DOE/PC/40801--T4

RECEIVED BY

OCT 19 1982

FOURTH QUARTERLY TECHNICAL PROGRESS REPORT

MASTER

FOR

DOE/PC/40801--T4

DE83 001030

SOLVENT AND CHEMICAL-REACTION EFFECTS
IN SUPERCRITICAL EXTRACTION OF COAL

DOE Grant No. DE-FG22-81PC40801
(Identification No. U8107293NFP)

JUNE 1, 1982 to AUGUST 31, 1982

Submitted to: U. S. Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Principal Investigator: Nicholas P. Vasilakos
Department of Chemical Engineering
University of Texas at Austin
Austin, TX 78712

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

During the fourth quarter of the project approximately thirty-five (35) experimental runs were carried out, in order to study the non-reactive solvent effects in supercritical extraction of coal. The number of experiments conducted is less than the projected number (50) in our last report, due to unexpected problems encountered with our experimental system, mainly gaseous solvent leaking from the autoclave reactor during a run. This problem (which has been resolved) caused also the delay in the preparation of this report, because we decided to go ahead and complete an integrated series of experiments, even by falling behind schedule, before reporting the results.

1. Technical Progress

Our research efforts have concentrated on studying two non-reactive solvent characteristics that can affect the efficiency of supercritical coal extraction:

- a) Physical solvent parameters. Molecular size and critical properties (T_c , P_c).
- b) Synergistic effects of solvent mixtures, in particular polar/nonpolar combinations.

A third, and very interesting solvent characteristic, namely polarity, is currently under experimental investigation.

1.1 Experimental Procedure

An Illinois No. 6 bituminous coal, 100x200 mesh size, was used in all the experiments. The coal was dried under vacuum for 24 hours at 110°C before every run.

In each run a certain amount of solvent, corresponding to the

desired supercritical density, was first measured into a 1000 cm³ (free volume: 910 cm³), 316 ss AE MagneDrive 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 confusion of results where a significant fraction of the coal would be soluble under supercritical conditions but insoluble when the system was brought back to ambient temperature and pressure, 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 (1). 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 the next pages 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 are currently being analyzed for elemental composition, heating value, pyridine solubility, and BET surface area. The analyses will be included in our next report.

1.2 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 and also depicted on Figure 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. (2) suggested that the solvent

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

power of a supercritical medium is directly related to its solubility parameter, δ . Using the van der Waals equation, they developed the following correlation:

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

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

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

and ρ_ℓ 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 (1), 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 $2.75 \frac{\text{moles}}{\text{liter}}$. The results are given in the last column of Table 2. Weight-percent extraction is plotted

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)	$a(x10^9)^1$ ($\frac{\text{cm}^6 \cdot \text{atm} \cdot ^\circ\text{K}^{1/2}}{\text{mole}^2}$)	b^1 ($\frac{\text{cm}^3}{\text{mole}}$)	Extraction Pressure (psig) ²	Solubility Parameter ($\text{cal}^{1/2}/\text{cm}^{3/2}$) 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

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:

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

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):

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

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 eqs. 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.; (3)) that extraction yields may be affected by molecular size, and that the longest dimension of each solvent molecule should be considered when

HOMOLOGOUS SERIES OF N-PARAFFINS

FIG. 1

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

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

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

$$\text{and } b = \frac{0.0867 R T_c}{P_c},$$

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 $\rho = 2.75 \frac{\text{moles}}{\text{liter}}$ or $\hat{V} = \frac{1}{\rho} = 363.6 \frac{\text{cm}^3}{\text{mole}}$.

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. The estimated and the experimentally observed values of the extraction pressure are also depicted in Figure 2 versus the solubility parameter of the supercritical solvent.

Figure 2 shows 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 ($\sim 1.8 \frac{\text{moles}}{\text{liter}}$ in our case), dodecane becomes an excellent supercritical solvent for coal, both in terms of the highest extraction yield

FIG. 2

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

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).

1.3 Polar Effects in Supercritical Coal Extraction

We are currently investigating the effect of increased solvent polarity on coal extraction yields using a homologous series of halohydrocarbons. Table 4 includes the results of a few 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 water density of 8.25 $\frac{\text{moles}}{\text{liter}}$ the coal extraction

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

yield is 34.0 wt% compared with 20.9 wt%, which is the value calculated from eqs. (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 (34 wt% 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 that can yield products completely different from simple supercritical extracts (4), is not clear at this point.

We are currently investigating the mechanism of supercritical water/coal interactions using a model-compound system, namely anthracene/ H_2O , under similar reaction conditions ($T=400^\circ C$; $P_r \approx 1.1$). 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.

1.4 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 given in Tables 5 and 6, and 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. (3) 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.

Table 5. Supercritical extraction of coal with toluene/
methanol mixtures at 400°C and at a (constant)
solvent density of 6.75 moles/liter.

Mole Percent Toluene	Weight Percent Extraction	Extraction Pressure (psig)
0	20.6	3610
5	20.0	3640
15	24.5	3670
30	28.8	3510
50	34.8	3600
66	37.0	3660
80	35.8	4080
90	35.0	4340
100	36.0	5140

TOLUENE-METHANOL MIXTURES

FIG. 3

Table 6. Supercritical extraction of coal with toluene/acetone mixtures at 400°C and at a (constant) solvent density of 4.0 moles/liter.

Mole Percent Toluene	Weight Percent Extraction	Extraction Pressure (psig)
0	4.0	2180
10	8.8	2140
30	13.3	2010
50	17.7	1880
70	20.2	1700
90	24.6	1520
100	27.6	1440

TOLUENE-ACETONE MIXTURES

FIG. 4

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 cm³ 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	Wt. 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	" "	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.

Finally, it is important to report here that part of the supercritical extract recovered in the toluene phase after cooling the reactor 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.

2. Future Work

During the fifth quarter of the project our efforts will concentrate on studying experimentally non-reactive, polar solvent effects in supercritical extraction of coal. Organic solvents of increased polarity and simple inorganic polar molecules (H_2O , SO_2 , NO_x , NH_3 , BF_3 , and CO_2) will be systematically evaluated in terms of both extraction efficiency and quality of the supercritical extract.

Nicholas P. Vasilakos
Assistant Professor

Austin, 10/11/82

References:

1. Blessing, J.E. and Ross, D.S., "Supercritical Solvents in the Dissolution of Coal and Lignite," in "Organic Chemistry of Coal," Larsen, J.W. (ed.), ACS Symposium Series No. 71, Washington, D.C., 1978, pp. 171-185.
2. Giddings, J.C., et al., "High Pressure Gas Chromatography of Nonvolatile Species," Science, 162, 67(1968).
3. Fong, W.S., et al., "Experimental Observations on a Systematic Approach to Supercritical Extraction of Coal," paper presented in the 1981 AIChE annual meeting, New Orleans, Louisiana, November 8-12, 1981.
4. Modell, M., Reid, R.C. and Amin, S.I., U. S. Patent No. 4113446, 1978.