

## Characterisation of Reactants and Products in Coal-Petroleum Co-processing

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### INTRODUCTION

Over the last few years a number of processes have been developed for the direct liquefaction of coal to distillate fuels. Typically these processes involve thermal degradation of the macromolecular coal structure followed by hydrogenation to stabilise the degraded material and adjust the hydrogen to carbon ratio of the products. One such process, developed by British Coal, is Liquid Solvent Extraction (LSE) (1). This is a two stage process in which coal is firstly digested in a process derived solvent. The resulting coal liquids are then hydrocracked and distilled to give a range of light oil fractions and a residue which is recycled to the extraction stage. Since the solvent stream is generated from the final coal-derived products the extent of hydrocracking has to be limited. In principle this problem could be alleviated by supplementing or replacing the recycle solvent stream with heavy petroleum fractions which are cheap and have a higher H/C ratio than the coal derived solvents.

In this paper we report on the preliminary results from an EEC funded project to examine the viability of incorporating petroleum oils into the existing LSE process. Methods have been developed for the characterisation and assesment of potential solvent streams and also for the determination of product distributions in co-processed mixtures.

### SAMPLES AND EXPERIMENTAL

The petroleum samples investigated so far include two atmospheric residues ('A' and 'B'), one vacuum residue ('C') and two whole crudes ('O' and 'M'). The crudes O and M were distilled to give vacuum residues boiling > 475°C whilst the three distillation residues were investigated as received.

The distillation residues were characterised by fractionation on silica into saturate, aromatic and polar compound classes (2). The aromatic fractions were further separated into mono, di and poly aromatics on neutral alumina (3). The C-5 and C-7 asphaltene contents of the crudes and residues were also determined. The <sup>1</sup>H NMR spectra of all fractions were recorded and form the basis for assessing solvent quality.

Point-of-Ayr (POA) coal was co-processed in two and three component systems containing petroleum fractions and petroleum fractions/anthracene oil respectively under a range of conditions. This work forms a separate part of the project and is discussed more fully in a separate paper by Caygill *et al* (4).

In order to assess the relative contributions of coal and petroleum derived asphaltenes in the co-processed residue size exclusion chromatography has been used. Briefly, mixtures with differing proportions of coal and petroleum derived asphaltenes were introduced onto an analytical scale PL Gel SEC column with UV detection. From the combined, overlapping, coal and petroleum peak areas a calibration graph was constructed and used to determine the relative contributions of the two asphaltenes to the co-processed residues.

To make a direct comparison between differing solvents a Solvent Dissolving Index was determined for the POA coal. Essentially, the coal was processed in a tubing bomb reactor (420 °C for 60 mins.) using hydrogenated anthracene oil (HAO) as a hydrogen donor solvent. In a series of runs the HAO was progressively diluted with naphthalene thus causing a progressive dilution of hydrogen donors.

## RESULTS AND DISCUSSION

Chromatographic analysis of the petroleum residues (eg. atmospheric residue A; Table 1) indicates that they contain a large amount of saturates. Although these materials are generally regarded as not participating in the liquefaction reactions, if present in large quantities they may have an anti-solvent effect and therefore their removal is desirable (5). Whilst removal of n-alkanes is facilitated by the use of urea adduction, removal of branched and cyclic alkanes presents more of a problem.

Table 1  
Analytical Data For Atmospheric Residue A

	Total	Asph.	Sats.	Arom.	Polars	
%	-	21.2	13.6	54.3	15.8	-
C	83.3	83.0	86.7	84.0	80.2	80.4
H	10.0	8.25	12.9	10.1	9.6	9.5
N	0.8	1.35	0.3	0.5	1.2	0.7
S	6.4	8.05	0.0	3.8	4.5	5.5
H/C	1.44	1.19	1.79	1.44	1.44	1.42
H <sub>AR</sub>	6.1	9.3	1.8	8.5	7.5	7.0
H <sub>α, 2</sub>	0.5	1.9	0.0	2.0	3.0	1.9
H <sub>α</sub>	16.0	18.9	6.5	23.6	20.6	16.3
H <sub>β</sub>	57.3	51.9	63.9	55.3	53.9	56.6
H <sub>γ</sub>	20.2	18.1	27.8	10.6	15.0	18.2

Removal of asphaltenes from the residues reduces the aromaticity of the remaining material. This is likely to make the remaining n-pentane solubles less suitable as a process solvent. Aromatic species probably participate in hydrogen shuttling reactions and increase radical lifetimes, thus enhancing the probability of radical stabilisation by hydrogen transfer (6). The nature of the aromatic groups in the asphaltene and polar fractions is currently being investigated by electrochemical methods (7).

Figure 1 shows the superimposed SEC traces obtained from a coal liquid and a petroleum derived asphaltene injected onto the column separately. Considerable overlap of the two components is evident and precludes the measurement of coal/petroleum asphaltene ratios in co-processed mixtures directly from the chromatogram. However, since the UV detector is more sensitive to coal derived asphaltenes than petroleum derived fractions, the total peak area is dependent on the ratio of the two types of asphaltene in the mixture. Figure 2 shows a plot of peak area verses percentage of coal derived asphaltene for mixtures of different coal and oil derived asphaltenes. It should be noted that, although the asphaltenes were obtained from different sources, all of the points fall broadly on the same straight line. A least squares treatment of the data gives a gradient of  $0.100 \pm 0.008$  %coal/unit area. For individual samples, however, the fit is significantly better (eg.  $0.090 \pm 0.002$  %coal/unit area). Using the plot as a calibration it is possible to estimate the proportions of petroleum and coal derived asphaltene in a co-processed product stream.

Atmospheric residue A was co-processed with Point-of-Ayr coal (48.7% POA/410 °C/30 mins.) and the asphaltenes separated from the product mixture. Using the

calibration it was estimated that, of the 8.1% of asphaltene obtained, 62% of it was coal derived. This result agrees well with the findings of Steer et al (8) using isotopic mass balance calculations. The high percentage of coal contributing to the asphaltene is likely arise from the progressive breakdown of the coal structure to preasphaltenes, asphaltenes and then n-pentane solubles thus causing a preferential increase in coal derived species in the high molecular mass fractions.

Figure 3 shows the SDI calibration for POA coal and HAO with naphthalene as a diluent. The horizontal region of the plot indicates that the solvent mixture contains an excess of hydrogen donors. At higher naphthalene concentrations the extraction yield gradually decreases until the minimum extraction is reached at 100% naphthalene (ie no hydrogen donors). The Solvent Dissolving Index is defined as 0 at 100% naphthalene and 20 at the onset of maximum extraction.

In the standard SDI method developed by Clarke et al (9) the test liquefaction solvent is diluted with naphthalene (typically 50%). For the analysis of potential petroleum derived solvents the presence of naphthalene may result in erroneously high dissolving index due to it increasing the average aromaticity of the solvent mix and, therefore, its ability to solubilise the highly aromatic coal derived species.

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#### REFERENCES

- 1) Davies, G.O. *Chem. and Ind.* 1978, 15, 560.
- 2) Marsh, M.K.; Smith, C.A.; Stokes, B.J.; Snape, C.E. *J. Chromatography* 1984, 283, 173.
- 3) Schiller, J.E.; Mathiason, D.R. *Anal. Chem.* 1977, 49, 1225.
- 4) Caygill, R. et al (These Preprints).
- 5) Winschel, R.A.; Robbins G.A.; Burke, F.P. *Fuel* 1987, 66, 654.
- 6) Derbyshire, F.J.; Whitehurst, D.D. *Fuel* 1981, 60, 655.
- 7) Bartle, K.D.; Gibson, C.; Mills, D.G.; Mulligan, H.J.; Taylor, N.; Martin, T.G.; Snape, C.E. *Anal. Chem.* 1982, 54, 1730.
- 8) Steer, J.G.; Ohuchi, T.; Muehlenbachs, K. *Fuel Processing Technol.* 1987, 15, 429.
- 9) Clarke, J.W.; Kimber, G.M.; Rantell, T.D. Round table meeting 'Chemical and Physical Valorization of Coal', Brussels, 24 Nov, 1983.

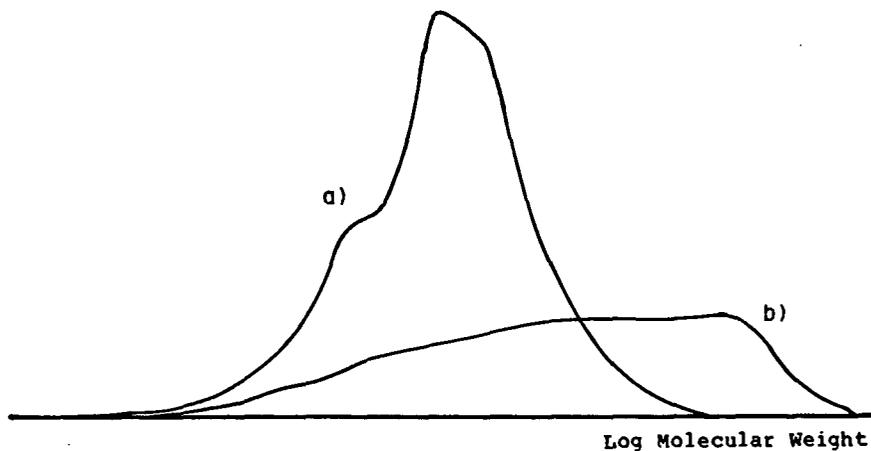


Figure 1. Superimposed SEC Traces from a) Coal Derived and b) Petroleum Derived Asphaltenes.

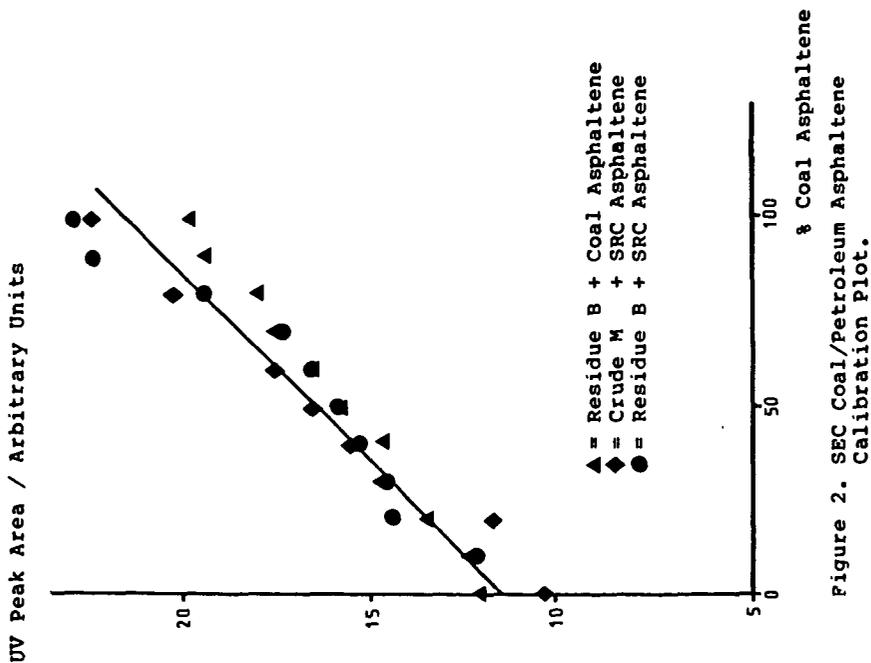


Figure 2. SEC Coal/Petroleum Asphaltene Calibration Plot.