Supercritical Solvent Extraction of Lignite to Form Carbonaceous Chars

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The supercritical extraction of lignite by n-pentane, n-hexane, benzene and water gave successively increasing yields up to destructive extraction. Thermal analysis showed that solvent extraction was not an exact duplication of pyrolysis.

Introduction

In order of increasing yield and temperature the solvent extraction of coals has been specified by the following categories (1,2): 1) Non-specific extraction, 2) specific extraction, 3) extractive disintegration, 4) extractive chemical disintegration. These categories are part of the macromolecular model for bituminous coal solvent extraction with a metaplast stage which occurs early in pyrolysis. The relationship of this model to lignite is uncertain but a comparison has been made between the residues obtained from the supercritical extraction of Indian Head lignite by using thermogravimetric analysis in an inert gas at atmospheric pressure. This on-going study has examined the residues obtained over a wide range of yields possible upto extractive disintegration. In the case of extractive disintegration, thermal decomposition and the release of gases and volatiles becomes important above 200°C.

Experimental

Chars were prepared from a North Dakota lignite (Indian Head mine, Zap, ND) by extracting the lignite in a semi-continuous supercritical extraction system. The critical parameters of the solvents used and examples of the percent conversions for each are given in Table I. Yields of the resulting extracts are slightly less than the conversions since some gaseous products were obtained in all the experiments. Soxhlet extractions using the same solvents gave a significantly lower yield than their supercritical counterparts.

Figure 1 shows the effect increasing operating pressure had on the conversions for a series of supercritical pentane experiments at a constant temperature. Likewise, Figure 2 shows the effect of increasing temperature at a constant pressure. The effect of lignite residence time for several supercritical water extraction experiments is presented in Figure 3. In general, the rates of conversion were rapid up to the maximum conversion. The aromatic content of the extract increased with increasing yield.

The thermogravimetric results of carbonizing the residues obtained from supercritical pentane, benzene and water experiments, which were performed at the same reduced temperature and pressure (Tr = 1.02, Pr = 1.50), are displayed in Figure 4. Figure 4 also shows TGA results for an original Indian Head lignite sample. Thermogravimetric analysis were performed using ∿25 mg samples with a 20°C/min heating rate. The results have been corrected to a maf basis of the original lignite to account for the weight loss that occurred during supercritical extraction. The results have been presented here as the differential weight loss versus temperature so that the area under the graph is proportional to the total weight loss.

Discussion

The conversion shown in Figure 1 displays a maximum similar to that found for South African bituminous coals in supercritical toluene (3). Hildebrand solubility theory predicts the maximum solubility will occur when the solubility parameters of the solvent and the solute are identical. Since the solubility parameter is primarily a function of the solvent density which in turn is dependent on the operating pressure, increasing the pressure has caused differences between the solvent and solute solubility parameters to occur. The observed minimum in Figure 2 was due to the decrease in solvent density that occurs with increasing temperature. The subsequent increase was due to increased thermal effects more than offsetting the decreased solvent density.

The low extract yields and the waxy nature of the extracts obtained would classify supercritical pentane as a nonspecific solvent even though at
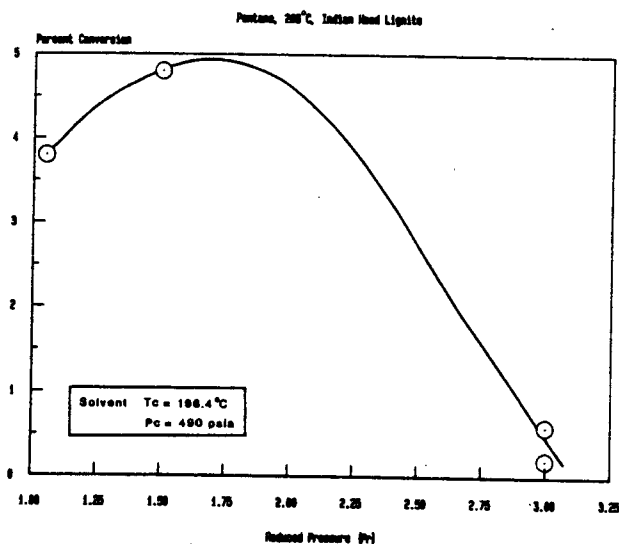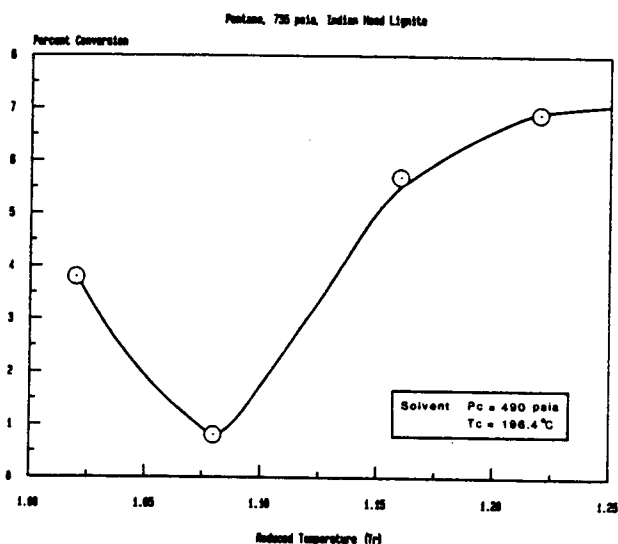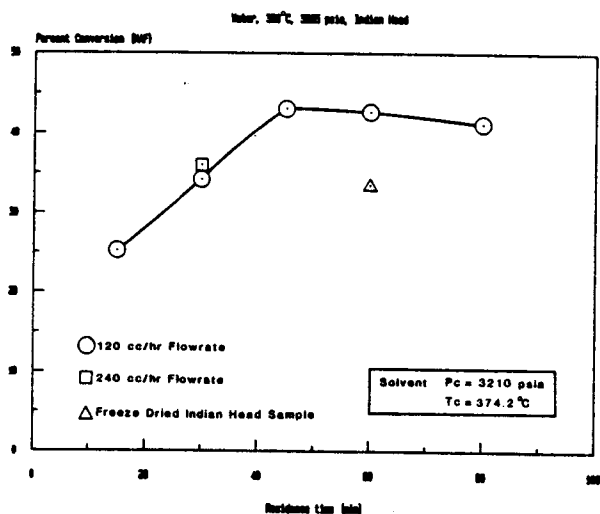
FIGURE 1

FIGURE 2

FIGURE 3

TABLE 1. EXAMPLES OF OPERATIONS PARAMETERS AND RESULTS FROM SUPERCRITICAL RUNS PERFORMED AT THE CONSTANT REDUCE CONDITIONS T_R=1.02, P_R=1.50

	n-Pentane	n-Hexane	Benzene	Water
Critical Temp., °C	196.4	234.2	288.9	374.2
Critical Pres., psia	490	431	710	3210
% Conversion,* maf	2.2	2.3	6.7	90.3
% Yield Extract, maf	1.2	1.0.	3.9	23.8
Soxhlet % Yield Extract, maf	0.26	0.17	0.75	--

*%Conversion = weight loss or original lignite =

$$\frac{\text{maf lignite - maf residue}}{\text{maf lignite}}$$
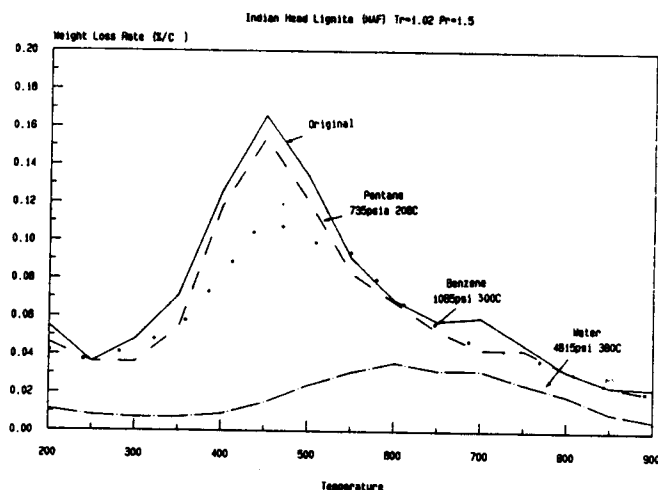

FIGURE 4

these extraction temperatures the supercritical pentane borders on the defined temperature range (200°-400°C) for extractive disintegration. This raises the question as to what part of the lignite the pentane is interacting with (ie., is it interacting with the macromolecular structure or just with the resins and the waxes residing among the coal matrix). Both the supercritical benzene and water are in the extractive disintegration temperature range although there is some evidence that supercritical water also acts as a reactant for the free radicals generated from the lignite at these temperatures. It can also be seen from the TGA curves that differences exist between the residual chars and the original lignite that are not consistent with wholly thermal disintegration.

References

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