

SUPERCRITICAL SOLVENTS AND THE DISSOLUTION
OF COAL AND LIGNITE

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The use of supercritical media as solvents in coal extraction is of interest because of their unusual solvent abilities. In a review of the general concept of supercritical gas extraction, Paul and Wise (1) discuss the solvent properties of materials above their critical temperatures (T_c). These supercritical vapors display unusual solvent powers when compressed to liquid densities. The solubility of naphthalene in supercritical ethylene (at 320 K), for example, is increased by a factor of 10^3 when the vapor density is increased from about 0.1 to about 0.6 g/cm³ (2).

Whitehead and Williams applied this principle to the extraction of coal with hydrocarbons in their supercritical state (3). They extracted about 20% of a coal containing 38% volatile matter into toluene at 350°C (T_c for toluene is 318°C), or a quantity of extract that was greater than the tar yield from carbonization of the same coal.

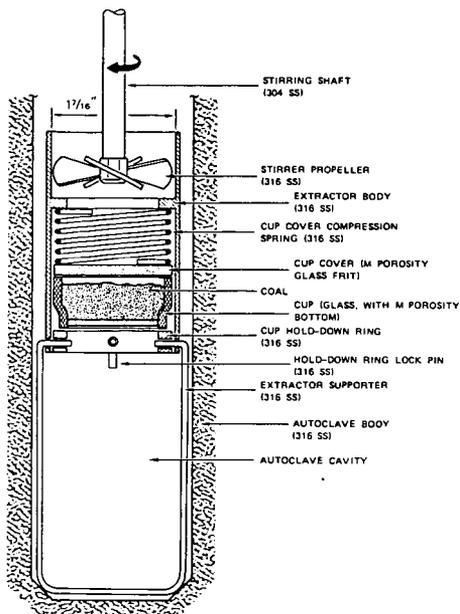
In the work discussed here, we used a number of different solvents as coal dissolution media, all at temperatures above their respective critical temperatures. Our objectives were to investigate a possible structure/solvent-power relationship and to determine if the solvent has to be strictly above its critical temperature to be effective. Our experiments are briefly described below.

Experimental

All experiments were carried out in a 300 cm³, 316 stainless steel, MagneDrive stirred autoclave from Autoclave Engineers. We used samples of beneficiated Illinois No. 6 coal, and a North Dakota lignite.* Most of the experiments were done at 335°C for 90 minutes.

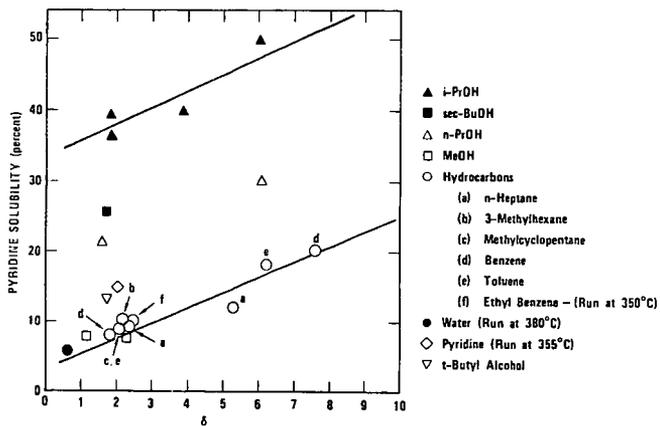
It was necessary under these test conditions to be able to separate any materials soluble in the media from the material insoluble during the experiment. This precaution would eliminate any confusion of results in cases where a significant fraction of the coal was soluble at test conditions but insoluble when the system was brought back to ambient temperature and pressure. Accordingly, we designed a coal filter "basket" for these experiments (Figure 1). Our procedure was to place the starting coal between two sintered glass discs within the autoclave so that any material dissolved under our supercritical conditions would be carried through these discs and found outside the basket after the experiment.

* The samples were provided by Pennsylvania State University, whose designation for the coal samples was PSOC-26 and for the lignite, PSOC-246.



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FIGURE 1 SUPERCRITICAL EXTRACTOR (TO SCALE)



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FIGURE 2 HILDEBRAND SOLUBILITY PARAMETER, δ , VERSUS PYRIDINE SOLUBILITY OF COAL PRODUCTS
Experimental conditions were 335°C, 90 min.

Results and Discussion

Supercritical Extraction

We performed a number of experiments with several media, both with and without the extraction apparatus (basket) in the reactor, and under identical experimental conditions. The results in Table 1 show that, first, the degrees of extraction are small, no more than about 13% for the best cases, and second, that the values for material dissolved in each medium after reaction are virtually the same both with and without the basket. Thus, the supercritical media are extracting up to about 13% of the substrate, and that extract in turn is soluble in the respective media at ambient conditions. The extraction for Run 86 is significantly low, perhaps because the lignite tended to agglomerate under the conditions of this experiment, thereby reducing circulation of i-propanol through the basket.

Clearly, filtration under supercritical conditions was not necessary to obtain the maximum dissolution, and the promise of supercritical extraction appeared diminished in view of the low extraction values. To confirm these findings, we made several additional runs with coal in a wide range of solvents without the basket at several different solvent densities.

We found it useful to consider all our extraction data in terms of the Hildebrand solubility parameter of the respective solvents. This parameter is a measure of the cohesive forces in a solution and is expressed by the relation $\delta = a^{1/2}/V$, where a is van der Waal's intermolecular term and V is the molar volume (4). In addition, the solubility parameter has been considered in terms of polar and nonpolar contributions [4(c)]. The application of the solubility parameter to coal processing has been discussed by Angelovich et al. (5), who concluded that solvents with a nonpolar solubility parameter of about 9.5 appeared to be most effective in coal dissolution.

Giddings et al. (6) found a correlation between solvent capabilities and δ values of a number of supercritical fluids at liquid densities. Their expression defining the parameter is

$$\delta = 1.25 P_c^{1/2} \rho_r / \rho(\text{liq}) \quad 1)$$

where P_c is the critical pressure in atmospheres, ρ_r is the reduced density, and $\rho(\text{liq})$ is the reduced density of liquids, assumed to be about 2.66. We can thus vary the δ value for a given medium simply by varying the experimental density.

The pyridine solubility of our starting coal is 13%. Figure 2 compiles all our extraction data and plots the total pyridine solubilities of the coal products versus the Hildebrand solubility parameter value for each medium, as determined by Equation 1. Each experiment yielded both a filtrate soluble in the reaction medium and a filterable residue. All filtrates were pyridine-soluble, and the solubilities in pyridine of each of the residues were determined at room temperature. The values used in the figure are the total solubilities, obtained by summing the fraction of the starting coal represented by the filtrate, and the pyridine-soluble fraction of the starting coal in the residue.

Table 1
 SUPERCRITICAL EXTRACTION OF ILLINOIS NO. 6 COAL AND
 NORTH DAKOTA LIGNITE (at 335°C for 60 min)^a

Run No.	Supercritical Medium		Mode	Recovered in medium ^b (%)	Mass Recovered (%)
	Type	(g/ml)			
Coal	55	iPrOH 0.3	Basket	11	97
	38	iPrOH 0.3	No Basket	11	97
	82	Benzene ^c 0.6	Basket	12	95
	60	Benzene ^c 0.6	No Basket	13	92
	58	MeOH ^d 0.4	Basket	12	97
	76	MeOH ^d 0.4	No Basket	8	94
Lig-nite	84	Toluene 0.2	Basket	3	87
	66	Toluene 0.2	No Basket	4	88
	86	iPrOH 0.1	Basket	5	86
	65	iPrOH 0.1	No Basket	12	85

^a 5 g coal or lignite; reactor volume, 280 ml.

^b Room temperature solubilities of the starting coal and lignite are less than 1% in all the test solvents.

^c 1 g coal, for 3 hr.

^d 1 g coal.

Table 2
 EXPERIMENTS ON ILLINOIS NO. 6 COAL WITH TOLUENE
 BELOW AND ABOVE ITS CRITICAL TEMPERATURES FOR 90 MINUTES

Run No.	Solvent	Experimental Conditions				Solubility (%)	
		P (g/ml)	Temp ^a (°C)	psig ^b	Filt ^c	THF	Pyridine
45	Toluene (subcritical)	0.65	305	2400	8	12	13
49	Benzene (supercritical)	0.70	305	2400	8	11	13
27	Toluene (supercritical)	0.65	335	3400	13	21	24
16	Benzene (supercritical)	0.70	335	4100	10	22	20

^a The critical temperatures for toluene and benzene are 320°C and 288°C, respectively.

^b The critical pressures of toluene and benzene are 630 psi and 720 psi, respectively.

^c The "Filt" values are the fraction of the product coal which is soluble in the test medium at room temperatures.

The plot may be roughly split into two regions. The upper region of relatively high pyridine solubilities represents data from previously discussed work with alcohols as H-donor solvents (7). The bulk of the data falls about the lower line. Most of the solubilities are below 13% or less than the solubility of the untreated coal itself in pyridine.

We used pressure ranging from about 700 psi for the lower δ values to about 4000 psi for the highest. Within the range of solvents studied, and with the exception of the H-donor alcohols, no gross differences are apparent between solvent types. For example, all the hydrocarbons (○), both aliphatics and aromatics, cluster well about the line, as does the single point for water (●). Methanol (□) is also close to the line and apparently does not serve as an H-donor* under these conditions. The two solvents a little above the line are pyridine (◇) and t-butyl alcohol (▽). Pyridine is a well known solvent in coal work; its extraction capability is apparently not enhanced by high pressures and temperatures and its supercritical state. The alcohol, on the other hand, cannot operate as an H-donor, and yet, unexpectedly, the plot shows it to be a better solvent than methanol.

The roughly linear correlation displayed by the data suggests that the dissolution process is not a function of the solvent type, but rather, is sensitive to the density (i.e., pressure) of the medium. Perhaps what we observe is an initial, reversible thermal fragmentation of a critical link in coal.



followed by some means of stabilization by solvent (S)



The nature of the stabilization process remains in question.

The positive slope of the lower line in Figure 2 suggests that greater degrees of extraction might be possible at higher δ values. The point labeled d in the figure is for a δ value of 7.5 and is taken from an experiment with benzene at 4100 psi. If we make the appropriate simplifying assumptions regarding liquid compressibility, we can calculate that for a δ value of 10, where by extrapolation we would expect a pyridine solubility of 25%, a pressure in excess of 7800 psi would be required. Clearly, extractions at this pressure would not be practical.

Effect of Supercritical State

Finally, to determine if the supercritical state is strictly necessary to obtain the small extractions discussed here, we compare the results of using toluene and benzene at 305°C and 335°C. These temperatures are above the T_c of

* We have recently found that with some bases present, methanol operates very well as an H-donor alcohol.

benzene (288°C), but below and above, respectively, the T_c of toluene (320°C). The results of this series of runs are presented in Table 2.

The benzene in Runs 49 and 16 is supercritical. With increasing temperature, a small increase can be seen in the tetrahydrofuran (THF) and pyridine values. Similar changes can be seen for toluene in Runs 45 and 27 over the same temperature range, where toluene is below and above its T_c , respectively.

The changes observed are due to temperature differences alone. These conversions are thus due to the presence of a dense medium at high temperatures. We conclude, therefore, that whether an extraction medium is strictly supercritical, that is, above the critical temperature, is of little consequence.

Acknowledgement

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REFERENCES

1. P. Paul and W. Wise, "The Principles of Gas Extraction," Mill & Boon Ltd., London, 1971.
2. Yu, Tsekhanskaya, M. Iomtev, and E. Mashkina, Zh. Fiz. Khim., 38, 2166 (1964).
3. J. Whitehead and D. Williams, J. Inst. Fuel, 182 (December 1975).
4. (a) H. Hildebrand and R. Scott, The Solubility of Nonelectrolytes, Reinhold, New York, 1950.
(b) C. Hansen and A. Beerbover, "Solubility Parameters" in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Suppl. Vol., John Wiley, 1971.
(c) R. Blanks and J. Peausnitz, Ind. Eng. Chem. Fundamentals, 3, 1 (1964).
5. J. Angelovich, G. Pastor and H. Silver, Ind. Eng. Chem. Process Des. Dev., 9, 106 (1970).
6. J. Giddings, M. Myers, L. McLaren, and R. Keller, Science, 162, 67 (4 October 1968).
7. D. S. Ross and J. Blessing, "Isopropyl Alcohol as a Coal Liquefaction Agent," Fuel Division Preprints for the 173rd National Meeting of the American Chem. Soc., New Orleans, LA, March, 1977.