

SOLVENT EFFECTS IN SUPERCRITICAL EXTRACTION OF COAL

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INTRODUCTION

Supercritical gas extraction is particularly suitable for the recovery of the liquids formed when coal is heated to above 400°C. These liquids are normally too involatile to distill at this temperature. If the temperature is increased, they polymerize to form heavier and larger molecular species and evolve as gases and liquids. Only a relatively small amount of the coal distills as tar from the decomposing material. Supercritical gas extraction affords a means of recovering these liquids as they are formed while avoiding the undesirable decomposition reactions (1). Supercritical fluids have a density of about 30% of that of a normal fluid, which is high enough to provide for good solvent capability, but also low enough for high diffusivity and rapid mass transfer throughout the complex coal matrix.

The use of supercritical fluids for the recovery of hydrocarbons and related compounds from coal was pioneered by the National Coal Board (NCB) in Britain. Over a number of years, NCB has investigated the direct extraction of coals using light aromatic solvents (mostly toluene) under supercritical conditions. In a recent NCB report, Whitehead (2) summarized the experimental data on supercritical extraction of coal, obtained both on bench-scale units and on a 5 kg/h continuous pilot plant operated in Britain by the Coal Research Establishment. According to these data, the residence time of coal under supercritical conditions was the variable which most influenced the extract yield. The influence of pressure and temperature on the yield was also substantial, and an extract yield of 35% by weight of the dry, ash-free coal could be obtained using toluene at 420°C and 27.5 MPa pressure. It was also determined that it was not essential for the extracting fluid to be above its critical temperature to be effective. For a given operating pressure, the advantages of operating in a supercritical state were associated with the lower density and viscosity of the fluid compared with a subcritical fluid.

In another coal-related effort in the United States, Kerr-McGee Corporation has developed a new solid-liquid separation technique utilizing the unique solvent capabilities of supercritical fluids (3). The process, called Critical Solvent Deashing (CSD), is used to separate mineral matter and unreacted coal from coal liquids. A two-stage CSD pilot plant (integrated into an SRC process unit) has been operated for the last four years at Wilsonville, Alabama.

Despite the strong industrial interest and the extensive research activity in the field of supercritical extraction, much remains to be learned in the application of supercritical fluids to coal processing. An important feature of supercritical coal extraction that has received little attention in the literature concerns the specific characteristics (physical and/or chemical) of the supercritical solvent and solvent mixtures that can affect the yield and the quality of the coal extracts. Paul and Wise (4) in their excellent monograph on gas extraction used the semiquantitative approach of Rowlinson and Richardson (5) to show the strong dependence of supercritical solubility on the cross-virial coefficient B_{12} of the solvent-substrate gas phase. They also discussed empirical correlations for calculating these coefficients in relatively simple cases of nonpolar molecules. The existing B_{12} correlations, however, are most likely to prove completely unsatisfactory for polar solvents, or for solvents that are chemically (as well as physically) involved in the mechanism of coal extraction. Polar or hydrogen bonding solvents, for example, may exert a stronger dissociating or depolymerizing action on coal during the thermal fragmentation stage than nonpolar solvents, thus increasing the yield of extractable coal material.

The present paper discusses some results from the first phase of our experimental investigation into solvent and chemical-reaction effects in supercritical coal extraction. The second phase currently under way is concerned with the combination of supercritical extraction and specific chemical treatment of the coal (such as

catalytic depolymerization, alkylation, hydrogen-donor activity, etc.) to increase the yield of coal extracts and decrease the severity of the extraction conditions.

EXPERIMENTAL

All supercritical extraction experiments were carried out in batch mode, in a 1000 cm³ (free volume: 910 cm³), 316SS AE MagneDrive autoclave equipped with a digital temperature controller/indicator and a digital pressure transducer/indicator in the 0-10,000 psi range (Autoclave Engineers, Model DPS-0201). An Illinois No. 6 bituminous coal, 100x200 mesh size, was used throughout this investigation. Its proximate and ultimate analyses are included in Table 5. The coal was dried under vacuum at 110°C for 24 hours before every run.

In each run a certain amount of solvent, corresponding to the desired supercritical density, was first measured into the autoclave. Then a fine-mesh basket containing 20 grams of the dried and sized coal was suspended at the top of the autoclave, so that no actual contact between the liquid solvent and the coal sample was possible. We took this precaution to eliminate any ambiguity in the results, where a significant fraction of the coal would be soluble under supercritical conditions but insoluble when the system was brought back to ambient conditions, thus precipitating on the extracted coal and causing the extraction yields (which are based on the weight loss of the raw coal) to appear low (6). In our system any material dissolved under supercritical conditions is carried through and recovered outside the basket after the experiment, whether or not this material is still soluble.

After sealing and purging, the reactor was heated for about 1.5 hr to reach extraction temperature (400°C). Following 2 hrs of extraction, the system was cooled to room temperature (2 hrs). Yield was defined as the weight loss of the vacuum dried (24 hrs, 110°C), char-containing basket expressed as a percentage of the raw, dry-coal weight.

The results on weight-percent extraction reported in this paper were reproducible within ±0.5 wt% (absolute). Solvent recoveries after extraction ranged between 96 and 100%. Decreasing the particle size and the amount of coal sample (for a given solvent density), and increasing the extraction time had no effect on extraction yields. Therefore, the reported results reflect a condition of equilibrium extraction with no mass transfer or solvent-saturation limitations.

The extracted coal samples, as well as the supercritical extracts, were analyzed for elemental composition, heating value, and pyridine solubility.

RESULTS AND DISCUSSION

1. Non-polar Solvent Effects

To determine the effect of the physical parameters of the supercritical solvent on coal extraction, coal samples were extracted with a homologous series of n-paraffins (from pentane to dodecane), at 400°C and at a constant solvent density of 2.75 moles/liter. Results on weight-percent extraction and final extraction pressure (which is generated by the supercritical solvent itself) are given in Table 1. The critical parameters of the paraffinic solvents are listed in Table 2.

The results indicate that extraction yield increases with increasing molecular weight of the solvent, dodecane being the best supercritical solvent under the given experimental conditions. On the other hand, extraction pressure displays an interesting behavior, decreasing with increasing molecular weight of the solvent (at constant temperature and molar density), then passing through a minimum (for nonane), and finally increasing with increasing molecular weight.

Based on their experimental results on high-pressure gas chromatography, Giddings et. al. (7) suggested that the solvent power of a supercritical medium is directly related to its solubility parameter, δ . Using the van der Waals equation, they developed the following correlation:

$$\delta \left(\frac{\text{Cal}}{\text{cm}^3} \right)^{1/2} = 1.25 P_c^{1/2} \frac{\rho}{\rho_\ell} \quad 1)$$

where P_c is the critical pressure of the solvent in atmospheres,

ρ_r is its reduced density $\Delta \frac{\rho}{\rho_{\text{critical}}}$, and

ρ_λ is the reduced density of liquids, taken to be about 2.66.

It is important to note here that the above correlation is likely to prove satisfactory for non-polar solvents, but its value in predicting solvent capabilities when special solvent effects are present (polar clustering, hydrogen bonding, etc.) is very much in doubt. Blessing and Ross (6), based on a limited number of supercritical extraction experiments on coal and lignite, concluded that the extraction yield is an almost linear, universal (for a given coal) function of the solubility parameter of the solvent as calculated by the Giddings correlation, and that regardless of their structural differences, all compounds largely perform in accordance with their solvent capabilities. This is a rather arbitrary statement, taking into account the fact that only one polar solvent (methanol) was included in their plot of coal extraction versus solubility parameter of the solvent.

Using Giddings' correlation, solubility-parameter values for the homologous series of n-paraffins were calculated at the experimental solvent density of 2.75 moles/liter. The results are given in the last column of Table 2. Weight-percent extraction is plotted against solvent solubility parameter in Figure 1. As can be seen from the figure, the plot is highly linear (correlation coefficient 0.987), yielding the following correlation:

$$(\text{wt\% extraction}) = 3.05\delta + 11.2 \quad 2)$$

Table 4 includes the results on supercritical coal extraction at 400°C and three different solvent densities, for another nonpolar hydrocarbon solvent, namely toluene. Solubility-parameter values calculated from Giddings' correlation are given in the last column of Table 4. Linear regression on the toluene runs yields the following correlation (correlation coefficient 0.986):

$$(\text{wt\% extraction}) = 3.96\delta + 10.9 \quad 3)$$

A measure of the accuracy of the experimental results is the predicted value for the extraction yield at the limit $\delta \rightarrow 0$ (vacuum pyrolysis of coal), which should be the same for all solvents. Equations 2 (n-paraffins) and 3 (toluene) predict extraction limits very close to each other (11.2 and 10.9 weight percent respectively). However, contrary to the conclusion of Blessing and Ross, the extraction yield depends also on the solvent functionality. By comparing equations 2 and 3 it can be seen that toluene is a better solvent in supercritical coal extraction than straight-chain aliphatic hydrocarbons, for the same value of the Giddings solubility parameter. As we will show later the effect of functionality is even stronger for polar solvents.

It has also been suggested (Fong, et.al, (8)) that extraction yields may be affected by molecular size, and that the longest dimension of each solvent molecule should be considered when comparing the coal extraction efficiencies of various supercritical solvents. The implication here is that penetration of the micropore structure of the coal can be achieved more easily by the smaller molecules. Our results on the homologous series of n-paraffins, where dodecane, the longest molecule, proved to be the most effective extraction solvent, certainly do not support this suggestion. Mass transfer limitations do not appear to be significant in supercritical coal extraction, at least under the given experimental conditions.

The behavior of the extraction pressure at constant temperature and molar density in the homologous series of n-paraffins is worth further consideration from the standpoint of optimizing the extraction conditions. Our results, for example, indicate that n-nonane is a superior solvent than n-pentane in supercritical coal extraction, not only in terms of the higher extraction yield, but also in terms of the considerably lower extraction pressure.

The Redlich-Kwong equation of state

$$P = \frac{RT}{\hat{V}-b} - \frac{a}{T^{1/2}\hat{V}(\hat{V}+b)} \quad 4)$$

where

$$\hat{V} = \text{molar volume} = \frac{1}{\rho} \quad (\rho = \text{molar density})$$

$$a = \frac{0.4278R^2T_c^{2.5}}{P_c}, \text{ and}$$

$$b = \frac{0.0867RT_c}{P_c},$$

was used to examine the extraction-pressure trends in the homologous series of n-paraffins, under the given experimental conditions: $T = 400^\circ\text{C}$ and $\rho = 2.75$ moles/liter or $\hat{V} = \frac{1}{\rho} = 363.6 \text{ cm}^3/\text{mole}$. Critical parameters for the n-paraffins, as well as calculated values for a and b, and estimated (eq. 4) values for the extraction pressure are given in Table 2. These data show that, despite the considerable differences between estimated and observed values of the extraction pressure, especially for the higher paraffins, the Redlich-Kwong equation is able to predict the pressure minimum at almost the same solubility-parameter value as the experimental one. The structure of the Redlich-Kwong equation, and the strong dependence of the pressure on the $(\hat{V}-b)^{-1}$ term in particular, suggests a very interesting path for optimizing extraction conditions. In Table 3 we list estimated extraction pressures and solubility-parameter values for the homologous series of n-paraffins, in supercritical coal extraction at 400°C and two other molar densities. As can be seen from the table, by decreasing the molar density, the pressure minimum shifts towards the heavier hydrocarbons, which still possess the higher solubility-parameter values. Thus, by proper selection of the experimental solvent density (1.8 moles/liter in our case), dodecane becomes an excellent supercritical solvent for coal, both in terms of the highest extraction yield in the hydrocarbon series, and also in terms of the lowest generated extraction pressure.

The same solvent density considerations can, of course, be applied to any other homologous series of nonpolar compounds (e.g. aromatic hydrocarbons).

2. Polar Effects in Supercritical Coal Extraction

We are currently conducting an extensive experimental investigation on the effect of increased solvent polarity on coal extraction yields. A wide range of supercritical solvents is being studied, including simple inorganic molecules (CO_2 , H_2O , NH_3 , BF_3 , etc.), and polar hydrocarbons, particularly alcohols. Table 4 gives the results of some preliminary supercritical extraction experiments at 400°C with simple polar compounds, such as methanol, acetone and water.

Methanol gives a slightly lower extraction yield (20.6% versus 21.3%) than estimated from the Giddings correlation and equation 2. From a practical standpoint, however, methanol is far inferior a supercritical solvent than aliphatic hydrocarbons, because it gives lower extraction yields at much higher extraction pressures (20.6% at 3610 psig compared with 21.2% at 1290 psig for n-nonane).

The predictive value of equation 2 when coupled with the Giddings correlation breaks down completely for a polar solvent such as acetone, which shows anomalously low coal extraction yields at 400°C . These low yields can only in part be attributed to acetone decomposition that was experimentally observed at 400°C .

Water, on the other hand, displays large positive deviations from the estimated extraction values. For example, at 400°C and a supercritical density of 8.25 moles/liter the coal extraction yield is 34.0 wt% compared with 20.9wt%, which is the value calculated from equations 1 and 2. The results in Table 4 seem to indicate that water is an even better supercritical solvent than toluene for coal extraction, affecting high extraction yields at moderately high pressures (34wt% at $T_r=1.04$ and $P_r=1.12$). A very interesting feature of the supercritical water runs is that the extract-containing aqueous phase, when brought back to ambient conditions is an almost clear, strongly smelling solution with a minimal amount of precipitate, and in any case it is completely different from the black coal solutions obtained in supercritical toluene runs. Whether this is a result of supercritical water extracting selectively a different portion of the coal material (e.g. more of the polar, phenolic fraction) than toluene, or it is mainly a result of high-pressure reforming reactions of coal organics with supercritical water than can yield products completely different from simple supercritical extracts (9), is not clear at this point.

We are currently investigating the mechanism of supercritical water/coal interactions using model-compound systems, under similar reaction conditions ($T=400^{\circ}\text{C}$; $P_r=1.1$). We are also in the process of characterizing the toluene, methanol and water supercritical coal extracts by GPC and other analytical techniques, that will enable us to determine the differences in structure and functionality of these extracts.

3. Synergistic Effects of Solvent Mixtures

Possible non-ideal effects arising from polar/nonpolar solvent combinations were studied in supercritical extraction of coal at 400°C and constant total molar density for a series of toluene/methanol and toluene/acetone mixtures. Extraction yields and generated pressures are depicted in Figures 3 and 4.

Figure 3 for the toluene/methanol mixtures reveals a very interesting feature of the extraction curve, which passes through a maximum at a composition of approximately 70 mole% toluene and then descends slowly to the pure toluene value. This extraction maximum, which is higher than the extraction yield of either solvent alone (synergistic effect), is of even greater importance, because it is attained at a pressure much lower than the pressure generated in pure toluene extraction under similar conditions (3700 psig as compared with 5140 psig). Fong et. al. (8) observed a similar maximum-extraction effect in supercritical extraction of coal with toluene/methanol mixtures at 360°C and at a constant pressure of 2000 psig, but their results are of limited practical value, because of the constant-pressure condition that was employed (rather than constant solvent density).

Toluene/acetone mixtures, on the other hand, display almost linear dependence of both the extraction yield and the extraction pressure on molar composition. No synergistic effect is present under the given experimental conditions, so that pure toluene becomes a far superior supercritical solvent than pure acetone or any toluene/acetone mixture, effecting much higher coal extraction at a considerably lower extraction pressure.

4. Physical and Chemical Changes in Coal Structure during Supercritical Extraction

Table 5 gives proximate and ultimate analyses and heat content values for selected coal samples that were extracted with pure supercritical solvents under a variety of experimental conditions. The analysis of the raw coal that was used in all these experimental runs is also included.

The data show a drastic (more than 60% in most cases) reduction in the volatiles content and a consequent increase in the fixed-carbon content of the coal after supercritical extraction. The reduction in volatiles is accompanied by a significant increase in the C/H atomic ratio of the treated coal, thus indicating a progressive extraction of hydrogen-rich fractions from the coal matrix. It is interesting to note, however, that even at high extraction levels, the extracted coal retains most of its fuel value, as indicated by a moderate C/H ratio and a high heat-content value. For example, coal extracted with supercritical toluene at 400°C and at a solvent density of 6.75 moles/liter retains 94.7% of the specific heating value of the raw coal, despite a 36% extraction loss and a corresponding 61.7% loss of volatiles.

The data indicate, once again, that supercritical water may be one of the most promising solvents in supercritical coal extraction, affecting higher extraction yields at much lower heat-content and H/C losses (for the extracted coal) than hydrocarbon solvents (for example, compare the results of the pure toluene and the water runs).

A very interesting selective desulfurization effect is observed in supercritical extraction of coal with methanol-based solvents, and to a lesser extent with acetone and water. Ideally, if there is no special affinity of the supercritical solvent towards sulfur (or other heteroatom), the extraction of sulfur fractions from the coal matrix should be non-selective, so that the sulfur content of the extracted coal, as well as that of the extract, is in every case the same with the sulfur content of the raw coal. Our data show that, although this is true for nitrogen, sulfur undergoes strong selective extraction in the presence of methanol-based solvents.

Supercritical extraction of coal with pure methanol results in a 31.8% level of selective sulfur reduction, while the other two oxygenated solvents, acetone and water, also display significant ($\approx 23\%$) desulfurizing action on extracted coal samples. Chemical participation of the methanol in the coal-pyrolysis stage, that enhances selectively the fragmentation of sulfur clusters in the coal molecule and their subsequent extraction in the supercritical phase is proposed to be the main cause of this effect.

Finally, surface areas of extracted coal samples were measured by nitrogen adsorption at -196°C to determine the effect of possible changes occurring in the physical structure of the coal during supercritical extraction. The results are given in Table 6. A sharp decrease in the available surface area of the coal is observed in all the extracted samples, and this decrease, at least for the paraffinic series, is progressively more pronounced at higher extraction levels. Methanol-extracted coal, on the other hand, shows a higher surface-area reduction than hexane-extracted coal, despite the lower extraction level. The surface-area-reduction effect may be attributed to a shift in the pore-size distribution of the coal caused by the extractive action of the supercritical solvent. The removal of coal material from the solid matrix may result in the progressive opening of larger pore spaces, thus shifting the pore-size distribution towards the macropore range, generally associated with low specific surface areas. Swelling phenomena in the coal matrix caused by strong H-bonding solvents, such as methanol, can contribute further to the closing of smaller pores and, thus, to additional collapse of the microporous network. Fong et. al. (8) proposed a different explanation based on the retention of extract in the pores. At the end of an extraction cycle, the removal of the volatile supercritical solvent from the pores could result in partial condensation of the coal extract and, thus, in extensive pore blockage.

Concluding this section we would like to report some results on the pyridine solubility of raw and extracted coal samples. The pyridine solubilities of dried samples were determined by stirring 0.5 grams in 50 cm^3 pyridine for 2 hrs at room temperature, then filtering and evaporating the solvent, and drying the solid residue under vacuum at 110°C for 24 hrs. Results for the raw coal and for the pure toluene and pure methanol runs are given below:

Supercritical Solvent	Extraction Conditions	Weight Percent Extraction	Pyridine Solubility of Extracted Coal (%)
R A W C O A L			11.2
Toluene	400°C , 6.75 $\frac{\text{moles}}{\text{liter}}$	36.0	0.8
Methanol	400°C , 6.75 $\frac{\text{moles}}{\text{liter}}$	20.6	2.4

The pyridine solubility of coal decreases sharply after supercritical extraction, indicating that most of the coal material that is soluble in pyridine at room temperature dissolves in the supercritical solvent during the high temperature extraction.

It is also important to report here that part of the supercritical extract recovered in the toluene phase after cooling the reactor's contents to room temperature, is in the form of a precipitate, fully soluble in pyridine, and amounting to approximately 8 wt% on the basis of raw dry coal. Therefore, contrary to the claim of Blessing and Ross, a significant part of the coal material which is soluble in the solvent under supercritical conditions, becomes insoluble when the solvent is brought back to ambient conditions.

SUMMARY

The specific physical and chemical characteristics of supercritical solvents and solvent mixtures that can affect the yield and the properties of coal extracts were experimentally investigated. Strong non-ideal interactions, such as polar forces and hydrogen bonding, as well as synergistic interactions in multicomponent solvent mixtures, were shown to produce large deviations from the simple, density-driven supercritical solubility. These interactions can be manipulated to optimize supercritical coal extraction by reducing the severity of the extraction conditions (pressure in particular). Physical and chemical changes occurring in the coal structure during supercritical solvent extraction were also examined.

ACKNOWLEDGEMENTS

This work was supported by the United States Department of Energy under Grant No. DE-FG22-81PC40801 and by the Center for Energy Studies, Austin, Texas. The support of the two agencies is gratefully acknowledged.

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Table 1. Supercritical extraction of coal with a homologous series of n-paraffins at 400°C and at a (constant) solvent density of 2.75 moles/liter.

Solvent	Weight Percent Extraction	Extraction Pressure (psig)
Pentane	18.43	2032
Hexane	19.26	1635
Heptane	19.70	1441
Octane	20.70	1393
Nonane	21.17	1290
Decane	22.75	1380
Undecane	23.16	1562
Dodecane	23.56	1768

Table 2. Physical solvent parameters for the homologous series of n-paraffins from pentane to dodecane.

Solvent	Critical Temperature (°C)	Critical Pressure (atm)	Critical Density (g/cm ³)	a ($\times 10^9$) ¹ (cm ⁶ .atm. ³ .°K ^{1/2}) mole ²	b ¹ (cm ³ /mole)	Extraction Pressure (psig) ²	Solubility Parameter (cal ^{1/2} /cm ^{3/2}) ³
Pentane	196.6	33.3	0.237	0.4137	100.36	1680.2	2.27
Hexane	234.2	29.9	0.233	0.5586	120.72	1531	2.61
Heptane	267.1	27	0.232	0.7238	142.35	1425.9	2.90
Octane	296	24.8	0.232	0.8977	163.27	1383.3	3.17
Nonane	321	22.5	0.231	1.1017	187.87	1492.5	3.42
Decane	344.4	20.8	0.231	1.3125	211.22	1755.3	3.65
Undecane	365.2	19.2	0.230	1.5446	236.53	2363.6	3.85
Dodecane	386	17.9	0.230	1.7951	261.98	3502.1	4.05

¹ Constants of the Redlich-Kwong equation of state

² Calculated from the Redlich-Kwong equation at the supercritical extraction conditions: 400°C, 2.75 moles/liter

³ Calculated from Giddings' correlation at the supercritical extraction conditions: $\rho = 2.75$ moles/liter

Table 3. Extraction pressures calculated from the Redlich-Kwong equation of state at 400°C and two different solvent densities.

Solvent	$\rho = 2$ moles/liter		$\rho = 3$ moles/liter	
	Extraction Pressure(psig)	Solubility Parameter ¹	Extraction Pressure(psig)	Solubility Parameter ¹
Pentane	1236.2	1.65	1849.3	2.48
Hexane	1106.3	1.90	1713.3	2.85
Heptane	978.8	2.11	1650.7	3.16
Octane	863.1	2.31	1687.4	3.46
Nonane	771.8	2.49	1974.5	3.73
Decane	705.9	2.65	2538.0	3.98
Undecane	690.8	2.80	3757.3	4.2
Dodecane	727.1	2.95	6239.7	4.42

¹ Calculated from Gidding's correlation

Table 4. Supercritical extraction of coal
with various solvents at 400°C.

Solvent	Weight Percent Extraction	Extraction Pressure ¹ (psig)	Solvent Density ¹ (moles/liter)	Solubility Parameter ²
Toluene	36.0	5140	6.75	6.46
"	27.6	1440	4.0	3.83
"	20.3	1260	2.75	2.63
Acetone	4.0	2180	4.0	2.69
"	7.3	3480 ³	5.5	3.70
Methanol	20.6	3610	6.75	3.31
Water	34.0	3580	8.25	3.17
"	29.5	3070	7.08	2.72

¹ Experimental value

² Calculated from Giddings' correlation

³ Significant decomposition of acetone was observed

TABLE 5. Proximate and ultimate analyses of coal samples extracted with supercritical solvents at 400 °C

Solvent	Pentane	Octane	Dodecane	Toluene	Toluene	Methanol	Acetone	Water
Supercritical Density (moles/liter)	2.75	2.75	2.75	4.0	6.75	6.75	4.0	7.08
Weight Percent Extraction	18.43	20.70	23.56	27.6	36.0	20.6	4.0	29.5
<u>Proximate Analysis¹ (%)</u>								
Volatiles	42.3	21.9	25.4	21.6	25.3	24.6	23.1	18.1
Fixed Carbon	43.6	59.4	55.4	58.0	53.4	57.5	60.4	64.0
Ash	14.1	18.7	19.2	20.4	21.3	17.9	16.5	17.9
<u>Ultimate Analysis¹ (%)</u>								
Carbon	62.9	62.2	67.8	61.8	63.6	56.9	53.2	55.6
Hydrogen	4.7	3.5	3.7	3.1	3.1	3.6	3.7	3.2
Nitrogen	1.1	1.1	1.2	1.1	1.1	1.1	0.8	1.0
Sulfur	4.4	4.1	4.2	4.1	3.9	3.0	3.4	3.4
Oxygen (by difference)	26.9	29.1	23.1	29.9	28.3	35.4	38.9	36.8
Heating Value (Btu/lb)	11415	11560	11510	10980	10805	11690	12280	11510
C/H ratio	1.11	1.48	1.53	1.66	1.71	1.32	1.20	1.45
‡ Sulfur reduction	0	6.8	4.5	6.8	11.4	31.8	22.7	22.7

¹On a dry basis

Table 6. Nitrogen-surface areas of coal samples extracted with various supercritical solvents at 400°C.

Solvent	Raw Coal	Hexane	Decane	Undecane	Dodecane	Methanol
Supercritical density ($\frac{\text{moles}}{\text{liter}}$)	-	2.75	2.75	2.75	2.75	6.75
Weight percent extraction	0	19.3	22.8	23.2	23.6	20.6
N ₂ surface area (m ² /g)	38.4	12.7	3.0	2.5	2.4	1.6
Surface-area reduction (%)	0	66.9	92.2	93.5	93.8	95.8

HOMOLOGOUS SERIES OF N-PARAFFINS

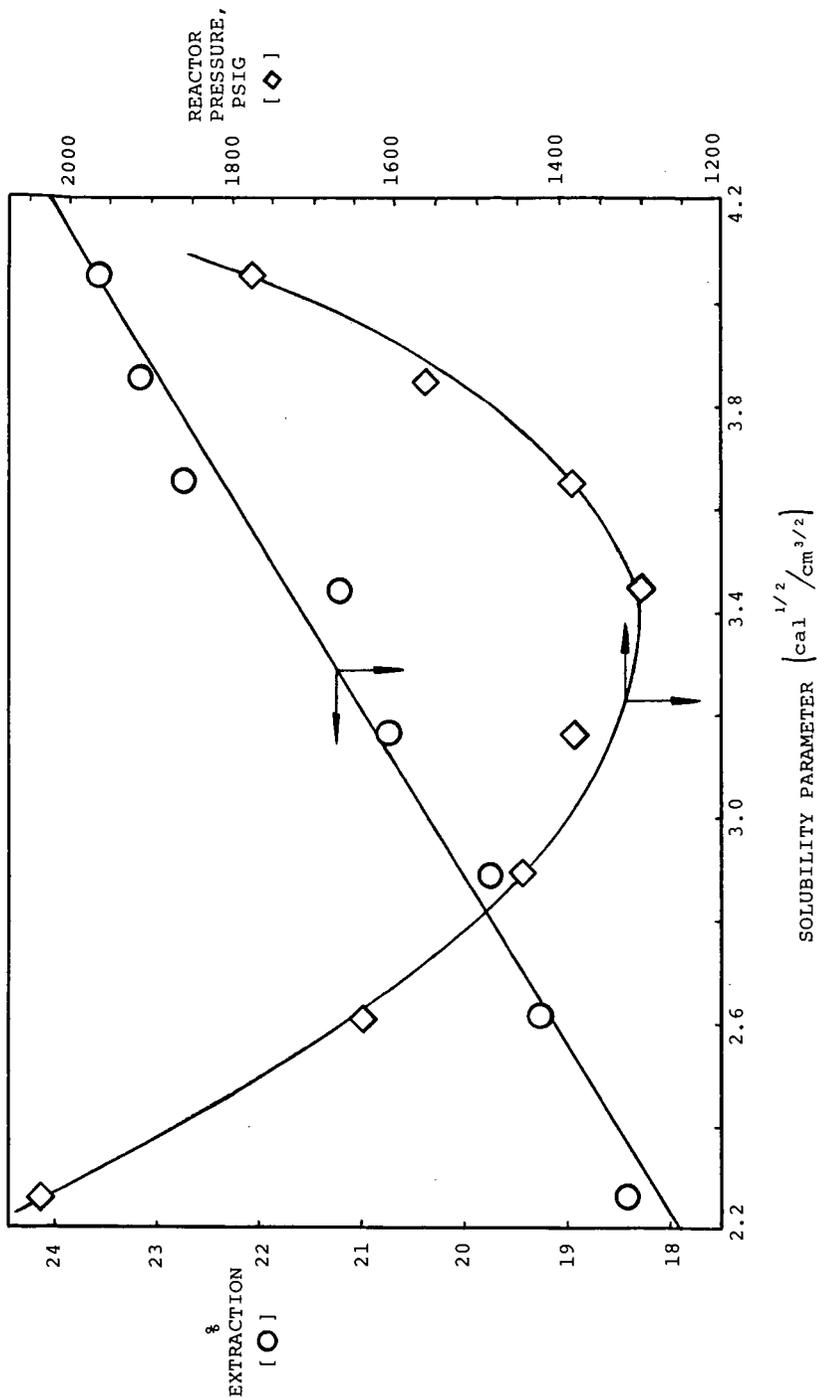
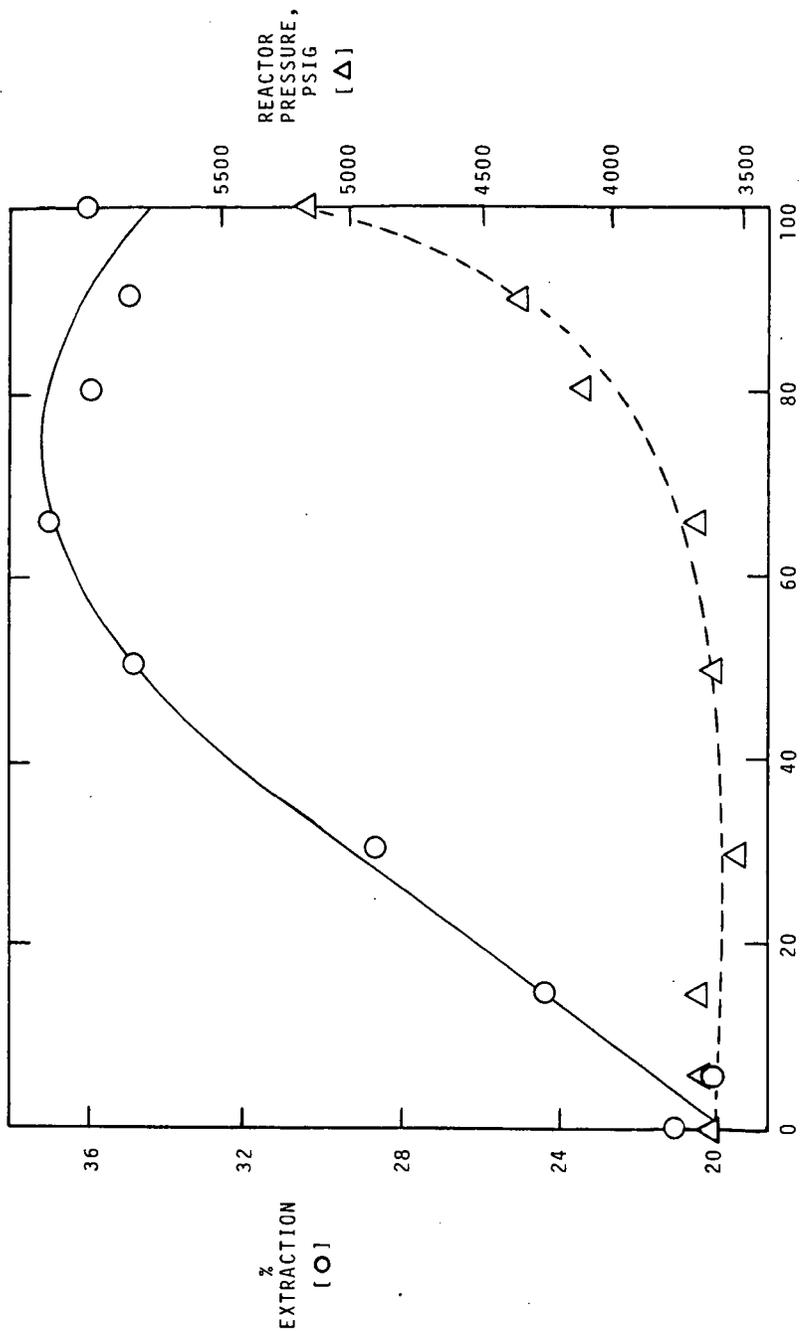


FIG. 1

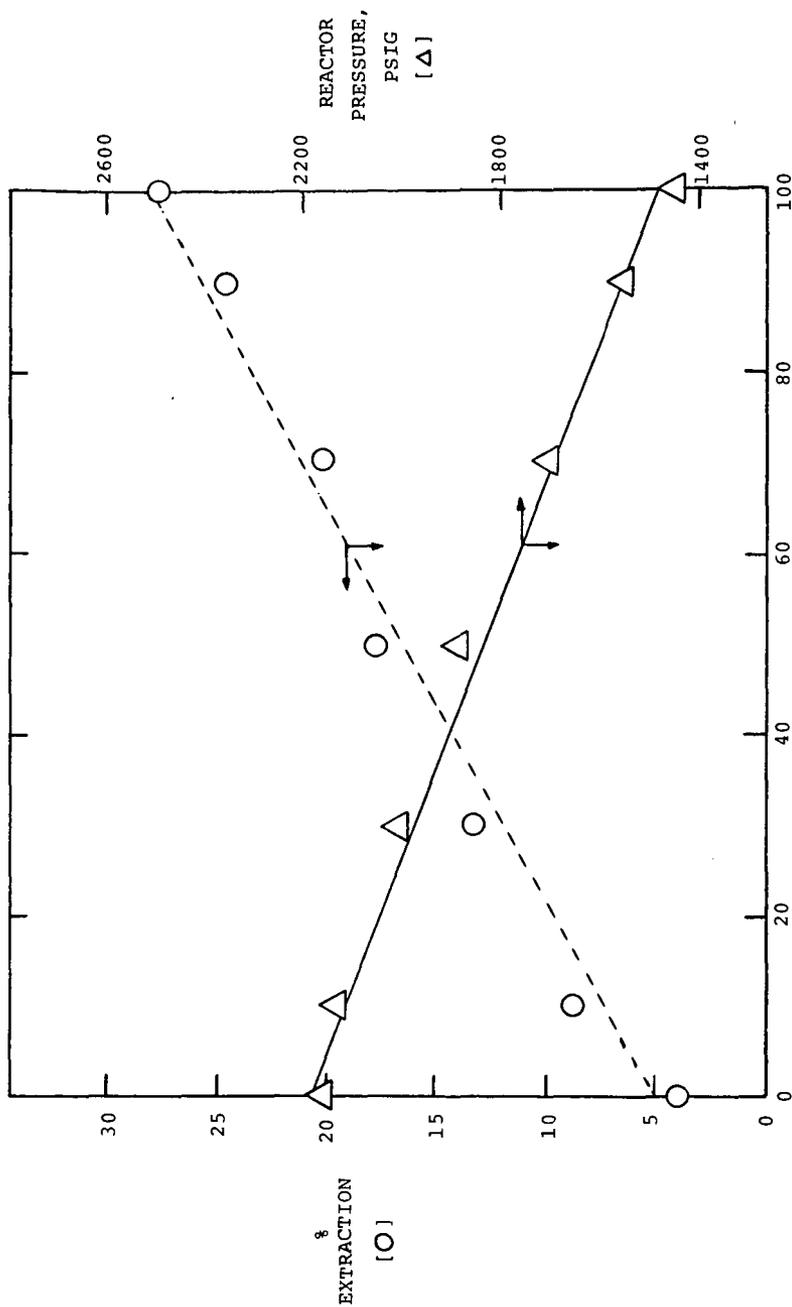
TOLUENE-METHANOL MIXTURES



MOLE % TOLUENE

FIG. 2

TOLUENE-ACETONE MIXTURES



MOLE % TOLUENE

FIG. 3

THE ROLE OF THERMAL CHEMICAL PROCESSES IN SUPERCRITICAL GAS EXTRACTION OF COAL

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INTRODUCTION

Many factors which limit the chemical conversion of insoluble, solid coal to soluble, smaller fragments are due to phenomena which are not routinely encountered in the chemical laboratory or in the chemical processing industry. In the first place, it often appears that the rate and extent of coal conversion is controlled by accessibility to reaction sites rather than by reaction energetics¹. Secondly, the chemical objective, depolymerization, is exactly the reverse of that of a major segment of the present chemical processing industry. While these observations are obvious, the implications for coal conversion are far reaching; and much of our recent research effort has focused on understanding the effects of these phenomena. Problems which limit the efficiency of current coal conversion processes are not necessarily amenable to solution using conventional solvents, standard reactor configurations, or other established chemical conversion concepts.

Currently, we are investigating supercritical fluids (SCF's) as solvents for extracting and chemically converting coal. The advantages of SCF's as solvents for coal extraction have been recognized for some time². Near the critical temperature, the solvent power, viscosity, and diffusion rates can be manipulated over wide ranges by relatively small changes in pressure or temperature³. Thus, SCF's have been touted as solvents which, by suitable manipulation of temperature and pressure, enhance both reagent access to interior reaction sites in coal and product removal from the microporous coal residuum. One of the primary objectives of the present research is to compare the efficacy of subcritical and supercritical solvents in this mass transport function.

In practice, most supercritical gas extractions (SGE's) of coal have been conducted at temperatures above 325°C⁴. While some investigators have acknowledged a thermal chemical contribution to these extractions⁵, others have reasoned that thermal processes are unimportant at 350°C⁶. Still others have sought to elucidate the thermal behavior of coal by investigating model compounds⁷. In any case, the thermal chemical component in SGE of coal has not been experimentally defined, and this is another important objective of our investigations.

Thermal conversion of coal to smaller fragments is best interpreted on the basis of three types of chemical processes. Primary reactions involving thermolysis of weak bonds generate smaller reactive fragments in conjunction with reactive sites within the coal residua. These reactive intermediates can then undergo two kinds of secondary reactions: stabilization to produce tar and light gases; and retrogressive recombination of the fragments and residua to produce refractory char. Obviously maximum liquid yields are obtained under conditions which promote stabilization reactions and inhibit retrogressive char-forming reactions.

In some liquefaction processes, the former objective has been accomplished by introducing a hydrogen donor stabilizing reagent into the conversion mixture^{8,9}. Other processes have sought to achieve the latter objective by heating the reaction mixture rapidly and limiting the reaction time⁹. While this approach has been partially effective, it does not address the root of the problem: intimate contact between reactive fragments and residua at elevated temperature for long periods.

Rapid vacuum pyrolysis of a thin bed of coal effectively minimizes retrogressive char-forming reactions by continuous removal of volatile tar fragments as they are generated¹⁰. Given the effectiveness of this approach to inhibiting char forming reactions, it is surprising that the concept has not been applied to other thermal liquefaction processes. Yet virtually all of these processes operate in the batch mode. Even those processes which purport to operate in a flow mode are not designed to quickly separate reactive coal fragments from reactive coal residua. Moreover, researchers in this area have directed little or no effort to exploring such ideas. Most investigators continue to employ batch mode techniques in which coal fragments and residua are mixed at elevated temperatures for substantial periods. Under such conditions, it is impossible to distinguish between primary and secondary products in a system as complex as coal. Therefore, a third important objective of this research is to develop a flow mode reactor system capable of rapidly separating coal fragments from residua and to investigate primary and secondary reactions in the chemical conversions of coal.

EXPERIMENTAL

General

Illinois #6 coal from the Ames Lab Coal Library was used in these studies. This coal has the following ultimate analysis (dmmf basis): 78.82% C; 5.50% H; 1.59% N; 2.29% S_{org}; and 10.05% ash. Prior to use, this coal was ground, sized to 60 x 100 mesh and dried at 110°C overnight under vacuum. Weight loss, extent of devolatilization, and extraction yields are reported on a raw coal basis.

Vacuum Pyrolysis

Vacuum pyrolysis experiments were conducted with a constant voltage heated grid apparatus¹¹ surrounded by a water jacketed condenser for collecting the tar and equipped with a liquid nitrogen cold finger condenser for collecting the light gases. In a typical experiment, 200 mg of Illinois #6 coal and a Chromel-Alumel microthermocouple were placed in the grid, and the system pressure was adjusted to 0.25 mm by bleeding He into the system. This slow He purge was maintained throughout the run, and the pressure and temperature were continuously monitored. The grid was then heated at an initial rate of approximately 200°C/min. to the programmed final temperature where it was maintained for 60 minutes. The extent of devolatilization was determined by measuring the weight of char remaining in the grid.

Coal Extraction with Methanol

Flow mode extraction of coal with methanol was carried out in the an apparatus described previously¹². A booster heating tape was wrapped around the reactor to provide rapid heat up capability. Coal (ca. 500 mg.) was placed in the tubular reactor, and the ends were sealed with 2 micron stainless steel frits. The free volume in the loaded reactor was found to be 0.70 ml. After connecting the reactor and purging the entire system with nitrogen, the apparatus was filled with methanol and pressurized. In rapid sequence, the reactor was inserted into the preheated furnace; and, as flow through the reactor was initiated, the reactor booster heater

was switched on. The heating profile for this reactor was approximately equivalent to that of the heated grid. A stable final temperature was attained in less than 5 minutes, and the booster heater was switched off. Throughout the extraction constant temperature, pressure, and flow rate (0.8-1.0 ml/min.) were maintained. After extracting for two hours, the system was purged with N_2 and cooled to room temperature. The reactor residuum was removed, dried in a vacuum oven at $110^\circ C$ overnight, and weighed to determine the extent of extraction.

Solvent Extraction of Coals and Residua

Coal (ca. 500 mg) or residuum (ca. 100 mg) was mixed with 10 ml of pyridine and ultrasonically irradiated under ambient conditions for 30 minutes. The resulting mixture was filtered with suction through a 3 micron Millipore filter, and the solid was washed with an additional 10 ml of solvent. After drying overnight at $110^\circ C$ under vacuum, the solid was weighed to determine the extent of extraction.

RESULTS AND DISCUSSIONS

The primary objectives of our investigations of the SGE of coal are the following:

- (1) To differentiate the extractive and pyrolytic components of this process;
- (2) To explore flow mode concepts as a mean of inhibiting secondary reactions by rapidly removing products from the reaction zone;
- (3) To compare the effectiveness of subcritical and supercritical solvents in the extraction of coal.

Progress toward the first two objectives has been achieved through two parallel series of experiments.

Extractive and Pyrolytic Phenomena

In the first series of experiments, weight loss of an Illinois #6 coal was determined as a function of the final coal bed temperature using a heated grid vacuum pyrolyzer. The recorded bed temperature was up to $50^\circ C$ less than the blank grid temperature measured under the same conditions. While the experimental difficulty of measuring the actual bed temperature is recognized¹⁰, we have reported the bed temperature because the grid temperature is assuredly attenuated by heat transfer inefficiencies and because it is the bed temperature that actually effects the coal pyrolysis. The room temperature pyridine solubility of each of the grid residua was also determined. Results from these experiments are reported in Table 1 and plotted in Figure 1.

The occurrence of two types of thermal processes are revealed by Figure 1. The first process, which occurs at a final temperature of approximately $200^\circ C$, apparently alters the solid coal structure in a way that reduces its pyridine extractibility. While this may be a physical alteration, one chemical change which would explain this is the formation of crosslinks. Whatever the cause, heating and maintaining the coal at $200^\circ C$ decreases its ambient solubility in pyridine and, presumably, other solvents as well.

The onset of the second process, devolatilization, is clearly evident at 300 to $350^\circ C$. Such behavior has consistently been interpreted as resulting from thermalolysis of weak bonds in coal^{10,13}. An acceleration of these pyrolytic processes, as manifested by more extensive devolatilization, is evident at higher temperatures, e.g. 32% weight loss at $528^\circ C$. It is important to note that residua which derive from final temperatures above $350^\circ C$ are minimally soluble in pyridine.

A parallel series of experiments were conducted using a short residence time flow mode reactor. Flow rates were adjusted so that methanol residence times in

the reactor were less than one minute, and experiments were conducted to determine the effect of extraction time on SGE yields at 320°C and 3000 psi. These results, which are included in Table 2 (Runs 8 and 9), establish that over 90% of the ultimate extraction has been accomplished within 30 minutes under these conditions. On this basis, extraction times of two hours (corresponding to a total extraction volume of 100 to 120 ml) were used for the remainder of the extractions. The two hour extraction yields (at 3000 psi) were then determined as a function of temperature; and these results and the pyridine extractibility of the residua are included in Table 2 and plotted in Figure 2.

The weight loss-temperature profile from these experiments, shown in Figure 2, is remarkably similar to the profile generated by the heated grid experiments. By 200°C a chemical or physical change has occurred which depresses the total extractibility of the coal, and the onset of extensive pyrolysis is again evident above 325°C. The coincidence of these thermal phenomena in the heated grid pyrolyses and the methanol flow mode extraction of Illinois #6 coal is clear evidence that thermal decomposition processes cannot be ignored in SGE experiments conducted above 325°C. These results are in substantial agreement with those of Slomka and Rutkowski in their investigations of toluene ($T_c=320^\circ\text{C}$) flow mode extractibility of an equivalent Polish coal¹⁴. By determining the extraction yield as a function of time and temperature, they found these extractions to be controlled by two distinct energies of activation. Between 200 and 320°C, E_a was about 3kJ/mole which is consistent with the operation of diffusion controlled, physical dissolution process. At higher temperatures (350-410°C), E_a was found to be 101 kJ/mole, and this can be taken as clear evidence for the operation of chemical processes.

In fact when considered in conjunction with the investigations of Slomak and Rutkowski, our experiments provide compelling evidence that, above 350°C, the SGE of coal is controlled by thermal decomposition processes rather than physical extraction processes. In light of this finding, it is surprising to discover a correlation between conversion yields and Hildebrand solubility parameters (δ) for the SGE of coal above 325°C^{4,5}. Yields should be influenced by the chemical nature of the solvent in this temperature range, and any correlation with δ must be coincidental or due to secondary effects.

Flow Mode vs. Batch Mode Extraction

In the flow mode extraction of coal with methanol utilized for these studies, the coal extract, once generated, is in contact with the residua for less than a minute. Although this time is long by molecular standards, it is short compared to contact times (45-100 minutes) in batch extraction of coal. While these considerations are not important below 325°C, they can certainly determine the efficiency and extent of SGE at higher temperatures. At 400°C, one can hardly expect a coal-like fragment to be chemically inert under conditions which cause coal to react or during various encounters with other fragments, residua, and reactive intermediates derived from these species.

The efficacy of flow mode extraction in minimizing secondary, char-forming reactions is demonstrated by the experiments reported here. Previous investigators⁴ have reported maximum methanol extraction yields of 19% at 450°C. In the present investigation a yield of 31% was obtained, indicating that, in the batch mode, at least one-third of the liquid product is lost to char.

Finally, other investigators⁵, using batch mode extraction, have been able to extract up to 12% of the extraction residua with pyridine. Presumably, this is due to extraction inefficiencies and to redeposition of solubilized material. Our results clearly show that this residual pyridine soluble material can be removed using flow mode extraction.

ACKNOWLEDGEMENT

This material was prepared with the support of the U. S. Department of Energy, Grant No. DE-FG22-82PC50786. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE.

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TABLE 1. THERMAL CONVERSION OF ILLINOIS #6 COAL BY HEATED GRID VACUUM PYROLYSIS

Run No.	Final Bed Temperature °C	Weight Loss: ^a RVP ^b %	Weight Loss: ^a PyE ^c %	Weight Loss: ^a Total %
Coal	-	-	10.2	-
1	191	0.2	8.6	8.8
2	248	0.8	6.0	6.8
3	326	6.1	-	-
4	337	5.7	2.3	8.0
5	448	19.7	1.0	20.6
6	448	21.1	0.9	22.0
7	528	32.3	0.7	33.0

^aWeight loss based on raw coal.

^bRapid vacuum pyrolysis.

^cPyridine extractibles.

TABLE 2. FLOW MODE EXTRACTION OF ILLINOIS #6 COAL WITH METHANOL

Run No.	Extraction Temperature °C	Extraction Pressure psi	Weight Loss: ^a FME ^b %	Weight Loss: ^a PyE ^c %	Weight Loss: ^a Total %
1	25	3000	2.6	9.7	12.3
2	100	3000	4.0	7.8	11.8
3	220	3000	7.4	0.6	8.0
4	270	1325	5.6	-	-
5	270	2000	8.3	-	-
6	270	3000	12.0	(0.9) ^d	12.0
7	270	4000	12.3	-	-
8	320	3000	12.0 ^e	-	-
9	320	3000	13.0	1.1	14.1
10	370	3000	22.0	-	-
11	420	3000	31.0	0.9	31.9

^aWeight loss based on raw coal.

^bFlow mode extraction.

^cPyridine extractibles.

^dWeight increase due to pyridine retention by the residuum.

^eExtraction time 30 minutes.

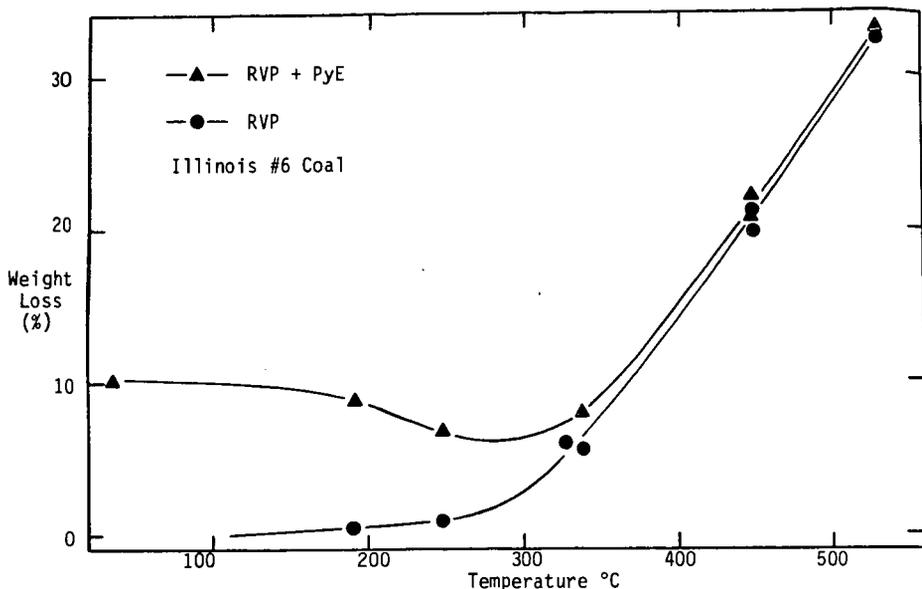


FIGURE 1. Effect of Final Temperature in Rapid Vacuum Pyrolysis

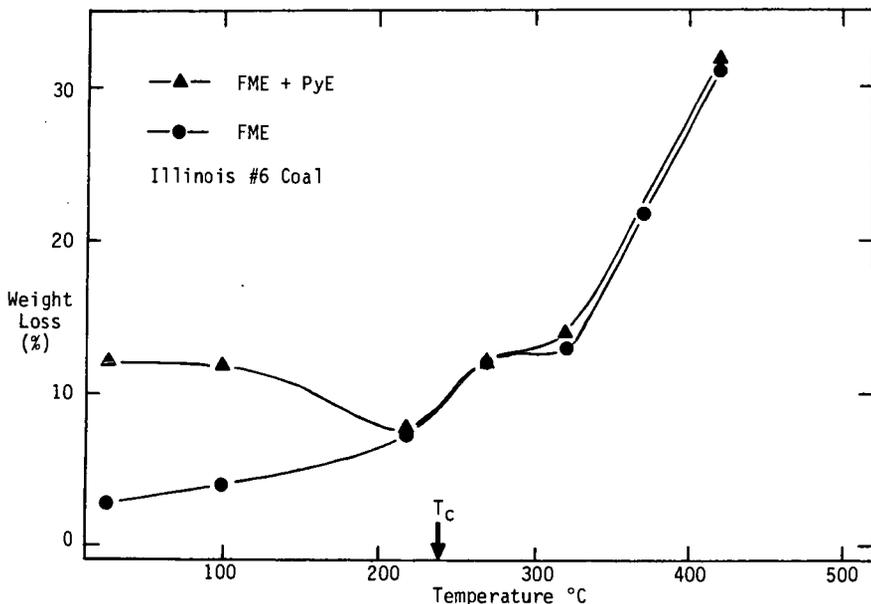


FIGURE 2. Effect of Final Temperature in Methanol Flow Mode Extraction

SUPERCRITICAL FLUID METHODS FOR COAL EXTRACTION, SEPARATION, AND ANALYSIS
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INTRODUCTION

Supercritical fluids are attracting increased interest for media for coal liquefaction and gasification, the basis for new separation techniques, and in new analytical techniques for the separation and characterization of coal-derived products. On-going research at Pacific Northwest Laboratory (PNL) is examining a range of supercritical fluid applications, including their use as a reaction media for coal liquefaction and for separation of fuels and coal-derived products. Other programs at PNL are studying the applications for analysis of fuel samples using supercritical fluid chromatography (SFC), the new technique of direct fluid injection-mass spectrometry (DFI-MS), and their combination (SFC-MS). In this report we will present an overview of the range of supercritical fluid applications at PNL related to coal and fuel separation and characterization.

EXPERIMENTAL

Two similar instruments have been utilized in our supercritical fluid studies to date. The first is a micro-scale supercritical fluid extraction/reaction facility designed to allow the rapid study and characterization of the fluid phase under a wide range of conditions. The second instrument is utilized for analytical studies which include direct fluid injection-mass spectrometry⁽²⁾ and capillary column supercritical fluid chromatography-mass spectrometry⁽³⁾. The instrumentation has been described previously⁽¹⁻³⁾. Figure 1 shows a schematic illustration of the DFI-MS instrumentation. Instrumentation for direct supercritical fluid extraction involves replacement of the injector by an extraction cell containing the material to be studied, while SFC-MS involves addition of a suitable open tubular capillary column between the injector and DFI probe⁽³⁾.

RESULTS AND DISCUSSION

The direct fluid injection (DFI) method allows any compound soluble in a supercritical fluid to be transferred to the gas phase for ionization using conventional methods⁽²⁾. Recent work at PNL has led to the design and development of Supercritical Fluid Extraction-Mass Spectrometer (SFE-MS) utilizing the DFI concept. The DFI method has the following advantages: quantitation is straightforward; the process is applicable to essentially any compound; various CI reagents may be selected to vary the degree of spectral complexity (fragmentation); and the technique is inherently sensitive.

The DFI probes have been designed to couple with the direct probe inlet of a modified "simultaneous" chemical ionization-electron impact (CI-EI) ion source⁽¹⁻³⁾. Chemical ionization provides both excellent sensitivity and flexibility due to the potential for the addition of different or mixed CI reagent gases. For cases where additional structural information is necessary for identification one can use either more energetic mixed CI reagents or the collision-induced-dissociation (CID) capability of the tandem quadrupole analyzer. The use of CI analysis for coal extraction is particularly attractive since the gentle ionization mechanism produces primarily protonated molecular ions (MH^+), which allows information on the molecular weight distribution to be obtained directly from the mass spectra. The DFI interface has also allowed the first practical supercritical fluid chromatography (SFC) -mass spectrometer instrumentation to be developed⁽³⁾. The combi-

nation of the selective extraction from substrate materials and detection with more selective collision induced dissociation tandem mass spectrometric methods (e.g., MS/MS) offers a particularly effective rapid analytical method for complex coal extraction and related coal-derived mixtures.

The last few years have seen a dramatic growth in the application of supercritical fluid extraction methods to a variety of extraction, separation, and process areas. The strong and often selective solvating power of supercritical fluids under controlled conditions often allows extraction of specific compounds (e.g., caffeine from coffee, PCB's from transformer oils, etc.) from complex matrices, as well as efficient extraction of a wide range of compounds under more severe conditions. Under more extreme conditions the "extraction" process for materials such as coal is undoubtedly a combination of chemical reactions resulting in breakdown of the complex matrix combined with the extraction-distillation process of the supercritical fluid.

The present methods for direct analysis of coal supercritical fluid extraction (SFE) processes involves the continuous removal of a small sample from an extraction cell for direct mass spectrometric analysis. A high pressure syringe pump, modified for pressure regulation, is used to maintain the desired pressure in the extraction cell. The extract is transported using a 25 cm length of 100 μm I.D. platinum-iridium tubing through the DFI probe which is maintained at the same temperature as the extraction cell. The entire sample line volume is approximately 2 μL and, for our typical flow rates of 10-30 $\mu\text{L}/\text{min}$, the time from extraction to analysis is less than one minute. Fluid from the cell is injected directly into the CI region of a "simultaneous" dual EI-CI source where a constant pressure is maintained. The mass spectrometer, programmable pressure regulated pump, oven temperature controller and data acquisition hardware are all interfaced for complete computer control(3).

The supercritical fluid phase reaction or extraction process can be studied under both nonisothermal and nonisobaric conditions. Small extraction cell volumes allow evaluation of compounds extracted as a function of pressure for the determination of "threshold pressures" for the solubility of individual components. The effects of catalysts can be studied in the extraction cell or a subsequent separate reaction cell. Large reaction volumes allow one to observe the fluid phase processes as a function of either temperature or pressure, where the parameter is varied in some known fashion with time. For large reaction cells (>50 mL) the actual loss due to mass spectrometric sampling (<25 $\mu\text{L}/\text{min}$) can be made insignificant for reasonable reaction times.

An example of preliminary nonisobaric studies is given in Figure 2. A 40 mg sample of a bituminous coal, sized to approximately 80 μm average particle size and previously washed with pentane, was packed into a 75 μL cell for these experiments. The extraction temperature was 280°C and the solvent was a 95% n-pentane-5% 2-propanol mixture; thus the temperature was maintained well above the estimated critical temperature of the solvent mixture. The "gentle" CI conditions result in little molecular fragmentation and a dominant protonated molecular ion, greatly simplifying mass spectral interpretation. The experiment shown in Figure 2 involved an initial 2 hr period at 10 atm after which the pressure was increased at a rate of 0.4 atm/min between 10 atm and 100 atm. Figure 2 gives reconstructed single ion profiles for several typical ions in the mass spectra and the total ion current (TIC) or extraction profile, which serve to illustrate the solubility of extractable components as a function of pressure. Large groups of compounds are clearly extracted in the 10-13 atm and 25-28 atm ranges and similar results showing greater structure are obtained with slower pressure ramps. Between 40 and 80 atm a large amount of complex higher molecular weight material is extracted. Mass spectra for these conditions show that species having molecular weights extending to over 1400

are extracted(1). These results demonstrate the potential for direct mass spectro-metric monitoring of supercritical fluid extraction of coal and other related processes. Initial experiments show significant structure in the extraction profiles, suggesting that the potential exists to readily alter the extracted product slate and to obtain significant product fractionation. Approximately 20% of the coal is extracted under these conditions, in reasonable agreement with previous studies.

An example of the application of DFI-MS for fuel characterization is given in Figures 3 and 4. These figures give DFI-mass spectra for four fractions of two diesel fuel marine (DFM) samples, obtained by an alumina column fractionation method, which has been described previously(4). These DFM samples, designated 81-5 and 81-6, represent a typical fuel (81-5) and a fuel which has been determined to exhibit considerable instability and particulate formation (81-6). The first two (less polar) fractions (A-1 and A-2) contain materials which appear to be nearly totally soluble in supercritical carbon dioxide (34°C, 450 atmospheres), and mass spectra representative of the mixtures are obtained (Figure 3). In contrast, however, the more polar A-3 and A-4 fractions exhibit very limited solubility in supercritical CO₂. Good spectra are obtained, however, in supercritical ammonia (134°C, 400 atmospheres). Since these spectra were obtained using relatively "gentle" chemical ionization reagents (isobutane for the A-1 and A-2 fractions and ammonia for the A-3 and A-4 fractions) only limited ionic fragmentation is anticipated in the spectra, with domination by the protonated molecular ion, (M+1)⁺. Thus, the DFI mass spectra provide a good measure of the molecular weight distribution of these materials. Comparison of the two relatively non-polar fractions, A-1 and A-2, indicates these fractions, which account for the bulk of the DFM, are quite similar. In contrast, however, comparison of the polar fractions (the A-3 and more polar A-4 fraction) indicates that fuels having greater instability have significantly greater contributions in the 150 to 300 molecular weight region in the A-3 fraction, and substantial contribution in the 300 to 500 molecular weight region, essentially absent for more stable fuel. These results are consistent with the greater amount of material observed in these fractions for the unstable DFM and with the gas chromatography results for the portions which are chromatographable. Research is presently in progress to apply supercritical fluid chromatography techniques using more polar fluids for separation of these materials, in conjunction with analysis by on-line DFI-MS. The much higher chromatographic efficiencies possible with SFC, in conjunction with DFI-MS analysis, promises significant advances for characterization of fuels and coal-derived materials.

ACKNOWLEDGEMENTS

This work has been supported primarily by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Portions of this work have also been supported by the Naval Research Laboratory. We wish to thank Dr. R. N. Hazlett of the Naval Research Laboratory for providing DFM samples and for helpful discussions.

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DIRECT FLUID INJECTION - MASS SPECTROMETER

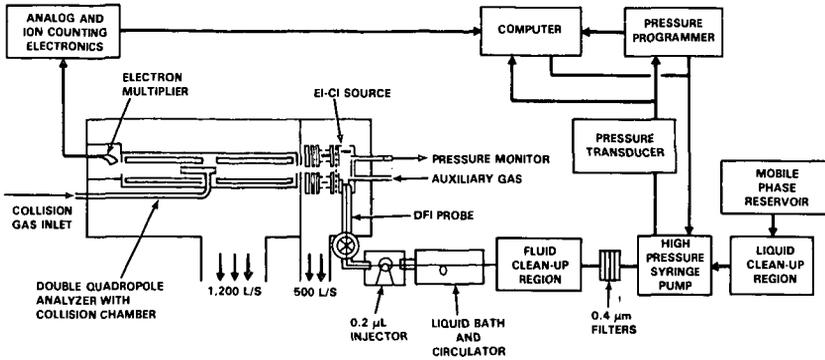


FIGURE 1. Schematic Illustration of the Direct Fluid Injection-Mass Spectrometer. Similar Instrumentation is Used for SFC-MS and Direct Supercritical Fluid Extraction Studies.

SUPERCritical COAL EXTRACTION PROFILES AT 280°C

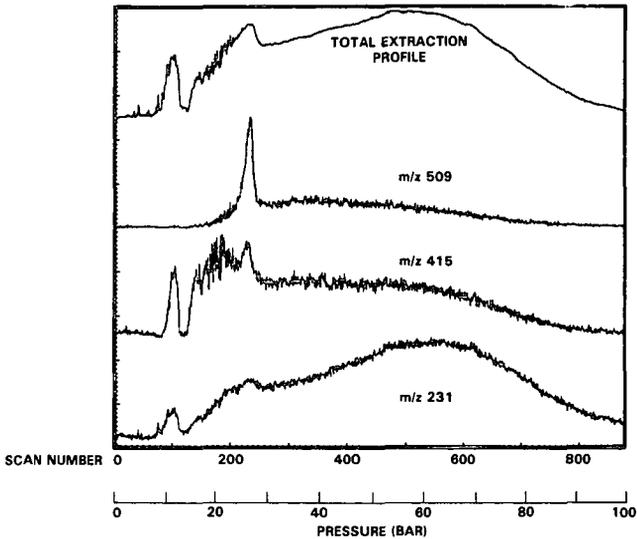


FIGURE 2. Selected Ion Profiles and Total Extraction Profile for a Nonisobaric Supercritical Fluid Coal Extraction Study Using a 95% Pentane-5% 2-Propanol at 280°C.

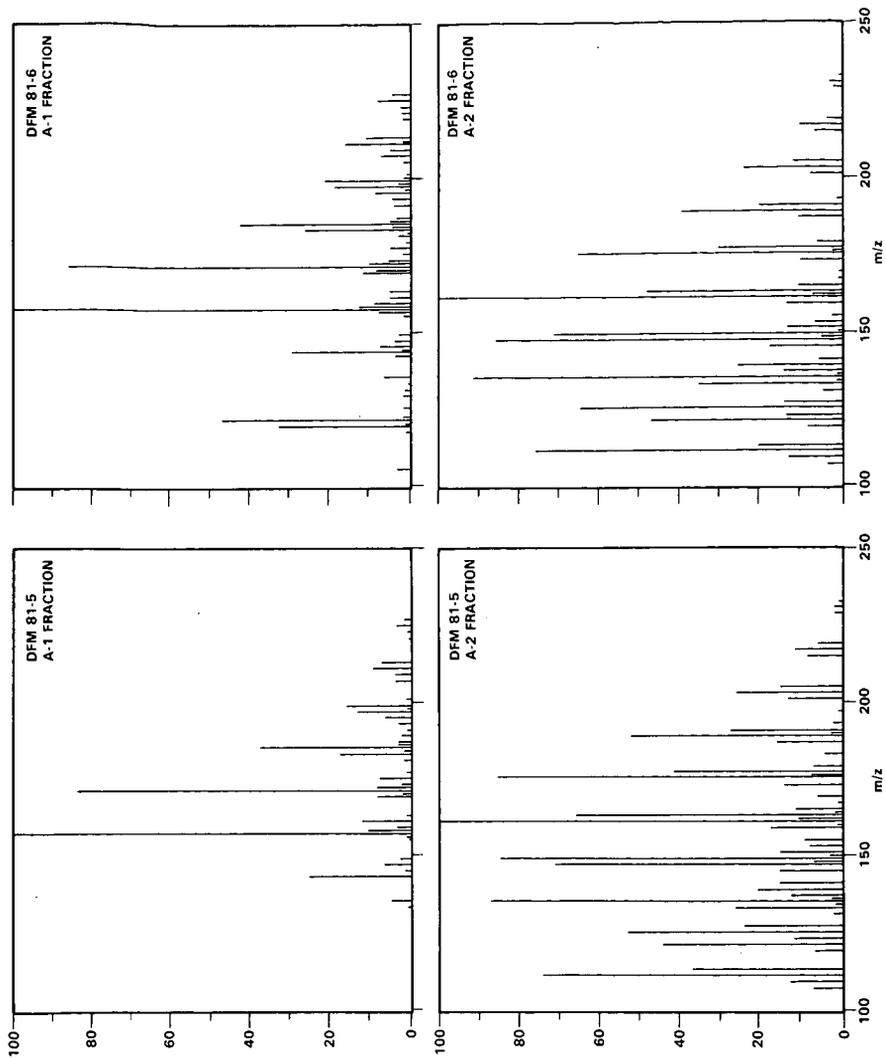


FIGURE 3. DFI-Mass Spectra Using Supercritical CO₂ for the A-1 and A-2 Fractions of Two Diesel Fuel Marine Samples.

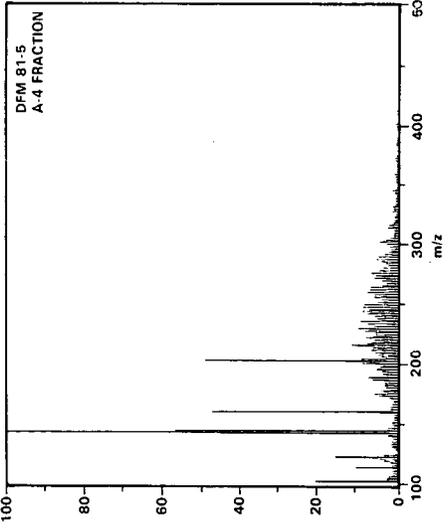
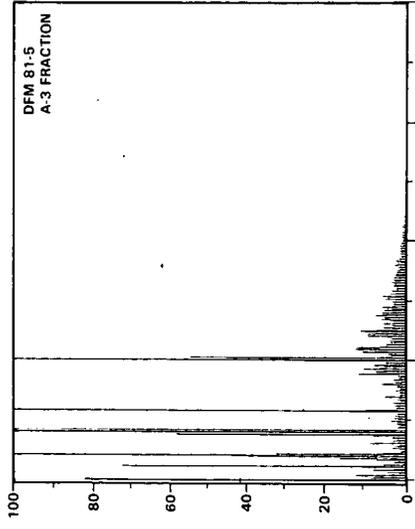
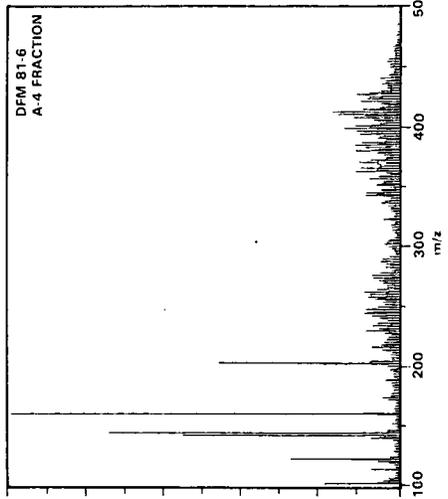
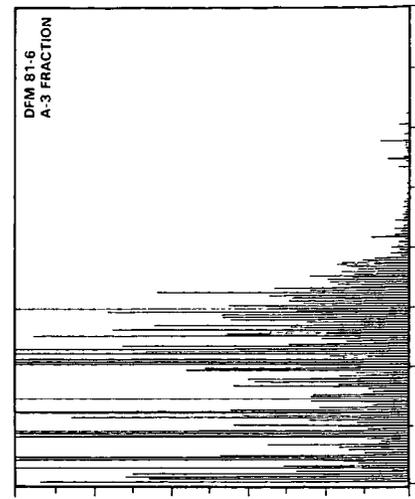


FIGURE 4. DFI-Mass Spectra Using Supercritical NH₃ for the A-3 and A-4 Fraction of Two Diesel Fuel Marine Samples.