).

Pressure (atm)	Percent Recovery (wt%)		
	80°C	140°C	200°C
200	1.8	4.7	7.0
300	2.9	12.8	13.6
400	4.6	14.2	18.8*

**Table 3.** Temperature and modifier effects on extraction efficiency from Ashland-240 petroleum pitch (1 ml modifier, 400 atm, 30 minutes dynamic extraction).

Modifier	Percent Recovery (wt%)		
	80°C	140°C	200°C
None	5.2	5.0	6.4
Toluene	4.6	14.2	18.8*
Heptane	2.5	13.7	18.1
Pentane	2.4	12.9	17.1
Methanol	1.3	11.9	14.6

**Table 4.** Effects of temperature and modifier on extraction efficiency from coal tar pitch (1 ml modifier, 400 atm, 30 minutes dynamic extraction).

Modifier	Percent recovery (wt%)		
	80°C	140°C	200°C
None	2.5	16.5	26.0
Heptane	3.5	20.0	33.1*
Methanol	3.3	18.3	28.1

## Analysis of pitches, extracts and residues by SEC

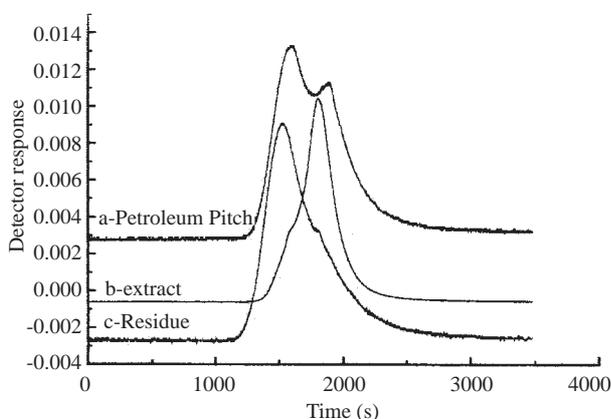
To determine the effectiveness of the extraction process, samples of the original Ashland-240 petroleum pitch and coal tar pitch extracts and residues were analysed by SEC to compare the molecular weight distributions. The range of molecular weights covered by the SEC column overlaps that of normal GC in the lower range. This provides a convenient means of detecting the presence of any heavier components which do not elute from the GC column.

Figure 1 shows the SEC chromatogram for the Ashland-240 petroleum pitch, SFE extract (1 ml toluene, 400 atm, 200°C and 30 minutes dynamic extraction) and the residue after extraction. When compared with polystyrene standards, this range corresponds to molecular weights from 100 to 7000. The

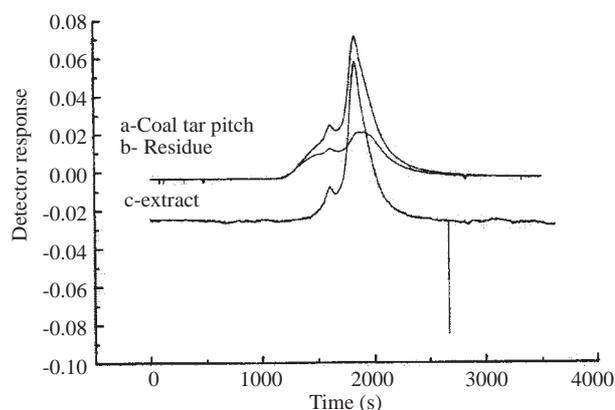
SEC effluent contains two fractions; the first fraction is a high molecular weight material with molecular weight distribution of around 500-7000. The second fraction has a molecular weight distribution between 100 and 500. Comparison of the molecular weight distributions of the three chromatograms confirms that a significant fraction of the low molecular weight species have been removed from the Ashland-240 petroleum pitch by SFE. The process looks very promising and the residue is ready for heat treatment.

Figure 2 displays the SEC for the coal tar pitch, SFE extract (1 ml heptane, 400 atm, 200°C and 30 minutes dynamic extraction) and the corresponding residue. The SEC chromatogram of coal tar pitch can be divided into three fractions. The first fraction has a small amount of high molecular weight material (molecular mass distribution is around 2500-5000), the second fraction contains a molecular weight distribution of 500-2500 and the third fraction contains a large amount of low molecular weight material (ca. 100-500). It can be seen from the chromatogram that the coal tar pitch contains a large amount of low molecular weight compounds. CO<sub>2</sub> modified with heptane or methanol did not extract the light fraction successfully. The residue still contains light material, which may interfere with the mesophase formation during the heat treatment.

Examination of the molecular weight distribution of the Ashland-240 petroleum and coal tar pitch extracts and residues from chromatograms (Figures 1 and 2) shows that a significant fraction of the low molecular weight species have been removed using SFE. For the Ashland-240 petroleum pitch, SEC of the residue clearly indicates that predominantly the low molecular weights are successfully being removed (18.8%). The coal tar pitch residue still contains low molecular weight compounds, although a considerable amount of them have been removed (33.1%).



**Figure 1.** Size exclusion chromatograms of Ashland-240 petroleum pitch, extract and residue (1 ml toluene, 400 atm, 200°C and 30 minutes dynamic extraction).



**Figure 2.** Size exclusion chromatograms of coal tar pitch, extract and residue (1 ml heptane, 400 atm, 200°C and 30 minutes dynamic extraction).

**Table 5.** Elemental analysis of Ashland-240 petroleum pitch, coal tar pitch and their residues after extraction.

Element (%)	Sample			
	Ashland-240 pitch	Ashland-240 residue	coal tar pitch	coal tar pitch residue
C	91.05	92.4	91.8	92.75
H	5.35	5.05	4.25	4.2
N	trace	0.45	1.0	1.3
S	2.2	2.3	0.4	0.65
H/C	0.059	0.055	0.046	0.045

## Conclusion

The purpose of this work is the production of high quality mesophase pitch from Ashland-240 petroleum and coal tar pitches using SFE. Light fractions were removed from the sample matrix by SC-CO<sub>2</sub> with the addition of organic modifiers. Methanol, heptane, pentane and toluene were successfully used as modifiers. Higher temperatures and pressures enhanced the extraction recovery of light molecular weight compounds using pure CO<sub>2</sub>, but modifying the CO<sub>2</sub> with co-solvents had a greater effect. Approximately 19% and 33% of light fractions were removed from the Ashland-240 petroleum pitch and the coal tar pitch, respectively. Following the extraction, both pitches, extracts and residues were characterised by SEC. The aromatic character of the pitches had increased in both cases. This characterisation of pitches, extracts and residues has shown that Ashland-240 petroleum pitch seems a very promising starting material from which to produce high performance mesophase pitch.

## Acknowledgements

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