EXTRACTION OF A NORTH DAKOTA LIGNITE WITH SUPERCRITICAL ALIPHATIC SOLVENTS

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Introduction

Extraction of coal with various solvents has been a commonly used method for obtaining knowledge about the structure of coal and its chemical composition. Solvent extraction of coal has been classified into four different types by Oele and others (1), and Dryden (2,3). A recent review of solvent extraction was prepared by Pullen (4).

1. Nonspecific extraction - nonspecific solvents extract only a small percentage of the coal. These solvents tend to primarily dissolve the waxy and resinous compounds which reside in the coal's physical structure in the form of resin bodies and particles.

2. Specific extraction - specific solvents extract a larger portion of the coal (up to ~40%) with the extracted material closely resembling the insoluble coal residue. The effectiveness of these solvents has been attributed to the existence of an unshared pair of electrons on nitrogen or oxygen in the solvent molecule thereby making the solvent behave as a polar fluid (3,4).

3. Extractive disintegration or degradation - this type of extraction occurs at temperatures between 200° and 400°C where the percent extraction is dependent on the production of smaller soluble fractions by the thermal decomposition of the coal. Solvents under these conditions can dissolve up to ~40% of the coal at temperatures of 400°C.

4. Extractive chemical disintegration - these extractions dissolve the coal by thermally decomposing and chemically reacting with the coal to form smaller molecular fragments (1). Most of this work involves using hydrogen-donor solvents (i.e., solvents that can either donate hydrogen to the various reactive coal species or at least act as a hydrogen transfer agent) to manufacture liquid products from the coal.

Interest in the extraction of coal (and other substrates) with supercritical solvents has been increasing rapidly over the past fifteen years. This interest is primarily due to the enhanced solubility of substrates in the fluid phase that occurs at or above the critical point. Also, the solvent power of the solvent (which depends on the solvent density) can be conveniently controlled over a large range with small changes in the solvent pressure or temperature (5,6). Most of the coal extractions using supercritical fluids have been performed at temperatures above 350°C. Squires and others (7) reported that thermal decomposition processes were becoming significant above 325°C for the extraction of an Illinois No. 6 coal with supercritical methanol. This suggests that results from supercritical fluid extractions above this temperature are a combination of physical and chemical solvent-coal interactions.

The twofold objectives of this research are to investigate, in the context of the solvent extraction model presented above, the fundamental principles of solute-solvent interactions at or above the solvent critical point and to use supercritical solvent extraction (SCSE) as a method for determining various molecular fractions present in low-rank coals. In order to minimize the thermal decomposition component in the supercritical fluid extraction of low-rank coals, solvents were selected with critical temperatures below the temperature at which volatile matter is evolved by destructive distillation (i.e., <325°C).

Experimental

Materials

The solvents used were n-pentane through n-octane and cyclohexane available commercially in HPLC grade. The coal used was Indian Head lignite (Indian Head mine, Zap, ND) vacuum dried for at least a week at 10 micron Hg and room temperature. The proximate and ultimate analyses for this lignite are shown in Table I.

Table I. Proximate and Ultimate Analyses for Indian Head Lignite (mf basis).

Proximate Analysis	
Volatile Matter	39.8
Fixed Carbon (By difference)	46.7
Ash	13.5
Ultimate Analysis	
Hydrogen	3.85
Carbon	60.79
Nitrogen	1.47
Sulfur	0.89
Oxygen (By difference)	19.51
Ash	13.5

Supercritical Fluid Processing

Extractions of Indian Head lignite samples were performed using the aliphatic solvents mentioned above. These experiments were performed using a semicontinuous supercritical solvent extraction system. A flow sheet for this system is shown in Figure 1. In this system a fixed bed of coal (~50 gm) was contained in a 25.4 cm by 1.75 cm ID section of high pressure tubing by one micron sintered metal frits. The preheating coils and fixed bed of coal were then immersed in a preheated fluidized sand bath where supercritical conditions were achieved in less than seven minutes. A Ruska positive displacement pump and high pressure accumulator were used to provide a pulseless flow of solvent through the system once supercritical conditions were reached. A solvent flow rate of 120 mℓ/hr was maintained for two hours. The pressure of the supercritical solvent was reduced to atmospheric pressure after passing a back pressure regulator. The extract and solvent were collected in a chilled sample

vessel. The noncondensable product gas was measured and collected for subsequent analysis.

Analytical

After each experiment, the extracted lignite residue and solvent-extract mixture were rotary vacuum distilled at ~30 mm Hg and 80°C and weighed. This procedure insured that a solvent and moisture-free product was obtained for material balance purposes. The collected product gases were analyzed by gas chromatography. Residues were analyzed by thermogravimetric analysis (TGA). Proximate and ultimate analyses were performed on selected samples.

Analysis of the solid extracts obtained by the supercritical hydrocarbon extractions were accomplished by column separations, infrared spectroscopy, 60 MHz proton NMR and capillary GC. Separations of the acids from the extracts was acomplished by the following procedure. The extract was dissolved in a warmed chloroform-methanol mixture (1:1). The soluble portion was added to a column containing Sephadex A25 ion exchange resin. The eluent from the column was evaporated and the acid-free fraction was weighed. The column was eluted again with a solution of formic acid (7 mℓ) in chloroform-methanol (1:1, 33 mℓ). Evaporation of this eluent gave a fraction consisting of fatty and resin acids. The acid-free wax was dissolved in carbon tetrachloride and analyzed by an infrared calibrated for the ester carbonyl peak and the alcohol OH-stretching peak.

Discussion and Results

Temperature and Pressure Effects

As mentioned above, one of the potential advantages of supercritical fluid extraction is the relatively large change in the solute solubility that can be achieved with small changes in solvent pressure or temperature. This premise was tested in the following way. A series of isobaric experiments using supercritical pentane to extract Indian Head lignite at various temperatures was carried out to investigate the effects of operating temperature on the percent conversions. The operating conditions of these runs and their resulting conversions are shown in Table II. As shown in

Table II. Operating Conditions and Results for Supercritical Pentane Extractions of Indian Head Lignite at Constant Pressure, P_r = 1.50.

Operating Temp., °C	T_r**	Operating Pressure (Psia)	% Conversion (maf)*	% Yield (maf)*
206	1.020	735	1.50	1.1
235	1.083	735	1.50	0.34
270	1.158	735	1.50	1.4
300	1.222	735	1.50	0.63 (?)

*% conversion $\frac{\text{wt maf coal - wt maf residue}}{\text{wt mf coal}}$; % yield = $\frac{\text{wt maf extract}}{\text{wt maf coal}}$

**$T_r = \frac{\text{operating temperature of solvent (°K)}}{\text{critical temperature of solvent (°K)}}$; $P_r = \frac{\text{operating pressure of solvent (psia)}}{\text{critical pressure of solvent (psia)}}$

Figure 2, the percent conversion initially decreased with an increase in operating temperature up to 235°C. This decrease was caused by the decrease in the solvent density that occurs with increasing temperature. The conversion then increased with further increases in the operating temperature up to 270° and 300°C, respectively. These increases were due to increased thermal effects in the coal which more than offset the decrease in solubility caused by the decreased solvent density.

Table III shows how temperatures affected the percent conversions and yields of three (two hexanes and one heptane) supercritical extractions. These results also indicate that percent conversions increase with increasing temperature. However, the differences observed between the isothermal hexane and heptane experiments indicate that higher conversions are obtained as the operating temperature approaches the solvent critical temperature (i.e., T_r goes to one). These results are consistent with those reported by Blessing and Ross (8).

Table III. Operating Conditions and Results for Supercritical Hexane and Heptane Extractions of Indian Head Lignite at Constant Reduced Pressure, P_r = 2.0.

Solvent	Operating Temperature (°C)	T_r	Operating Pressures (Psia)	% Conversion (maf)	% Yield (maf)
n-Hexane	244	1.020	860	3.1	1.3
n-Hexane	278	1.087	860	5.3	1.6
n-Heptane	278	1.020	795	6.5	1.7

The effect of pressure on supercritical fluid extractions was investigated by performing a series of isothermal extractions using supercritical hexane at various pressures to extract Indian Head lignite. The operating conditions and results of these experiments are shown in Table IV. The percent conversions and yields for these experiments are plotted in Figure 3. The results displayed in Figure 3 suggest that a maximum in the solubility of Indian Head lignite in supercritical hexane occurs in the vicinity of P_r = 2.0. The existence of a maximum in solute solubility occurring as a function of pressure have been reported for a South African coal in supercritical toluene (9) and for biphenyl in supercritical CO_2 (10). The reasons stated for these maxima were the differences between the pressure dependent solubility parameters of the coal and the solvent or by performing extractions at pressures above the upper critical region end point together with "free volume" effects (size asymmetry between the solute and solvent) as in the case of the biphenyl - CO_2 system. Figure 4 illustrates the improved solvent power that resulted from small increases in the solvent pressure from P_r = 1.5 to 2.0 for the extractions using supercritical heptane, octane and cyclohexane. This figure also suggests that changes in the operating pressure have a larger effect on the solvent power of the supercritical solvent at higher operating temperatures. It appears from the data presented above that the yields from the extraction of Indian Head lignite with supercritical aliphatic solvents were not affected to a large extent by either the operating temperature or pressure. This could be due to a limited amount of compounds present in the coal which are selectively extracted by aliphatic solvents under 325°C. The differences between the percent yield and conversion data were due to the production of gas (primarily CO_2) and the formation of water from the coal.

Table IV. Operating Conditions and Results for Supercritical Hexane Extraction of Indian Head Lignite at Constant Temperature, T_r = 1.02.

Operating Temp. (°C)	Operating Pressure (Psia)	P_r	% Conversion (maf)	% Yield (maf)
244	450	1.05	2.2	0.9
244	650	1.50	2.3	1.0
244	860	2.00	3.2	1.4
244	1080	2.50	2.6	1.3
244	1295	3.00	3.0	1.1

Analytical Results and Discussion

The effect of supercritical extraction on the thermal characteristics of the resulting residues was investigated using thermogravimetric analyses. Table V shows the operating conditions and conversions obtained for each of the residues analyzed by TGA. Figure 5 displays the differential weight loss for the five supercritical fluid extracted residues as functions of the sample temperature. A sample of the vacuum dried "as run" Indian Head lignite was also plotted for comparison purposes. This figure suggests that the supercritical fluid solvents used in this paper were extracting more of the compounds that would devolatilize below ~400°C with the increased operating temperature necessary with the longer solvent chain length.

Table V. Operating Conditions and Results for Supercritical Extraction of Indian Head Lignite at Constant Reduced Temperatures and Pressures, T_r = 1.02, P_r = 2.0.

Solvent	Operating Temp (°C)	Operating Pressure (Psia)	% Conversion (maf)	% Yield (maf)
n-Pentane	206	980	3.1	0.6
n-Hexane	244	860	3.2	1.3
n-Heptane	278	795	6.5	1.7
n-Octane	307	720	9.8	2.2
Cycohexane	291	1180	9.1	2.5

The analyses of the extracts revealed the presence of aliphatic esters, alcohols, acids and alkanes with little or no aromatics being extracted. Separations and quantitative infrared spectroscopy have been performed on the chloroform-methanol soluble fractions (~50 wt %) from the supercritical pentane and hexane extractions to date. The yields from this preliminary data averaged 0.19%, 0.06%, and 0.26% for the waxy esters, aliphatic alcohols and the fatty acids, respectively. Proton NMR showed that the aromatic content of the extracts tended to increase slightly with increasing operating temperature. Capillary GC analyses on whole samples and silica gel column separated samples using a 15 m SE-54 column provided data on the distribution of normal

and cyclic alkanes, waxy esters, and fatty alcohols and acids. The series of n-alkanes occurred between C_{21} and C_{33} with a maximum concentration of the C_{29} alkane. A number of triterpanes and C_{15} to C_{20} cyclic alkanes were present. The fatty alcohols were found to be mainly C_{24}. The fatty acids were converted to their methyl esters for analysis. A series of esters was observed with maximum concentration at C_{24} and C_{26}. From the composition and yield data, it appears that extraction of Indian Head lignite with supercritical aliphatic solvents with critical temperatures below 325°C still has the characteristics of nonspecific extraction.

Acknowledgment

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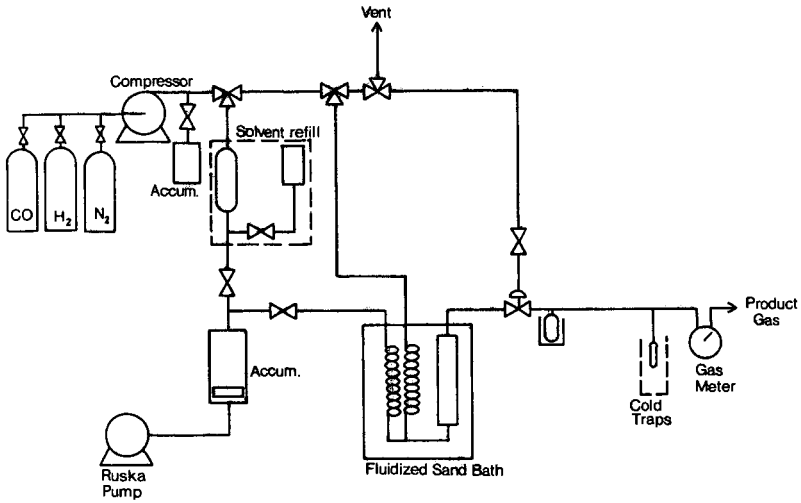

Figure 1. Equipment flowsheet for the semi-continuous supercritical solvent extraction system.

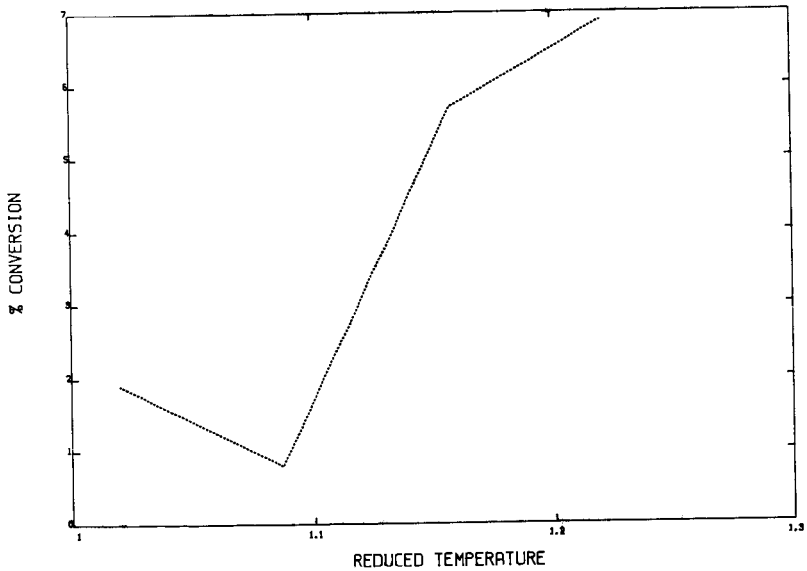

Figure 2. Temperature effects of supercritical pentane extraction on conversions.

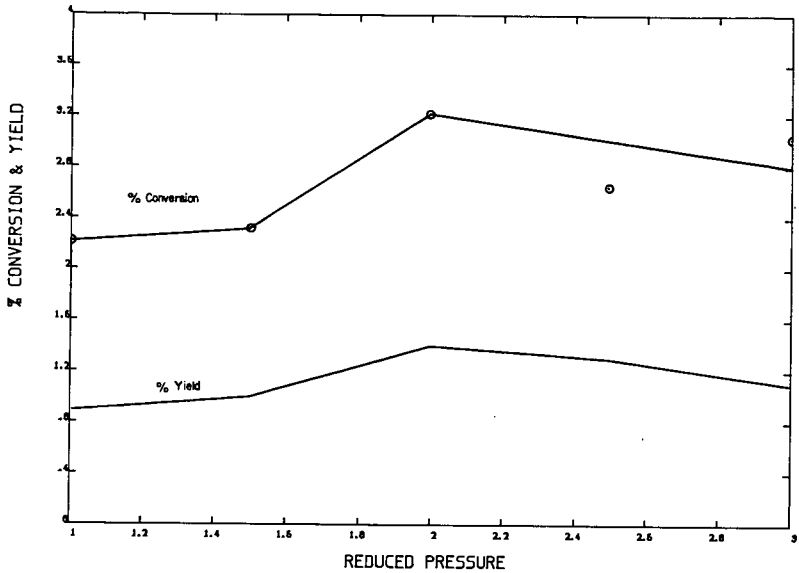

Figure 3. Pressure effects of supercritical hexane extractions on conversions and yields.

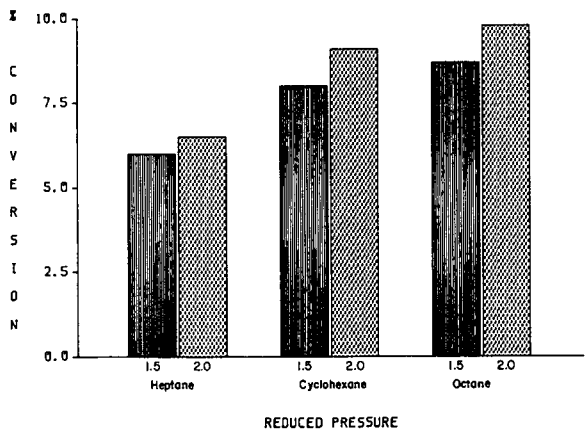

Figure 4. Pressure effects of heptane, cyclohexane and octane supercritical extractions on conversion.

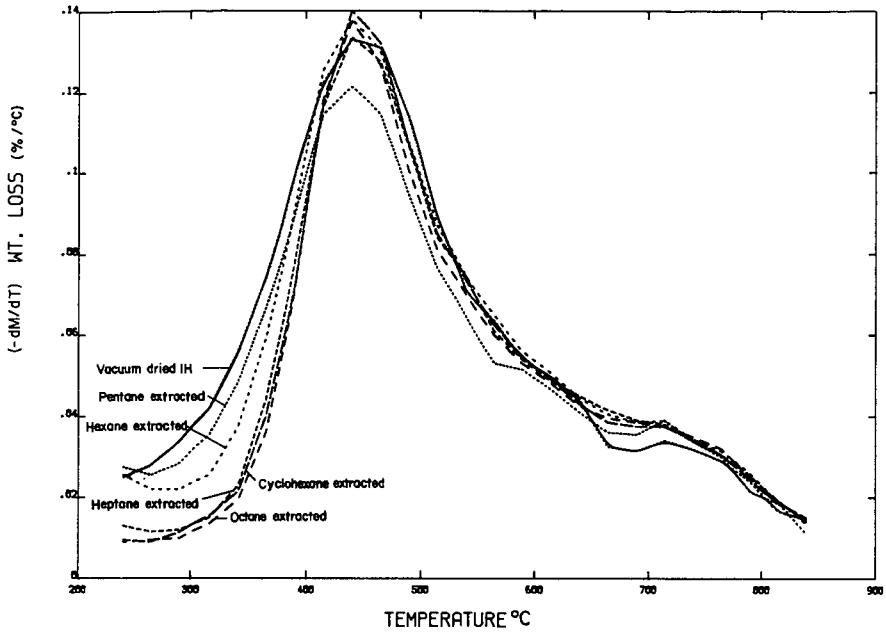

Figure 5. TGA rate of weight loss for supercritical solvent extracted residues.