

# IMPROVED SIZE EXCLUSION CHROMATOGRAPHY OF COAL DERIVED MATERIALS USING N-METHYL-2-PYRROLIDINONE AS MOBILE PHASE

Barry R. Johnson, Keith D. Bartle, Alan A. Herod\* & Rafael Kandiyoti\*  
School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

\*Department of Chemical Engineering, Imperial College, London SW7 2BY, UK

Keywords Size exclusion chromatography, molecular mass distribution, coal derived materials

## INTRODUCTION

A detailed knowledge of the molecular mass distribution (MMD) in coal and its derived products is essential for a fundamental understanding of coal structure, and of the processes occurring during pyrolysis, liquefaction and combustion. Indeed with increased economic and environmental pressure to use natural resources more effectively such knowledge can be applied to gaining more from finite coal reserves. Of the methods available for determining MMDs size exclusion chromatography (SEC) is perhaps the most routinely employed. In SEC tetrahydrofuran (THF) is the most commonly employed mobile phase. However THF has limited solvating power for coal derived materials and consequently a significant proportion of such materials goes undetected. In addition the interpretation of chromatograms with reference to calibration of the column with polystyrene standards is flawed<sup>1</sup>. By comparison, N-methyl-2-pyrrolidinone (NMP) is capable of solvating more of the coal sample and therefore gives the opportunity to determine an improved MMD. In this contribution the extended capabilities of NMP as the mobile phase are demonstrated primarily through the analysis of a coal tar pitch. Both NMP and THF are used as mobile phases for SEC using a number of detection techniques, allowing comparison and evaluation of different chromatographic systems to the analysis of coal derived materials.

## EXPERIMENTAL

The principle coal product used in these investigations was a high temperature coal tar pitch, with observations confirmed by similar experiments on a Point of Ayr Pilot Plant extract of Point of Ayr (PoA) coal, and a synthetic pitch. Neither pitch sample was wholly soluble in THF, unlike the PoA sample. The systems developed were then applied to the examination of char material from the British Coal, Coal Technology Development Division (CTDD) Gasification Pilot Plant (Stoke Orchard). The gasifier feed stock was power station grade Daw Mill coal. Char samples were derived from experiments at atmospheric pressure and 960°C. Organic material was extracted from the char using three different techniques. Supercritical fluid extraction, carbon dioxide with toluene modifier (400atm, 200°C), and liquid solvent extraction (1:1 NMP:CS<sub>2</sub> and sonication) both produced greater yields than the more conventional soxhlet extraction. However, in each case the yield was low indicating destruction of potential tar forming materials within the gasifier.

The chromatographic analyses and separations were performed on three systems:

For the THF based analytical system two Jordi gel (5µm, polydivinylbenzene packing) analytical SEC columns (250 x 10 mm, 500 & 100-Å<sup>0</sup>), with guard column, were operated at room temperature with a THF flow rate of 1.0ml/min. Detection was through fixed wavelength (254 or 280 nm) uv absorption and evaporative light scattering detection (ELSD).

Fractionation of the coal tar pitch was performed on two PL Gel (10 µm, styrene-divinylbenzene copolymer packing) preparative scale (600 x 25 mm, 500 & 100-Å<sup>0</sup>) columns. 40 mg of the pitch, in THF, was injected onto the columns with a THF flow rate of 10 mL/min and uv absorption detection used at 254 nm. Using this apparatus the pitch eluted over a volume range of some 40mL. A continuous series of aliquots of the column effluent were collected for each of 22 separate injections. The fractions from the same collection times were then combined and dried in a vacuum oven to remove the solvent.

The NMP based apparatus consisted of a single PL gel (3µm, styrene-divinylbenzene copolymer packing) SEC column (250 x 10 mm, Mixed Bed E) with guard column connected in series to a variable wavelength uv absorption detector (260-700 nm) and a uv/vis fluorescence detector (280-750 nm). Columns were operated at a temperature of 80°C, with an NMP flow rate of 0.5 mL/min.

All SEC apparatus were calibrated using narrow polystyrene standards (162 - 410,000 g/mol, Polymer Labs Ltd). Injection volumes were 20-µl of a 1-10 mg/mL solution for the analytical systems, and 2ml for the preparative scale experiments.

## RESULTS AND DISCUSSION

The THF-SEC chromatograms, from both uv absorption and ELSD, of the THF soluble portion of the soft pitch are shown in Figure 1. The range of the calibration with polystyrenes is marked on the figure. This clearly illustrates the difficulties being addressed in the present work<sup>1,2</sup>. However before these are examined two other interesting features are revealed in this figure. The two monitoring wavelengths employed give very similar profiles, and so are detecting similar material. The ELSD chromatogram shows material eluting over the same time range, but gives a different profile, and therefore more

information, at the shorter elution times. This ELSD detection method produces excellent results for the heaviest material within the sample, a portion often underestimated by other detectors.

Returning to the main point of Figure 1. The pitch sample elutes over a much greater time range than the calibrants. In fact the majority of the pitch sample elutes at retention volumes greater than the smallest calibrant. Obviously this 'late' material is not of very small mass, but is interacting with the column packing material, and so the separation occurring is through both adsorption and size exclusion mechanisms. This multimode separation phenomena is well documented<sup>1,2</sup> and means that a MMD cannot confidently be assigned to the sample.

The application of NMP as a mobile phase for analysing such material was investigated next. The dried THF extract of the coal tar pitch was redissolved in NMP, and appeared to be completely soluble. This was analysed on the NMP-SEC apparatus together with the NMP extract of the pitch. The resulting chromatograms are presented in Figure 2. The polystyrene calibration for this apparatus gave an exclusion limit at ~550s and a total permeation limit (peak of toluene elution) at ~1365s. The NMP extract shows two unresolved maxima in the chromatogram. The first is at the exclusion limit indicating large molecular material, with the second within the columns resolving range. The important feature to note here is that there is no material eluting after the total permeation limit. This observation is repeated in the fluorescence detected chromatogram. In the case of the THF extract of the soft pitch, again there are two maxima, one at the exclusion limit and one within the columns resolving range. However, here the two peaks are baseline resolved. Again there is no material eluting after the total permeation limit.

These chromatograms indicate that the molecular material solvated by NMP has a continuous mass range limited only by the exclusion limit of the columns (~30,000 polystyrene equivalent mass units, p.e.m.u. - manufacturers figures). Indeed, by consideration of the intensity of the excluded peak a large proportion of the pitch has a high molecular mass. The majority of the THF soluble material has a much smaller mass, < 5000 p.e.m.u. The presence of the excluded material in this sample may be due to processes occurring during drying and removal of the original THF. A similar effect has been reported during experiments to measure molecular mass by vapour pressure osmometry, where accurate weighing of solvent free sample is essential.

The examinations in Figures 1 & 2 raise an important question about the mechanism of separation occurring in the THF and NMP systems<sup>2,3</sup>. Clearly there is adsorption chromatography occurring within the THF system, so what effect is this having on the size separation mechanism of the porous column packing? Figure 3 presents some results from an investigation of the order of elution of coal derived material with NMP or THF as the mobile phase. The preparative scale separation of the coal tar pitch produced narrow retention volume defined fractions with known elution order, confirmed on the analytical THF system. These fractions were dissolved in NMP and injected on to the NMP-SEC system. Figure 3 illustrates the finding that the elution order remains largely the same. There is however a greater peak broadness in this NMP system for each individual fraction.

These observations indicate that the non-size exclusion contribution to the separation mechanism is much less when NMP is the chromatographic mobile phase. This may well be due to both the greater solubilising powers of NMP and the higher temperatures at which the NMP columns are operated. This is supported by the fact that no thermally treated coal derived material has been found to elute after the retention time of toluene.

We now turn to an examination of material extracted from the gasifier char. The supercritical fluid extraction, Figure 4, yields material which is generally of low molecular weight. There is no excluded peak. This is consistent with previous SFE of coal and environmental materials<sup>4</sup>. Also illustrated is the extension of extraction to larger molecules as more modifier is used. It is interesting to note that SFE produces material up to the total permeation limit of the column.

Chromatograms produced from the analysis of the mixed solvent extract are shown in Figure 5. This is a powerful technique capable of solvating 60% of some raw coals<sup>5</sup>. This increased extraction power over SFE is seen by the presence of a large peak in the chromatogram corresponding to excluded material. Indeed there appears to be more excluded than retained material. The lowest molecular weight material indicated by Figure 4 to be present in the original char may well be lost from the material examined in Figure 5 by the processes used to remove CS<sub>2</sub> from the extract filtrate. This last figure also illustrates that the excluded material is absorbing significant amounts of uv light at 500nm. The corresponding fluorescence chromatograms show very little fluorescence at any wavelength. This supports the assumption that this excluded material consists of larger molecular structures and not aggregated low molecular weight compounds which generally have strong fluorescence spectra.

## CONCLUSIONS

From the results reported here it is clear that NMP surpasses THF as a mobile phase for SEC of coal derived materials. It offers the opportunity to analyse more of the sample, and has shown much reduced adsorption effects. Investigation has shown that this technique can be applied to materials of industrial relevance. Polystyrene calibration for these materials remains a source of error particularly for higher mass materials, but is probably less inaccurate for low masses with NMP-SEC. The combination of

NMP-SEC and new MS techniques (LIMA, MALDI), might provide a possible route to the manufacture of relevant coal calibrants and thus accurate MMDs.

#### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the permission given by CTDD allowing collection and analysis of the gasifier samples and supply of the PoA liquefaction extract, in particular Drs Nigel Patterson and Sam Moore. We would also like to thank the EPSRC and ETSU for funding this work.

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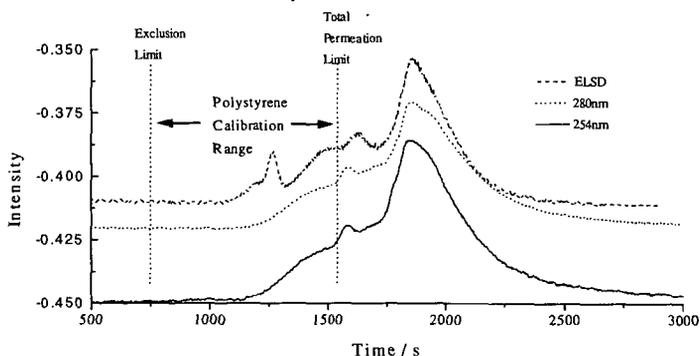


Figure 1 Size exclusion chromatographic analysis of coal tar pitch using multiple detectors with tetrahydrofuran as the mobile phase.

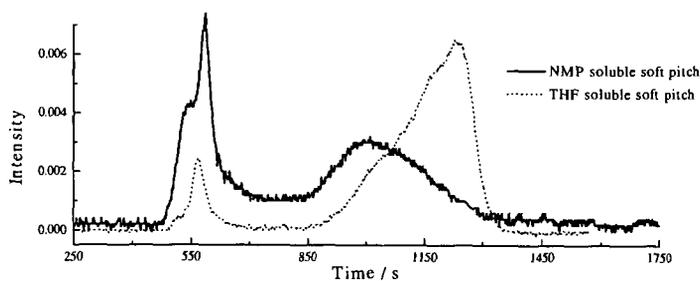


Figure 2 SEC chromatograms of solvent separated coal tar pitch fractions using uv absorption detection at 280nm and N-methyl-2-pyrrolidinone as the mobile phase.

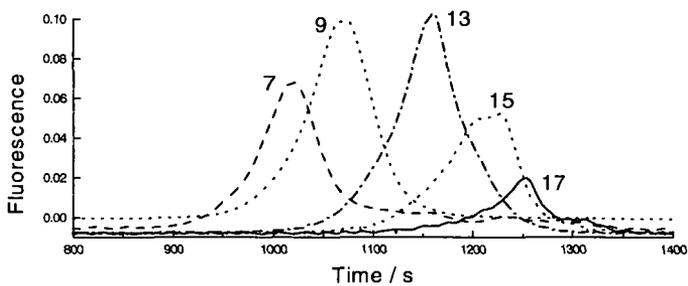


Figure 3 NMP-SEC chromatograms of pitch fractions from preparative scale THF-SEC.

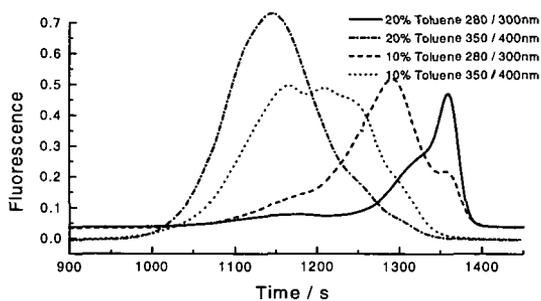


Figure 4 Chromatograms of supercritical fluid extracts from gasifier char.

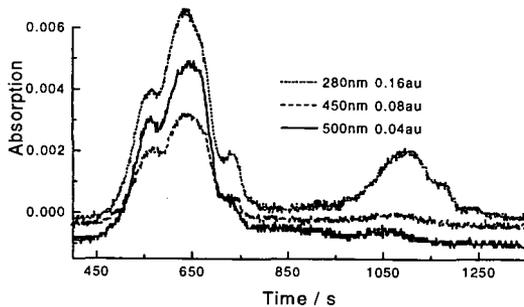


Figure 5 Chromatograms of mixed solvent extract from gasifier char.