SAND--89-1217C

DE89 013586

INFLUENCE OF ORGANIC COAL STRUCTURE ON LIQUEFACTION BEHAVIOR: AN UPDATE WITH EMPHASIS ON LOW-SEVERITY CONDITIONS*

C. E. SNAPE[1], F. J. DERBYSHIRE[2], H. P. STEPHENS[3], R. J. KOTTENSTETTE[3] and N. W. SMITH[4].

[1] University of Strathclyde, Dept of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL (UK)

[2] Sutcliffe Speakman Carbons Ltd, Guest Street, Leigh, Lancashire WN7 2HE (UK)

[3] Sandia National Laboratories, Albuquerque, New Mexico 87185 (USA)

[4] University of Leeds, Dept of Physical Chemistry, Leeds LS2 9JT (UK)

SUMMARY

The influence of coal structure on primary conversions and oil yields in thermolytic extraction with different H-donor and non-H-donor solvents and in dry catalytic hydrogenation has been investigated. Pre-soaking of coal/H-donor solvent slurries at 250°C increased conversions and the level of hydrogen transfer at short contact times (SCT, $\leq$ 10 min), demonstrating the importance of solvent accessibility. However, contrary to other studies, prior removal of THF-extractable material (mobile phase) from one bituminous coal actually gave rise to higher conversions to pyridine - solubles for non-donor polynuclear aromatic compounds (PAC), such as naphthalene, phenanthrene and pyrene. These findings highlight the difficulties in relating primary conversions to coal characteristics. In contrast, oil yields have been found to increase broadly with decreasing rank in both H-donor solvent extraction with a process solvent and dry catalytic hydrogenation. However, in SCT tetralin extraction where poor physical contact between coal and solvent exists, neither total conversion nor oil yield correlates with rank.

---

* Portions of this work were performed at Sandia National Laboratories, which is operated for the U.S. Department of Energy under contract number DE-AC04-76DP00789.

INTRODUCTION

The correlation of coal characteristics with liquefaction behavior has received considerable attention (see, for example, Refs. 1-3). However, apart from the lack of precise structural information on the nature of aromatic, aliphatic and heteroatomic groups and low molecular weight (MW) material (mobile phase) in coals, research has been hampered by the fact that the rate and extent of conversion are heavily dependent on the conditions used. Indeed, the recent review given by one of the authors ([1]) at the first Rolduc symposium indicated that a clear distinction has to be made between overall or primary conversions (typically pyridine, quinoline or THF-solubles) and distillate or oil yields (toluene- or alkane-soluble material). The profound influence of low MW material and the nature of H-donor and non-donor solvents on primary conversions were highlighted. In contrast, distillate or oil yields often correlate with parameters reflecting the aliphaticity of coals (H/C ratio - Ref. 4, decreasing vitrinite reflectance - Ref. 5, CH_2 content - Ref. 6).

In this paper, new findings on aspects of primary conversion in H-donor and non-donor solvents and in dry catalytic hydrogenation are discussed in the light of other recent work ([7-10]). Also, it is demonstrated that oil yields broadly increase with decreasing coal rank provided that retrogressive reactions are avoided in the initial stages of coal dissolution (see Ref. 20).

EXPERIMENTAL

Conditions used for the extraction and hydrogenation experiments are summarized in Table 1. H-donor solvent extractions of a Wyodak sub-bituminous coal (73% dmmf C), an Illinois No. 6 coal (78% dmmf C) and a UK bituminous coal (Pt. of Ayr, 87% dmmf C) were conducted using (i) a Lummus process - derived distillate (nominal boiling range of 340 to 400 °C, containing approximately 1% donatable hydrogen) as described previously ([11]) and (ii) tetralin with a short contact time (SCT, $\leq$ 10 min).

To investigate factors affecting the initial stages of coal dissolution, extractions were conducted on two UK coals (Linby 82% dmmf C, and Pt. of Ayr) at 400°C using a number of model compounds including tetralin, naphthalene, 9,10-dihydrophenanthrene, phenanthrene, and pyrene for periods up to 30 min. For Linby coal, the effect of Soxhlet extraction with THF on conversions was investigated (extract yield, 6% daf coal). Also, coal/solvent slurries were pre-soaked at 250°C in a number of experiments. For the model hydroaromatic compounds, the amount of H transferred during extraction was determined by GC analysis of the products.

Dry hydrogenations with and without a dispersed sulphided molybdenum (Mo) catalyst were carried out at 400°C ([12]) (Table 1) on a suite of four U.S. coals comprising a sub-bituminous coal (PSOC-1408, 72.9% dmmf C), two h.v.A bituminous coals (PSOC-1266 and 1296, 83% and 87% dmmf C, respectively) and an l.v. bituminous coal (PSOC-1325, 90% dmmf C).

RESULTS AND DISCUSSION

Primary Conversions and Influence of Mobile Phase

Yields for the various H-donor and non-donor solvent extractions of Linby coal at 400°C are summarized in Table 2; conversions for the THF-extracted coal include the extracted material. Surprisingly, pre-extraction with THF significantly increases primary conversions in the polynuclear aromatic compounds (PACs) investigated. These findings appear to be contrary to those of other liquefaction ([13]) and pyrolysis ([14]) studies where prior removal of chloroform-extractable material significantly reduced conversions. However, Rincon and Cruz ([15]) have reported recently that pre-swelling coals in THF increases conversions for both anthracene oil and tetralin. The fact that Pt. of Ayr (87% dmmf C) coal yielded over 80% pyridine-solubles in pyrene (C. Snape, unpublished data) without pre-extraction is consistent with the earlier results of Clarke et al. ([16]) for anthracene oil extraction where UK coals containing ~85-87% dmmf C gave the highest conversions. It was suggested previously by one of the authors that this could correspond to a minimum in the cross-linking density of bituminous coals (^{1}). However, these latest findings indicate that the mobile phase is merely limiting accessibility for larger PACs, such as pyrene, within lower rank bituminous coals, such as Linby.

Conversions to pyridine-solubles for non-THF-extracted Linby coal were much greater with naphthalene than with phenanthrene and pyrene (Table 2). Pre-soaking at 250°C had little effect on conversions (C. Snape, unpublished data) and, even after THF extraction, naphthalene conversions were comparable to those of pyrene. Although Neavel obtained high yields of pyridine solubles using naphthalene at short contact times for some U.S. bituminous coals (^{17}), conversions were much lower after longer extraction times. This trend is not evident for Linby coal where little variation in conversion to pyridine and THF-solubles is found for residence times between 10 and 30 min for both the initial and THF-extracted coal samples (Table 2). The trends reported here were certainly not anticipated from previous studies with model PACs (^{1,18}). The yields of THF-solubles for pyrene, however, were considerably greater than those obtained for either phenanthrene or naphthalene (Table 2). This evidence provides strong support for pyrene being an effective "hydrogen-shuttler" (^{18}); the available hydrogen in Linby coal is utilized more effectively with pyrene than with naphthalene and phenanthrene, generating significantly higher yields of THF-solubles.

As expected, tetralin and 9,10-dihydrophenanthrene gave much higher yields of THF-solubles after THF extraction than the PACs with the exception of pyrene (Table 2). Pre-soaking the coal/solvent slurries at 250°C increased SCT conversions for 9,10-dihydrophenanthrene but not tetralin, presumably due to poorer physical contact of tetralin with the coal; Narain et al. (^{19}) found similar improvements in SCT hydroliquefaction with 1-methylnaphthalene. For 9,10-dihydrophenanthrene, the higher conversion to THF-solubles was not accompanied by an increase in H consumption. However, the conversion at SCT (Table 3) was no more than that obtained after prolonged extraction (30 min., Table 2) with pyrene where no H donation can occur. This agrees with work by Baldwin and coworkers (^{20}), which showed that oil yields (Dichloromethane-DCM, toluene or alkane-solubles) provide more reliable indicators of H utilization than overall conversions to pyridine (or quinoline) or THF-solubles. The lower yields of pyridine-solubles obtained with tetralin compared to 9,10-dihydrophenanthrene (Table 2) and even to naphthalene and pyrene for the THF-extracted coal (Table 2) again are probably attributable to tetralin being largely vaporized at liquefaction temperatures. Indeed, different trends in primary conversion are evident for the SCT tetralin and the higher temperature process-solvent extractions (Table 3). The sub-bituminous coal (Wyodak) gives the highest yield of quinoline-insolubles with tetralin consistent with the general trend found in SCT hydroliquefaction by Whitehurst (1,21). In the case of the process solvent, yields of THF-insolubles increase with increasing rank (Table 3) although the trend is much smoother than could be realistically expected for a larger suite of coals. Nitrogen-containing solvents, such as indoline have also been found to give significantly higher primary conversions for Wyodak coal (22) than tetralin presumably due to the hydrogen-bonding/solvent interaction. Clearly, solvents which provide good physical contact are essential to minimize retrogressive reactions, particularly for low-rank coals.

In view of the compelling arguments recently put forward by McMillan and coworkers (9) in support of solvent-mediated hydrogenolysis, it is pertinent to consider whether chemical or physical factors for the different H-donors investigated are responsible for inefficient hydrogen utilization and, in particular, whether different conversions are evident for a given level of hydrogen donation. Majchrowicz et al. (23) demonstrated that by increasing the filling factor for tetralin in autoclaves so that more of the tetralin is in the liquid phase, conversions to THF-solubles increased but the level of hydrogen transfer remained constant. Table 2 indicates that when 0.5% hydrogen has been consumed, the yields of THF-solubles obtained with 9,10-dihydrophenanthrene are considerably higher than with tetralin. Despite the reservations over the use of THF-soluble yields as indicators of H utilization, these findings clearly indicate that cleavage of relatively stable C-C bonds via hydrogen radical transfer occurs to a significantly greater extent in 9,10-dihydrophenanthrene.

Oil Yields

Figure 1 gives the yields of chloroform - soluble liquid products obtained from the dry hydrogenation experiments at 400°C with the sulphided Mo catalyst. Table 3 lists oil and gas yields from the process solvent extractions at 450°C. In both regimes, oil yields (chloroform or n-heptane-soluble liquids) generally increase with decreasing rank. Again, the trends are probably much smoother than could be anticipated for a larger suite of coals. For sub-bituminous coals, it is probably more appropriate to express oil yields on a "CO_2 plus CO free" basis ([4]) (Table 3), a higher yield then being obtained for Wyodak sub-bituminous coal compared to Illinois No. 6 coal in the process solvent extractions (Table 3).

Although the yield of DCM-insolubles increases with increasing rank in SCT tetralin extraction (Table 3, QI + QS/DCM insols), the yields of DCM-soluble liquid product are similar for Wyodak and Pt. of Ayr coals even after correcting for the carbon oxides. Thus, retrogressive reactions encountered in SCT extraction with tetralin for Wyodak coal limit both primary conversions and oil yields. The relatively high concentration of solvent extractable material in Illinois No. 6 coal may be responsible for this coal giving the highest oil yield in SCT liquefaction. Also, for dry hydrogenation without catalyst, oil yields do not correlate with rank (Figure 1), the sub-bituminous coal giving a significantly lower oil yield than one of the h.v.A bituminous coals. Thus, the catalyst is needed to limit retrogressive reactions by promoting cleavage reactions probably by hydrogen radical mediated hydrogenolysis ([9]). These findings are in broad agreement with trends obtained under typical SRC-II processing conditions ([5]) where addition of pyrite is needed to give high oil yields for low-rank coals and clearly show the importance of limiting retrogressive reactions in the initial stages of liquefaction for low-rank coals.

ACKNOWLEDGEMENTS

The authors thank the U.S. Dept. of Energy (Grant Nos. DE-FE22-83PC60811 and DE-AC04-76DP00789) and the Science and Engineering Research Council with British Coal (CASC studentship for N.W.S.) for financial support.

REFERENCES

1. C. E. Snape, "Characterisation of Organic Coal Structure for Liquefaction," Fuel Process Tech., 15 (1987), pp. 257-279.

2. P. H. Given, W. Spackman, A. Davis and R. G. Jenkins, "Some Proved and Unproved Effects of Coal Geochemistry on Liquefaction Behaviour with Emphasis on U.S. Coals," in: D. D. Whitehurst (Ed.), Coal Liquefaction Fundamentals, Am. Chem. Soc. Symp. Series, 139 (1980), pp. 3-34.

3. R. M. Baldwin, K. J. Voorhees and S. L. Durfee, "Relationship of Coal Characteristics to Coal Reactivity for Direct Hydrogenation Liquefaction," Fuel Process Tech., 15 (1987), pp. 282-292.

4. P. Redlich, W. R. Jackson and F. P. Larkins, "Hydrogenation of Brown Coals, 9. Physical Characterization and Liquefaction Potential of Australian Coals," Fuel, 64 (1985), pp. 1383-1390.

5. G. Tomlinson, D. Gray, and M. Neuworth, "The Impact of Rank-Related Coal Properties on the Response of Coals to Continuous Direct Liquefaction Processes," Proc. Int. Conf. on Coal Science, Sydney, October 1985, Pergamon (1985), pp. 3-6.

6. J. T. Senftle, D. Kuehn, A. Davis, B. Brozoski, C. Rhoads and P. C. Painter, "Characterisation of Vitrinite Concentrates, 3. Correlation of FT-ir measurements to Thermoplastic and Liquefaction Behaviour," Fuel, 63 (1984), pp. 245-251.

7. R. A. Keogh, B. Chawia, K. J. Tsai and B. H. Davis, "Coal Liquefaction: Impact of Alkyl Substitution in Naphthalene Model Solvents," Prepr. Am. Chem. Soc. Div., Fuel Chem., 33(3) (1988), pp. 333-342.

8. I. Mochida, A. Yufu, K. Sakanishi, and Y. Korai, "Influence of Donor Amount in the Hydrogen-Transfer Liquefaction of Australian Brown Coal," Fuel, 67 (1988), pp. 114-118.

9. R. Malhotra and D. F. McMillen, "The Impact of Liquefaction Solvent Composition on Hydrogen Utilization Efficiency," Prepr. Am. Chem. Soc. Div., Fuel Chem., 33(3) (1988), pp. 319-324.

10. K. Chiba, H. Tagaya and N. Saito, "Liquefaction of Yallourn Coal by Binary Solvent System," Energy and Fuels, 1 (1987), pp. 338-343.

11. H. P. Stephens, "Two-Stage Liquefaction Without Gas-Phase Hydrogen," Prepr. Am. Chem. Soc. Div., Fuel Chem., 31(4) (1986), pp. 314-320.

12. F. J. Derbyshire, A. Davis, R. Lin, P. G. Stanberry and M. T. Terser, "Coal Liquefaction by Molybdenum Catalysed Hydrogenation in the Absence of Solvent," Fuel Process. Tech., 12 (1986), pp. 127-141.

13. J. W. Larsen, T. L. Sams, and B. R. Rogers, "Effect of Chloroform-Solubles in Coal Conversion in Non-Hydrogen Donating Solvents," Fuel, 59 (1980), pp. 666-667.

14. R. J. O'Brien, J. R. Gibbins, and R. Kandiyoti, "The Effect of Chloroform Extractables on Tar Formation in Flash Pyrolysis and Catalytic Flash Pyrolysis," Fuel Process. Tech., 15 (1987), pp. 71-82.

15. J. M. Rincon and S. Cruz, "Influence of Pre-Swelling on Liquefaction of Coal," Fuel, 67 (1988), pp. 1162-1163.

16. J. W. Clarke, G. M. Kimber, T. D. Rantell and D. E. Shipley, "Reactivity of British Coals in Solvent Extraction," in: D. D. Whitehurst (Ed.), Coal Liquefaction Fundamentals, Am. Chem. Soc. Symp. Series, 139 (1980), pp. 111-129.

17. R. C. Neavel, "Coal Plasticity Mechanism: Inferences from Liquefaction Studies," in: M. L. Gorbaty, J. W. Larsen, and I. Wender (Eds.), Coal Science, Vol 1, Academic Press (1982), pp. 1-19.

18. F. J. Derbyshire and D. D. Whitehurst, "Study of Coal Conversion in Condensed Polycondensed Aromatic Compounds," Fuel, 60 (1981), pp. 655-662.

19. N. K. Narain, H. R. Appell and B. R. Utz, "The Effect of Solvent Pre-Treatment on Coal Liquefaction," Prepr. Am. Chem. Soc. Div. Fuel Chem., 28(1) (1983), pp. 161-162.

20. S. C. Shin, R. M. Baldwin and R. L. Miller, "Effect of Radical Quenching on Hydrogen Activity: Model Compound and Coal Hydroliquefaction Studies," Energy & Fuels, 3 (1989), pp. 71-76.

21. D. D. Whitehurst, "A New Outlook on Coal Liquefaction Through Short Contact Time Thermal Reactions: Factors Leading to High Selectivity," in: D. D. Whitehurst (Ed.,) Coal Liquefaction Fundamentals Am. Chem. Soc. Symp., Series 139 (1980), pp. 133-164.

22. T. D. Padrick and S. J. Lockwood, "Liquefaction of Wyodak Coal in Indoline," Prepr. Am. Chem. Soc. Div. Fuel Chem., 29(5) (1984), pp. 92-98.

23. B. B. Majchrowicz, D. Franco, J. Gelan, and J. J. de Vlieger, "Effect of Tetralin-Coal Ratio and Temperature on Liquefaction Behaviour of a Bituminous Coal Using Different Batch Autoclave Systems," Proc. 1987 Int. Conf. on Coal Science, Elsevier (1987), pp. 207-210.

Table 1
Summary of Liquefaction Experiments

Experiment	Temp °C	Solvent	Solvent to Coal Ratio	Atmosphere Gas	Atmosphere Pressure (cold)
H-donor Solvent extraction					
1.	450	Lummus process-derived distillate	2:1	N_2	30
2.	400	Tetralin+ 9,10 dihydrophenanthrene+	2:1	N_2	1
Non-donor PAC extraction*	400	Naphthalene, phenanthrene, pyrene+	2:1	N_2	1
Dry catalytic hydrogenation	400	-	-	H_2	70

Experiment	Extraction time, min	Solvents used to determine conversions
H-donor solvent extraction		
1. 450°C	30	THF, n-heptane,
2. 400°C	7-30	Pyridine, quinoline, THF
Non-donor PAC extraction*	7-30	Pyridine/quinoline, THF
Dry catalytic hydrogenation	60	Chloroform

\+ - with and without a pre-soak period of 60 min, at 250°C
* - before and after THF-extraction of Linby coal

DISCLAIMER

Table 2
Primary Conversions for Linby Coal at 400°C

Solvents	Coal treatment	Time min.	Yields+ Pyridine sols.	THF sols.	Hydrogen consumption
Naphthalene	None	10	51	25	
	"	30	58	29	
	THF-ext.	7	81	24	
	"	30	76	26	
Phenanthrene	None	7,30	22	15	
	THF-ext.	7,30	38	30	
Pyrene	None	7,30	24	14	
	THF-ext.	10	60	47	
	"	30	83	60	
9,10 Dihydro-phenanthrene	THF-ext.	5	55	34	0.5
	"	30	88	83	2.1
	Pre-soak	5	88	53	0.4
	"	30	93	80	1.9
Tetralin	THF-ext.	7	38	25	0.5
	"	30	78	65	1.2
	Pre-soak	7	43	35	0.5
	"	30	75	66	1.3

+ = % daf coal

Table 3
H-Donor Solvent Liquefaction Results

Coal		Pt. of Ayr	Illinois No. 6	Wyodak
<u>SCT Tetralin</u>				
	QIs	8	5	26
% daf	QS/DCM insols	69	60	35
coal	DCM liquids*	20	32	20
				(24)
<u>Process Solvent</u>				
	THF Insols.	17.0	3.0	2.1
% daf	THF sols/C_7 insols.	47.5	47.1	35.3
coal	C_7 liquids*	27.6	41.5	39.5
				(47.5)
	$CO + CO_2$	1.6	1.5	16.8
	C_1 - C_3 gases	5.5	5.9	6.0

QI - quinoline insolubles
C_7 - n-heptane
( ) - "CO_2 + CO" free basis

QS - quinoline solubles
* - includes
DCM - dichloromethane

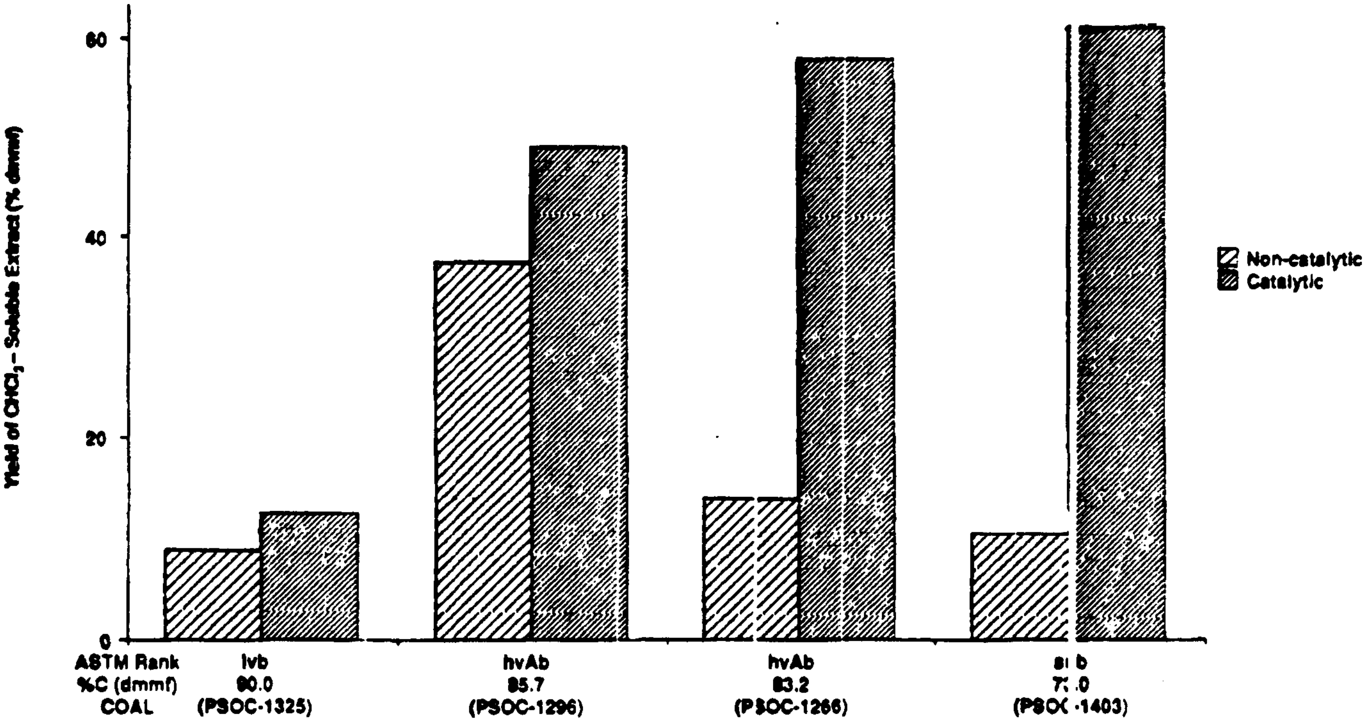

Figure 1 - Effect of Coal Rank and Sulphided Mo. Catalyst on Yield of Chloroform-Soluble Liquids in Solvent-Free Hydrogenation at 400°C