

## COAL LIQUEFACTION WITH MODEL SOLVENTS CONTAINING HYDROPHENANTHRENS AND/OR HYDROPYRENES

Kevin Bate\* and Graham Harrison

Department of Applied Sciences,  
Staffordshire Polytechnic,  
College Road,  
Stoke-on-Trent,  
ST4 2DE UK.

\*now at Point of Ayr, Coal Liquefaction Project,  
Flynngroew, Clwyd, North Wales, CH8 9JJ

Keywords: H-donors, hydrophenanthrenes, hydropyrenes.

### INTRODUCTION

The importance of the quality of the solvent in coal liquefaction is well known. Model solvent studies have helped to characterise and elucidate reactions occurring during coal liquefaction, particularly coal dissolution but have been limited in that the model solvents chosen have not been very representative of actual process solvents. Tetralin, the model solvent often used, is unlikely to be present in a significant concentration in recycle solvents which tend to contain mainly three and four ring compounds. Studies using hydroaromatic compounds with three and four rings are more representative but again hardly represent the complex nature of recycle solvents. Consequently, there is a need to undertake studies using more complex model solvents, particularly to evaluate the contribution from individual hydrogen donors to coal dissolution.

### EXPERIMENTAL

Samples of hydrogenated phenanthrene and hydrogenated pyrene were obtained by hydrogenating the parent aromatic compound using a CoMo catalyst under a high hydrogen overpressure at elevated temperatures. Some variation in reaction conditions did apply but typical conditions were: 200 bar H<sub>2</sub> at 400°C for 2h, 100g of aromatic and 5g of 3% Co/15% Mo catalyst. All hydrogenations were conducted in a spinning/falling basket autoclave with the catalyst contained in a squat wire mesh basket as described previously (1).

Coal dissolution experiments were also carried out in the spinning/falling basket autoclave. The experiments used 300g of solvent and 150 g of air dried Point of Ayr coal (supplied by CRE), mainly at 420°C with variation in run times from 1 to 6h. The proximate (mass %, air dried) and ultimate (mass%, dmmf) analyses of the coal sample were: proximate - ash 15.9, moisture 3.5 and volatiles 27.8%; and ultimate - carbon 84.6, hydrogen 4.6, nitrogen 1.3, sulphur 1.3 and oxygen (by difference) 8.2%. The solvents used were denoted as follows: solvent A - hydrogenated phenanthrene; solvent B - 50 mass % hydrogenated phenanthrene plus 50 mass % phenanthrene; solvent C - 50 mass %, hydrogenated phenanthrene plus 50 mass % pyrene; solvent D - hydrogenated pyrene; and solvent E - 50 mass % hydrogenated pyrene plus 50 mass % hydrogenated phenanthrene.

After the dissolutions, undissolved material was removed by elevated pressure filtration (2 bar N<sub>2</sub> at 200°C) through a special unit described elsewhere(2). The filter cakes were washed with dichloromethane (DCM) to remove entrained solvent at a DCM cake ratio of 5:1; the solvent was removed by vacuum filtration and the cake was washed with further portions of

DCM until the washings were colourless. Samples of dried washed filter cakes were analysed for their ash contents using a Leco Proximate Analyser.

The filtered coal liquid was separated by solvent fractionation into toluene-insoluble, toluene-soluble/hexane insoluble and hexane-soluble materials. The hexane-soluble materials were analysed by gc using an OV101 capillary column contained in a Perkin-Elmer Sigma 3B Chromatograph equipped with 'on-column' injection. Similar gc analysis was carried out on the starting solvents dissolved in hexane.

## **RESULTS AND DISCUSSION**

### Analysis of Solvents

The results of the quantitative gc analysis of the five model solvents are shown in table 1. The contents of the various hydroaromatics of phenanthrene and pyrene, including the separate geometric isomers as well as peaks characterised as products from cracking reactions during the hydrogenations (butyltetralin and biphenyl) have been quantified. Characterisation of the chromatograms made use of marker compounds and gc.ms information supplied by CRE. Unfortunately the peaks for the two geometric isomers of H<sub>6</sub>Py and H<sub>10</sub>Py could not be attributed to the specific isomers and are referred to as H<sub>6</sub>Py<sup>1</sup>, H<sub>6</sub>Py<sup>2</sup>, H<sub>10</sub>Py<sup>1</sup> and H<sub>10</sub>Py<sup>2</sup>.

In figure 1, the chromatogram of the most complex of the solvents (solvent E) is compared with that of a batch of recycle solvent (supplied by CRE). Although there was a difference in the ramp rates for the temperature programme for the two chromatograms (5°C min<sup>-1</sup> for the recycle solvent, 8°C min<sup>-1</sup> for solvent E), it is apparent that many of the peaks for the recycle solvent chromatogram were in common with those for the solvent E chromatogram, showing that solvent E would be very representative of an actual process solvent.

### Coal Dissolution - Comparison of Solvent Performances

The solvents were compared in a series of coal dissolution experiments conducted at 420°C for different times. The results for solvents A, B, D and E are illustrated graphically in figure 2. For solvent C only 2h duplicate experiments were conducted, giving dissolutions (calculated by ash balance and expressed on 'daf' basis) of 69.2 and 69.4%; duplicate experiments were also carried out the solvent A for the 2h run and gave identical dissolutions of 72.4%. In spite of the excellent repeatability of the results, it is considered that the value for solvent D at 2h was abnormally high.

The total hydrogen donor contents of the starting solvents were evaluated from their gas chromatograms. For the recycle solvents fractions after dissolution, it was assumed that the hexane-soluble material contained the recycle solvent only and hence their hydrogen donor contents were determined from the chromatograms of the hexane-soluble fractions see (figure 3). This assumption was reasonable since the starting solvents were soluble in hexane (>99.5%) but most of the coal fragments produced during dissolution would not be and mass balance calculation on the solubility results indicated that the proportion extracted by hexane corresponded well with the mass of solvent in the dissolution.

After one hour, solvent A (hydrophenanthrenes) dissolved 62.4% of 'daf' coal and its H-donor content was reduced from 2.3 to 1.4% i.e. by 39%. For solvent D after one hour, the H-donor content was reduced by 61% from 1.8 to 0.7% for a dissolution of 72.4%. After 4h dissolution with solvent A, dissolution increased to 72.4% but donor depletion was only 57%. Hence hydrophenyrenes induced a higher dissolution after 1h but used more of their H-donor content to produce the same dissolution, probably as a result of producing wasteful hydrogen gas through dehydrogenation without utilising the hydrogen for capping radicals.

Solvent E, which contained both hydrophenanthrenes and hydrophenyrenes, effected about the same dissolution as solvent D after 1h (71.9 vs. 72.4%) but utilised less of its H-donor content (49 vs 61%). Solvent B, which only has an initial H-donor content of 1.15%, showed the lowest dissolution (57.3% after 2h) whereas solvent C with the same initial H-donor content provided a dissolution of 69.2% after 2h. Therefore the addition of phenyrenes to hydrophenanthrenes induces a greater dissolution than the addition of phenanthrene, probable

because pyrene is more able to promote H-shuttling. The improved dissolution with solvent C was at the expense of a higher H-donor depletion (61 vs. 52%).

#### Coal Dissolution - Depletion of Individual Donors.

The variation of the contents of hydrophenanthrenes and phenanthrene with time is depicted in Figure 4 for solvents A and E. Figure 5 shows similar plots for the hydroxyrenes and pyrene for solvents E and D. The general trends in figure 3 are: a gradual rise on the phenanthrene content becoming linear after the first hour; a rapid fall on the H<sub>2</sub>P and s-HgP contents, particularly over the first hour, an initial rise in the content of H<sub>4</sub>P (due to it being produced from the dehydrogenation of s-HgP more rapidly than it being lost by dehydrogenation to H<sub>2</sub>P) followed by a gradual fall; an almost constant (solvent E) or small decrease (solvent A) in the content of a-HgP. The initial rapid decrease in the contents of s-HgP and H<sub>2</sub>P corresponded with the initial increase in the phenanthrene contents and the decrease was more rapid for solvent A because of the absence of hydroxyrenes which appear to have a larger contribution than hydroxyrenes in the early stages of dissolution.

The general trends in figure 4 are: a rapid increase in the pyrene content over the first hour after which the pyrene content seemed to approach a constant value; a rapid decrease in the contents of H<sub>4</sub>Py, the two H<sub>6</sub>Py isomers and the two H<sub>10</sub>Py isomers; and an initial decrease in the content of H<sub>2</sub>Py after which there was a tendency to approach a constant value, mirroring the Py content and suggesting that an equilibrium ratio of H<sub>2</sub>Py:Py was being approached.

Table 2 shows the percentage relative depletions of the various hydrogen donors for solvent E over 1h. It can be seen that, apart from H<sub>2</sub>Py, the hydroxyrenes were depleted by similar extents and to much larger extents than the hydrophenanthrenes. Therefore most of the hydroxyrene contents in the recycle solvent fraction will be lost more readily than the hydrophenanthrene contents and, after the early stages of dissolution, the only hydroxyrene remaining in a significant amount will be H<sub>2</sub>Py. For the hydrophenanthrenes, the H<sub>2</sub>P and s-HgP contents despite being reduced quite quickly will still be in sufficient quantities to provide a supply of donor hydrogen after most of the hydroxyrene content has been used. The concentration of a-HgP was not reduced, indicating it has a higher stability towards dehydrogenation. However, its content might become important in the later stages of dissolution when its rate of dehydrogenation might be sufficiently fast to provide hydrogen for capping the radicals produced from cleavage of the more stable bonds bridging aromatic centres.

In a two-stage liquefaction process, bridging bonds surviving dissolution will be mainly catalytically cracked and stabilisation of the carbocations produced should come from the hydrogen held as hydrides at the catalyst surface not demanding any solvent H-donation. However, the second stage is often operated at higher temperatures and some thermally promoted cracking might take place in the bulk phase in which case the likely presence of the donors H<sub>2</sub>Py and a-HgP could become important for further radical stabilisation.

#### CONCLUSIONS

The rate of coal dissolution is improved by the presence of hydroxyrenes but these hydroaromatic compounds utilise more of their hydrogen donor contents than do hydrophenanthrenes for the same level of dissolution. The best solvent is one containing both hydrophenanthrenes and hydroxyrenes and generally the contents of these compounds in actual process recycle solvent are high. Most of the coal is dissolved in the early stages and thereafter further dissolution becomes expensive in terms of consumption of hydrogen donors i.e. most of the donors are dehydrogenating at a much faster than the production of free radicals resulting in the generation of wasteful hydrogen gas. Therefore it might be economic to sacrifice some coal dissolution in order to maintain a better solvent quality.

Certain donors will be depleted more rapidly than others and, if dissolution starts to decrease with solvent recycle, it could be that the contents of the "faster donors" are not being properly made up during solvent rehydrogenation in the second stage rather than overhydrogenation of the solvent to saturates. Consequently it is important not only to monitor the total hydrogen donor content of the solvent but also to analyse the solvent for its content of the various

hydropyrenes and hydrophenanthrenes, a task that should be possible by gc analysis of the solvent. Based on these assessments it should be possible to control the second stage conditions to ensure the current balance between hydrogenation and hydrocracking.

### References

1. Doughty, P.W., PhD Thesis, Staffordshire Polytechnic (CNA), April 1988
2. Bate, R., PhD Thesis, Staffordshire Polytechnic (CNA), September 1990.

Compound	Composition (mass %)				
	A	B	C	D	E
P	23.0	61.5	11.5		11.7
H <sub>2</sub> P	2.2	1.1	1.1		1.1
H <sub>4</sub> P	17.8	8.9	8.9		9.0
s-H <sub>8</sub> P	27.9	14.0	14.0	2.1	14.8
a-H <sub>8</sub> P	11.6	5.8	5.8		5.8
iso-H <sub>8</sub> P	2.8	1.4	1.4		1.6
H <sub>14</sub> P	3.6	1.8	1.8		2.0
Py			50.0	29.3	14.9
H <sub>2</sub> Py				18.6	9.5
H <sub>4</sub> Py				3.6	1.9
H <sub>6</sub> Py <sup>1</sup>				18.7	9.5
H <sub>6</sub> Py <sup>2</sup>				13.4	7.0
H <sub>10</sub> Py <sup>1</sup>				7.1	3.7
H <sub>10</sub> Py <sup>2</sup>				3.9	1.9
BT	2.8		1.4		1.3
BP	1.3		0.6		0.6
T	0.2		1.1		

**Table 1. Composition of Model Solvents by G.C**

P - phenanthrene, H<sub>2</sub>P - dihydrophenanthrene, H<sub>4</sub>P - tetrahydrophenanthrene  
s - H<sub>8</sub>P - sym - octahydrophenanthrene, a - H<sub>8</sub>P - antisym - octahydrophenanthrene  
iso-H<sub>8</sub>P - isomerised octahydrophenanthrene, H<sub>14</sub>P - perhydrophenanthrene  
Py-pyrene, H<sub>2</sub>Py - dihydropyrene, H<sub>4</sub>Py - tetrahydropyrene, H<sub>6</sub>Py<sup>1</sup>, H<sub>6</sub>Py<sup>2</sup> -  
hexahydropyrene, H<sub>10</sub>Py<sup>2</sup> - decahydropyrene, BT - butyltetralin, BP - biphenyl, T - tetralin.

### Relative Depletion (%)

Hydrophenanthrenes				Hydropyrenes							
H <sub>2</sub> P,	H <sub>4</sub> P,	s - H <sub>8</sub> P,	a - H <sub>8</sub> P	H <sub>2</sub> Py,	H <sub>4</sub> Py,	H <sub>6</sub> Py <sup>1</sup> ,	H <sub>6</sub> Py <sup>2</sup> ,	H <sub>10</sub> Py <sup>1</sup> ,	H <sub>10</sub> Py <sup>2</sup>		
54.5	-3.3	50.0	0	51.6	89.5	85.3	88.7	89.2	89.5		

**Table 2. Percentage Relative Depletions of Individual H-donors for Solvent E Over One Hour**

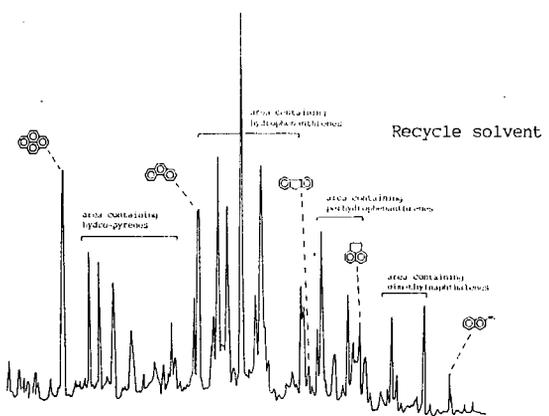
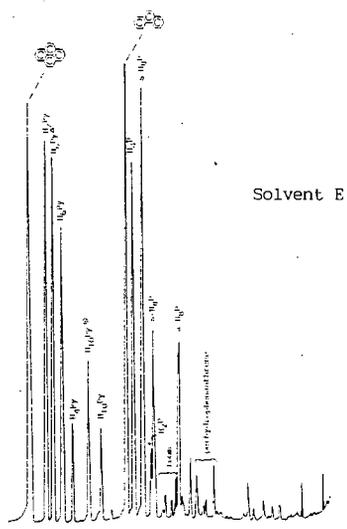


Figure 1. Gas chromatogram for solvent E (ramp rate  $8^{\circ}\text{C min}^{-1}$ ) and a recycle solvent (ramp rate  $5^{\circ}\text{C min}^{-1}$ )

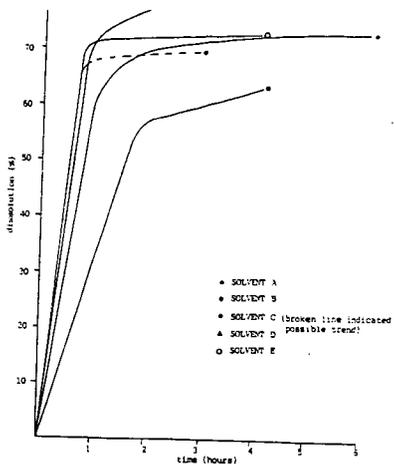


Figure 2. Plots of percentage dissolution vs time for the five model solvents A-E

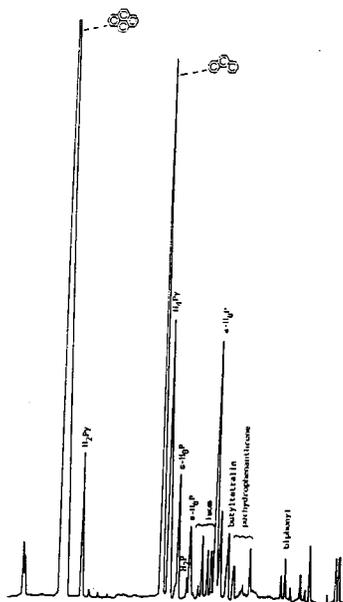


Figure 3. Gas chromatogram of a hexane-soluble material fraction of a coal liquid

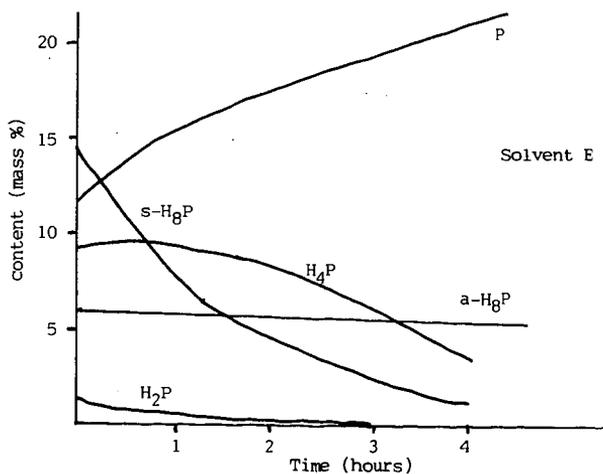
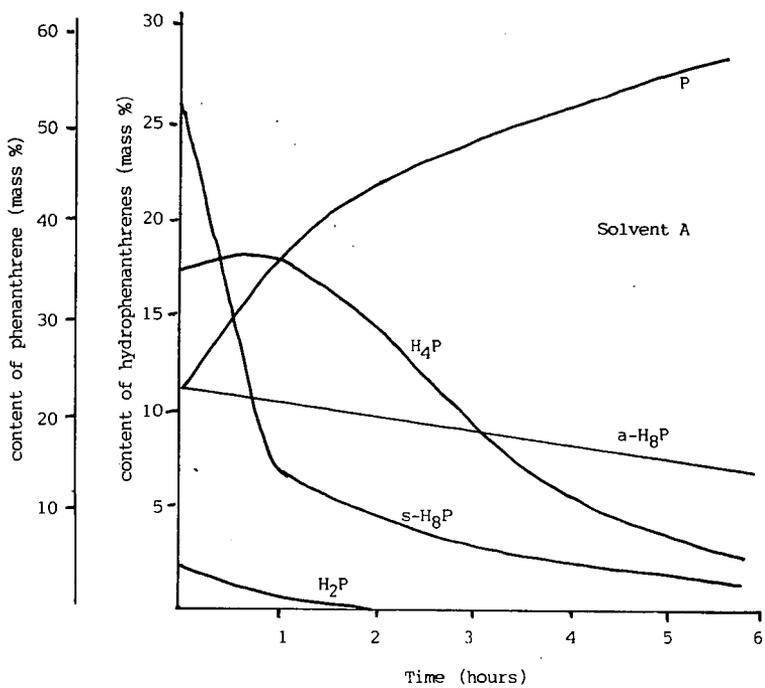


Figure 4. Variation of contents of phenanthrene and hydrophenanthrenes with dissolution time for solvents E (bottom) and A (top).

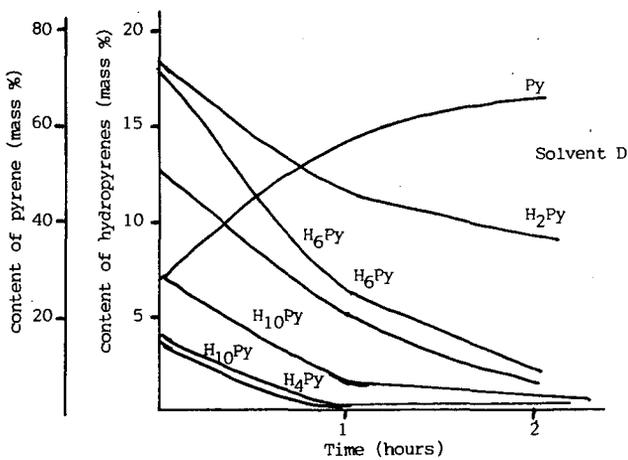
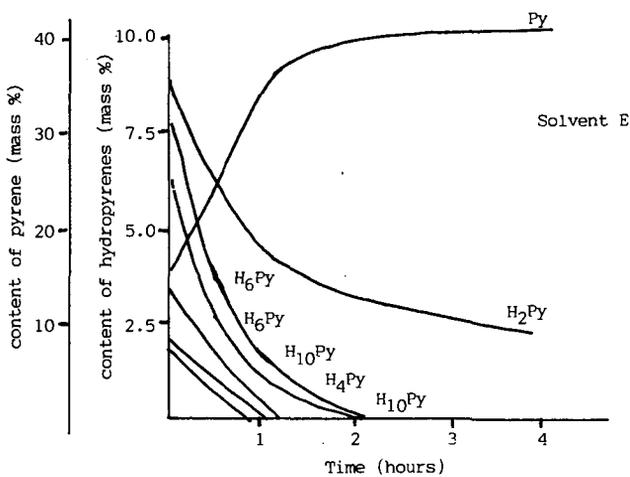


Figure 5. Variation of contents of pyrene and hydroxyrenes with dissolution time for solvents D (bottom) and E (top)