Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Supercritical Gas Extraction of South African Coals

John R. Kershaw[a,b]; Josef Jezko[a,c]
[a] Fuel Research Institute of South Africa, Pretoria, South Africa [b] CSIRO Division of Applied Organic Chemistry, Melbourne, Australia [c] B.C. Research, Vancouver, B.C., Canada

To cite this Article Kershaw, John R. and Jezko, Josef(1982) 'Supercritical Gas Extraction of South African Coals', Separation Science and Technology, 17: 1, 151 — 166
To link to this Article: DOI: 10.1080/01496398208058144
URL: http://dx.doi.org/10.1080/01496398208058144

SEPARATION SCIENCE AND TECHNOLOGY, 17(1), pp. 151-166, 1982

Supercritical Gas Extraction of South African Coals

JOHN R. KERSHAW* and JOSEF JEZKO**

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA
P. O. BOX 217,
PRETORIA 001, SOUTH AFRICA

ABSTRACT

The supercritical gas extraction of South African coals was carried out using semi-continuous reactors. The conversion (to liquid and gaseous products) increases as the volatile matter yield or the H/C atomic ratio of the coal increases and as the critical temperature or the Hildebrand solubility parameter of the solvent increases. The effect of pressure and temperature on the conversion is discussed. The chemical nature of the oils (hexane soluble product) from supercritical gas extraction at 350°C and 450°C is also reported.

INTRODUCTION

Extraction of coal with supercritical gases is a novel route for obtaining coal-derived liquids. It is envisaged that these liquids will be further processed by hydrogenation to transport fuels and chemical feedstocks. A number of papers have described the supercritical gas extraction of coal (1-4) and the chemical nature of the products obtained (5-10).

---

* To whom correspondence should be addressed. Present address: CSIRO Division of Applied Organic Chemistry, P.O. Box 4331, Melbourne 3001, Australia.

**Present address: B.C. Research, 3650 Wesbrook Mall, Vancouver, B.C., Canada

In this paper the effect that the coal properties, the properties of the supercritical fluid, the pressure and the temperature have on supercritical gas extraction of South African coals are discussed as well as the chemical nature of the oils (hexane soluble product) obtained on supercritical gas extraction of these coals.

EXPERIMENTAL

The proximate and ultimate analyses of the coals (0.59 to 0.25 mm fraction) used are given in Table 1.

Supercritical Gas Extraction

Method A

The extractions were carried out in a 1 liter stirred autoclave. The autoclave was charged with coal (25 g) and solvent (800 mL) and

TABLE 1

Analysis of South African Coals Used

	New Wakefield	Sigma	Waterberg
Moisture[a]	4.9	6.6	3.8
Ash[a]	14.9	29.6	11.7
Volatile Matter[a]	32.8	21.9	33.2
C[b]	79.2	76.7	80.7
H[b]	5.4	4.4	5.5
N[b]	2.1	1.6	1.4
S[b]	2.3	1.1	1.1
O[b] (by difference)	11.0	16.2	11.3

[a] wt%, air dried basis

[b] wt%, daf (dry,ash-free basis)

heated. When the temperature reached ca 150°C, solvent (4 L/h) was pumped via a dip tube, which acts as a pre-heater, into the bottom of the autoclave and through the coal bed. On reaching the final temperature of 450°C the extraction was continued until the condensate was clear. The pressure was maintained at 20 MPa during the extraction.

The residue was washed out of the reactor with the aid of toluene, filtered, washed with toluene and with acetone, and dried at 110°C.

Method B

The method is similar to Method A except that the 'hot-rod' reactor (11,12) was substituted for the autoclave. The coal (25 g) was mixed with sand (50 g, acid washed, 0.42 to 0.15 mm) to limit agglomeration (13) and was held within the reactor by steel wool plugs. The reactor was heated by direct resistance heating at a rate of ca 200°C/min to temperature. On obtaining the reaction temperature, toluene (4 L/h) was pumped through the reactor for 15 min after the required pressure was reached.

The work-up procedure was as for Method A. The overall conversion of coal to liquid and gaseous products was obtained from the formula:

$$\% \text{ Conversion} = 100 \left(\frac{\text{wt daf coal} - \text{wt daf residue}}{\text{wt daf coal}} \right)$$

(daf = dry, ash-free basis)

Method C

The autoclave (1 liter) was charged with coal (100 g) and toluene (600 mL) and heated to temperature (350° or 450°C). On reaching the desired temperature and pressure (17 or 20 MPa), toluene (ca 2 L/h) was pumped into the reactor and through the coal bed via a dip tube for 1 hour. The toluene extract was cooled at atmospheric pressure in a water-cooled condenser.

The extraction condensate was filtered to remove material which precipitated on cooling. The toluene was removed from the filtrate under reduced pressure. Hexane (250 mL) was added to the extract and it was allowed to stand for 24 h with occasional shaking. The solution was filtered to leave a residue (asphaltene) and the hexane was removed from the filtrate under reduced pressure to give the oil.

Fractionation of the Oils

The oils were fractionated by adsorption chromatography on silica gel. The column was eluted successively with 40-60°C BP petroleum ether (12 fractions), 40 to 60°C petroleum ether/toluene (increasing proportions of toluene, 5 fractions), toluene, chloroform and methanol. A total of 20 fractions were collected.

Analyses

IR spectra were measured as smears on sodium chloride plates using a Perkin-Elmer 567 grating spectrophotometer, while UV spectra were measured in hexane (spectroscopic grade) using a Unican SP 1700 instrument. Fluorescence spectra were recorded as very dilute solutions in hexane using a Perkin-Elmer 512 instrument, and phosphorescence spectra were similarly recorded using the phosphorescence accessory in EPA (a mixture of ether, isopentane and ethanol in the proportions by volume of 5:5:2) at 77°K.

^{1}H NMR spectra were recorded in deuterochloroform at 90 MHz with tetramethylsilane as an internal standard using a Varian EM 390 instrument. Broadband proton-decoupled pulse Fourier transform ^{13}C NMR were recorded in deuterochloroform at 20 MHz using a Varian CFT-20 spectrometer. Deuterochloroform provided the lock signal and the number of scans was ca 1000.

GLC analyses were carried out on a 50 m x 0.25 mm I.D. capillary column (wall-coated open tubular) with OV-101 silicone fluid stationary phase using a Perkin-Elmer 3920 chromatograph. GLC analysis was also carried out using 1.25 m x 3 mm I.D. stainless steel columns with 10% SP-2100 methyl silicone oil on 100/120 Supelcoport.

RESULTS AND DISCUSSIONS

Coal Properties

Supercritical gas extraction with toluene of a number of South African coals was carried out using Method A. A suite of fourteen South African coals were used in this study. These coals varied considerably in their volatile matter yield and hydrogen to carbon atomic ratio. The conversion increased with an increase in either the volatile matter yield or the hydrogen to carbon atomic ratio of these coals (see Fig. 1). Good correlations were found between these coal properties and the conversions.

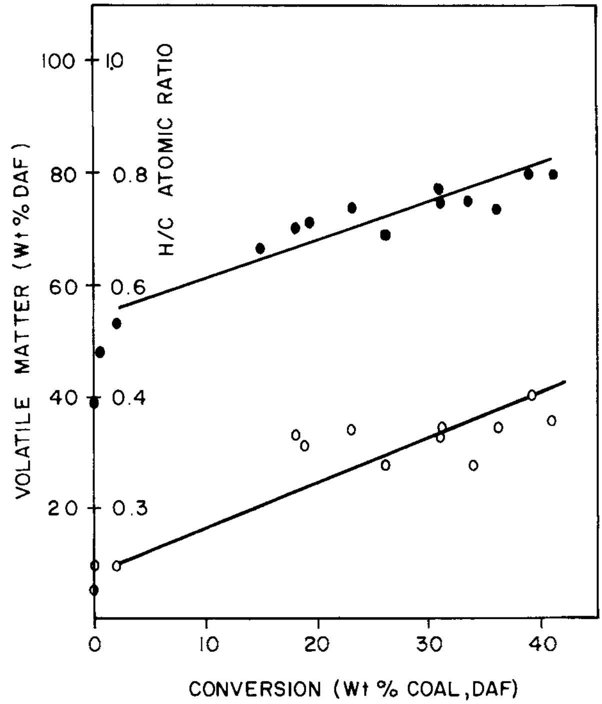

FIGURE 1. Conversion versus volatile matter yield (o) and H/C atomic ratio (•) at 450°C and 20 MPa using Method A. Conversion = 1.2 (V.M.) - 9.1; r = 0.90. Conversion = 104 (H/C) - 48.6; r = 0.92.

Solvent Properties

Most reports (1,2,5-10) of the supercritical gas extraction of coal have been limited to the use of toluene as the solvent. Williams and Whitehead (3) used n-dodecane, toluene, o-xylene and pyridine as solvents for supercritical gas extraction of a British coal. They obtained yields of 15, 29, 32 and 34% respectively under identical conditions. Ross and Blessing (4) reported a correlation between the extraction yield and the Hildebrand solubility parameter (δ) for a limited number of solvents.

In this work eighteen solvents were used for the supercritical gas extraction of Waterberg coal using Method A. The solvents used, their critical constants, the calculated values for the density and for the Hildebrand solubility parameter at the experimental conditions, together with the conversion data obtained are given in Table 2. At the temperature of 450°C all the solvents were above their critical temperature. The conversion increased as the critical temperature (T_c) or the Hildebrand solubility parameter (δ) at the experimental conditions increased (see Fig. 2), and good correlations were obtained between conversion and these parameters. Because of its unusual characteristics water was excluded from calculations of the regression lines in Fig. 2. The solvents used in this study varied considerably in their chemical nature. The values of critical temperature were obtained from the literature (14,15) while the Hildebrand solubility parameters at the experimental conditions were calculated according to the formula (4,16):

$$\delta \left((\mathrm{cal/cm}^3)^{\frac{1}{2}} \right) = 1.25\, P_c^{\frac{1}{2}}\ d_r/d_l$$

where P_c is the critical pressure of the solvent in atmospheres, d_r is its reduced density (the density divided by the critical density of the solvent), and d_l is the reduced density of liquids, taken to be 2.66 in all cases.

It is apparent from Fig. 2 that, generally, conversion data for a particular solvent can be estimated from the critical temper-

TABLE 2

Solvents, Their Critical Constants, Calculated Values of Density and Solubility Parameter, and Conversion Data

Solvent	Critical Temperature[a] (T_c) (K)	Critical Pressure[a] (P_c) (atm)	Critical Density[a] (d_c) (g/cm^3)	Density[b] (d) (g/cm^3)	Solubility Parameter[b] (δ) (cal/cm^3)$^{1/2}$	Conversion (wt % daf)
Aniline	699	52.4	0.34	0.62	6.2	75.0
Benzene	562	48.3	0.302	0.38	4.1	37.9
m-Cresol	706	45.0	0.346	0.65	5.9	79.7
Cyclohexane	553	40.2	0.273	0.38	4.2	41.8
Cyclohexanol	623	37	0.293	0.48	4.9	61.8
Cyclohexanone	629	38	0.273	0.47	5.1	68.4
Decalin	664	25.8	0.254	0.51	4.8	63.2
Ethanol	516	63.0	0.276	0.19	2.5	25.5
n-Heptane	540	27.0	0.232	0.36	3.8	24.1
Isobutanol	548	42.4	0.272	0.33	3.7	45.3
Isooctane	544	25.3	0.244	0.40	3.8	21.5
Isopropanol	508	47.0	0.273	0.24	2.8	28.8
Methanol	513	79.9	0.272	0.13	1.9	18.9
Pyridine	620	55.6	0.312	0.47	5.2	50.5
Tetralin	719	34.7	0.309	0.62	5.5	95.8
Toluene	592	40.6	0.292	0.44	4.5	39.2
Water	647	218.3	0.315	0.087	1.7	18.4
o-Xylene	630	35	0.284	0.48	4.7	46.7

[a] From references 14 and 15

[b] At experimental conditions of 450°C and 20 MPa

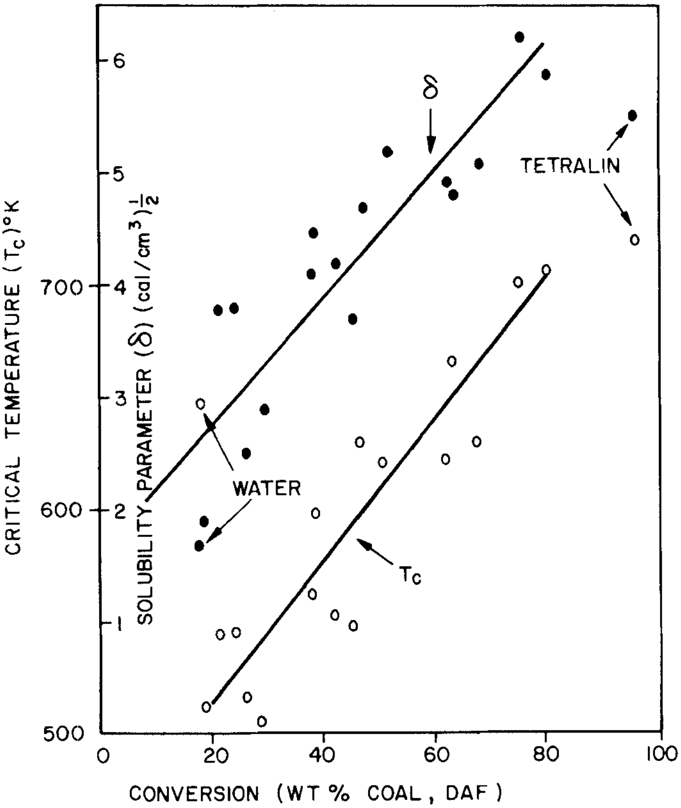

FIGURE 2. Conversion versus critical temperature (T_c) and Hildebrand solubility parameter (δ) for extraction of Waterberg coal at 450°C and 20 MPa using Method A. Conversion = $0.297\ T_c - 129.3$; $r = 0.94$. Conversion = $15.99\ \delta - 21.0$; $r = 0.84$.

ature of that solvent, thus allowing a simple means of estimating the potential of a solvent in supercritical gas extraction. Tetralin, with its hydrogen-donor capability, gave as expected higher conversion than estimated from its critical temperature or solubility parameter. Extraction with tetralin, probably, should be considered as hydrogen-donor hydrogenation rather than 'true' supercritical gas extraction.

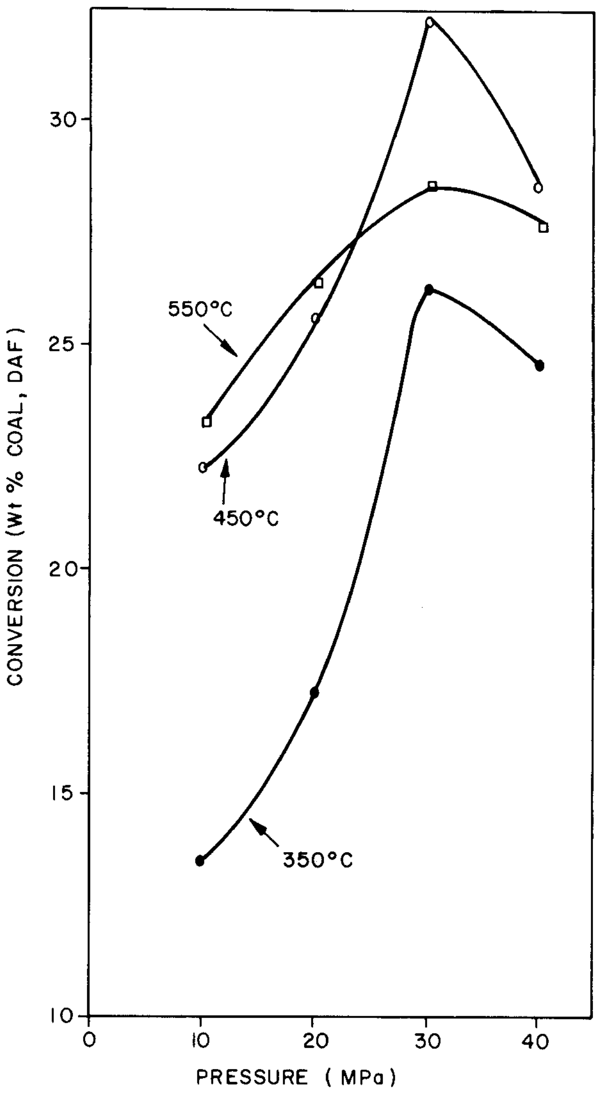

FIGURE 3. Conversion versus pressure for toluene extraction of New Wakefield coal.

Pressure and Temperature

The extraction of New Wakefield coal with toluene was carried out at pressures of 10, 20, 30 and 40 MPa using Method B and at temperatures of 350°C, 450°C and 550°C. At each temperature a maximum was found when conversion was plotted against pressure (see Fig. 3). In each case the maximum was at a pressure of 30 MPa and the conversion at the higher pressure (40 MPa) was lower. Each point on Fig. 3 was an average of at least five results.

The Hildebrand solubility parameter at reaction conditions depends on the density and, therefore, on the pressure of the solvent. Howard (17) has pointed out that the maximum extraction of coal at a constant elevated temperature should occur when the solubility parameters of the coal and the solvent are identical. Therefore, it would be expected, as we found, that at a particular temperature increasing the pressure increases the conversion until a maximum is reached when a further increase in pressure causes a reduction in conversion.

It can also be seen from Fig. 3 that there was a considerable increase in the conversion for supercritical gas extraction at 450°C compared to 350°C. There appears to be no advantage in working at higher temperatures than 450°C.

Chemical Nature of the Oils

The oils (hexane soluble product) from supercritical gas extraction of Sigma coal at 350°C and 450°C and at a pressure of 17 MPa, and New Wakefield and Waterberg coals at 450°C and 20 MPa using Method C have been studied. These oils were separated by elution chromatography on silica gel. The fractions from these separations were grouped as aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds.

Detailed GLC analyses of the aliphatic fractions were only carried out on the two oils from extraction of Sigma coal. These showed, as principal components, a regular series of peaks attributed to straight-chain alkanes. These were identified by comparing their retention times with those of standards and by co-injection. The distribution of the n-alkanes from supercritical gas extraction of Sigma coal at 350°C and 450°C are shown in Fig. 4 together with the n-alkane distribution for Soxhlet extraction of the same coal using choroform/methanol for 100 h. The odd over even composition of the n-alkanes from supercritical gas extraction at 350°C and the low concentration of n-alkanes below n-C_{16} indicates that little, if any, thermolysis is taking place during supercritical gas extraction at 350°C. Indeed the composition of the n-alkanes is very similar to that obtained by mild Soxhlet extraction (see Fig. 4).

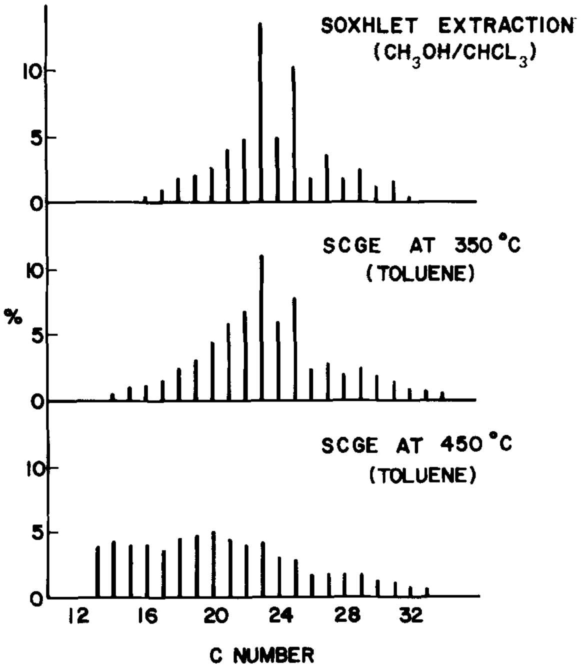

FIGURE 4. Distributions of n-alkanes in paraffin fractions of oils (% of total paraffins).

Bartle et al. (5) have also reported a similar distribution of the n-alkanes on supercritical gas extraction at about 350°C. At 450°C, however, there is considerable change in the composition of the aliphatic fraction, compared with Soxhlet extraction (see Fig. 4).

Vahrmann (18) suggested that a considerable amount of coal consists of small (molecular mass < 1000) compounds held in the coal pores rather than being part of the coal lattice, i.e., coal behaves as a molecular sieve. The penetration of the coal matrix with supercritical toluene under high pressure at 350°C to release a substantially unaltered product is in accord with the view that coal is, to some extent, a molecular sieve. Whereas, at 450°C the different composition of the n-alkanes indicates rather that the supercritical solvent is extracting the product formed on pyrolysis of the coal and that degradation of the coal matrix is taking place. The considerably higher amounts of both total aliphatics (0.5 % of coal at 450°C; 0.09 % at 350°C) and also n-alkanes (0.35 % of coal at 450°C; 0.06 % at 350°C) formed indicates that thermal cleavage of alkyl side groups is much more important at 450°C than 350°C.

The aromatic hydrocarbon fractions are complicated by the presence of substantial amounts of toluene pyrolysis products especially bibenzyl. The pyrolysis of toluene at 350°C and 450°C under conditions similar to those used in supercritical gas extraction has recently been reported (19). UV, fluorescence and phosphorescence spectra showed the presence of ten polyaromatic ring systems in all the oils. These were naphthalene, phenanthrene, anthracene, pyrene, triphenylene, benzo(a)pyrene, benzo(e)pyrene, perylene, dibenzo(def, mno)chrysene (anthanthrene) and dibenzo(b,def)chrysene. There was also evidence from IR studies of the presence of ether linkages and oxygen heterocyclic compounds in these fractions.

The IR spectra of the polar fractions of every sample studied showed strong hydroxyl and carbonyl adsorption. The IR spectra indicated the presence of both aromatic and aliphatic carbonyl groups.

^{13}C NMR spectra were recorded for the oils from New Wakefield and Waterberg coals. In the aromatic carbon region the most intense signals between 118 and 129 ppm from TMS arise from aromatic C-H; the less intense signals between 129 and 148 ppm are due to aromatic C-C (20,21). Part of the aromatic C-H band was shifted to higher fields (108-118 ppm) and may be attributed to aromatic C-H ortho to ether C-O or phenol C-OH (20,21). A relatively intense peak at 142 ppm was present in the spectra of these oils and is probably due to the C-1 carbons of bibenzyl (22). In the aliphatic region the spectra were dominated by two sharp lines at 38 ppm and 29.5 ppm. The line at 38 ppm is ascribed to the ethane carbons of bibenzyl (1,2-diphenylethane) (22). The line at 29.5 ppm is assigned to ε carbon of long aliphatic chains, while other less intense lines at ca 14, 23, 32 and 29 ppm correspond to α, β, γ and δ carbons of these chains (23). The ε band was approximately five times the intensity of the α and β bands, in the spectra of oils from both New Wakefield and Waterberg coal, indicating reasonably long aliphatic chains with an average chain length of about C_{18} (23). (For straight-chain alkanes, substituent effects are not normally transmitted through more than four bonds and, hence, the ε-carbon cannot be distinguished from the remainder of the interior carbons. The ratio of the intensity of the ε band due to the inner methylene carbons to that of the α and β bands indicates the average chain length).

The ^{1}H NMR spectra of the oils were complicated by the presence of toluene pyrolysis products. This was indicated by a strong signal at δ 2.85 which is ascribed to the protons on the CH_2 groups of bibenzyl (24) and signals at approximately δ 3.8 ppm which are probably due to the CH_2 group of diphenylmethanes (25). When the hot-rod reactor (Method B) was used, the oils contained much less toluene pyrolysis products (10) and this allowed meaningful assignments of the proton environments from the ^{1}H NMR spectra. The hydrogen distribution of the oils from supercritical gas extraction

TABLE 3

^{1}H NMR Spectral Data of the Oils [a]

Hydrogen Type	Oil from New Wakefield coal	 Waterberg coal
	% of total hydrogens	
Aromatic (δ 6.1 - 8.9 ppm)	29	29
Phenolic (δ ca 5.5 ppm)	2	2
Benzylic (δ 1.9 - 3.8 ppm)	31	32
Aliphatic (δ < 1.9 ppm)	38	37

[a] Spectra of samples corrected for bibenzyl.

of New Wakefield and Waterberg coals at 450°C and 20 MPa are given in Table 3.

CONCLUSIONS

Supercritical gas extraction of coal is a convenient way of obtaining reasonable yields of coal liquids without using hydrogen. By using a solvent with a higher critical temperature than toluene, much higher yields of extract can be obtained.

The distribution of n-alkanes in the extract indicates that at 350°C very little degradation is taking place during extraction and at this temperature the supercritical solvent is extracting molecules held in the coal pores, in agreement with Vahrman's 'molecular sieve' theory of coal. At the higher temperature of 450°C, however, the n-alkane distribution indicates rather that the supercritical solvent is extracting the product formed on pyrolysis of coal.

REFERENCES

1. J.C. Whitehead and D.R. Williams, J. Inst. Fuel, 48, 182 (1975).
2. R.R. Maddocks and J. Gibson, Chem. Eng. Prog., 73(6), 59 (1977).
3. D.F. Williams and J.C. Whitehead, U.S. Patent 3,970,541 (July 20, 1976).
4. J.E. Blessing and D.S. Ross, Organic Chemistry of Coal, ACS Symposium Series 71, (J.W. Larsen, ed.), American Chemical Society, Washington, D.C., 1978, p. 171.
5. K.D. Bartle, T.G. Martin, and D.F. Williams, Fuel, 54, 266 (1975).
6. J.R. Kershaw, S. Afr. J. Chem., 30, 205 (1977).
7. T. Tugrul and A. Olcay, Fuel, 57, 415 (1978).
8. K.D. Bartle, W.R. Ladner, T.G. Martin, C.E. Snape, and D.F. Williams, Fuel, 58, 413 (1979).
9. K.D. Bartle, A. Calimli, D.W. Jones, R.S. Matthews, A. Olcay, H. Pakdel, and T. Tugrul, Fuel, 58, 423 (1979).
10. J.R. Kershaw, G. Barrass, D. Gray, and J. Jezko, Fuel, 59, 413 (1980).
11. R.W. Hiteshue, R.B. Anderson, and M.D. Schlesinger, Ind. Eng. Chem., 49, 2008 (1957).
12. J.R. Kershaw, G. Barrass, and D. Gray, Fuel Process. Technol. 3, 115 (1980).
13. D. Gray, Fuel, 57, 213 (1978).
14. A.P. Kudchadker, G.K. Alani, and B.J. Zwozinski, Chem. Rev., 68, 729 (1968).
15. Landolt-Börnstein, Zahlenwerte und Funktionen, Vol. 2, Part 1, Springer-Verlag, Berlin, 1971, pp. 328-377.
16. J.C. Giddings, M.N. Myers, L. McLaren, and R.A. Keller, Science, 168, 67 (1968).
17. H.C. Howard, Chemistry of Coal Utilization, Supplementary Volume, (H.H. Lowry, ed.) Wiley, New York, 1963, pp. 340-394.

18. M. Vahrman, Fuel, 49, 5 (1970).

19. J.R. Kershaw, S. Afr. J. Chem., 31, 15 (1978).

20. K.D. Bartle, T.G. Martin, and D.F. Williams, Chem. Ind. (London), 313 (1975).

21. C.E. Snape, W.R. Ladner, and K.D. Bartle, Anal. Chem., 51, 2189 (1979).

22. T.W. Proulx and W.B. Smith, J. Magn. Resonance, 23, 477 (1976).

23. R.J. Pugmire, D.M. Grant, K.W. Zilm, L.L. Anderson, A.G. Oblad, and R.E. Wood, Fuel, 56, 295 (1977).

24. H.A. Szymanski and R.E. Yelin, NMR Band Handbook, Plenum, New York, 1968.

25. A.J. Gordon and R.A. Ford, The Chemist's Companion, Wiley, New York, 1972.

Received by editor November, 1980