

Effect of Solvent Density on Coal Liquefaction Under Supercritical Conditions

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ABSTRACT

Supercritical fluid extraction is an attractive process primarily because the density and solvent power of a fluid changes dramatically with pressure at temperatures near the critical. In complex supercritical extractions, such as the extraction of coal, the density of the supercritical fluid should also change the extractability of the coal. In this experiment a non-reacting supercritical fluid, toluene, was studied to determine the effect of density on the coal extraction/reaction process. Extractions were carried out for two to 60 minutes at reduced densities between 0.5 and 2.0 and at temperatures between 647 and 698K. the data obtained can be explained by the hypothesis that coal dissolution is required preceding liquefaction reactions and that the degree of dissolution depends upon solvent density and temperature.

INTRODUCTION

Earlier efforts aimed at understanding supercritical extraction of coal used both flow and batch reactors.

In the flow reactors⁽¹⁾⁻⁽⁵⁾, coal was packed into the reactor and the supercritical fluid was passed through the bed of coal until the condensed effluent was clear. The conversion was defined as the total weight loss of the coal due to extraction by the solvent.

In batch systems⁽⁷⁾⁻⁽¹²⁾, the coal and solvent were placed in a reactor and heated together to the reaction temperature.

More recent studies^{(13),(14)} have employed a rapid injection autoclave, where coal is injected into a preheated supercritical solvent. After the reaction is over the products are quenched by passing water through internal cooling coils.

The general trends observed in the studies discussed above do provide some important insights; higher temperatures and higher densities result in higher conversions partially because more coal dissolves in the supercritical solvent as temperature and density are increased. Blessing and Ross⁽⁶⁾ correlated the coal conversion to pyridine solubles with the Hildebrand Solubility Parameter, δ , which they defined as

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

where P_c is the critical pressure of the medium in atmospheres, ρ_r is its reduced density and ρ_g is generalized reduced density of liquids, taken to be 2.66. They found the product pyridine solubility to be a linear function of δ .

EXPERIMENTAL

Bruceton bituminous, a Pittsburgh Seam coal was used in the experiment. The chemical analysis of coal is given in Table I. The coal was dried in vacuum @ 343 K prior to use and stored in glass containers under nitrogen.

Supercritical Coal Liquefaction Procedure

The experimental apparatus is shown in Figure 1 and consists of a 1-L stainless steel autoclave equipped with a Magnedrive stirrer and a coal injection system. The reactor is charged with a known quantity of toluene depending on the fluid density desired for the experiment and is heated at 3-4 K/min to the temperature desired. Once this temperature is reached, ambient coal is injected into the reactor from a coal reservoir using high-pressure Argon. The average weight of injected coal was 30g. Reaction times are measured from the time at which the coal is injected.

The liquid and solid contents were collected from the reactor and placed in an extraction thimble which was then placed in a soxhlet unit. The contents were then extracted with toluene until the extractant was clear after which the thimble was dried and weighed. The weight of the dried product is designated as toluene insolubles.

The conversion, based on the extraction results, are defined below.

Gases, Oils and Asphaltenes (GOA), % = 100 x

$$\frac{(\text{coal injected (g)} - \text{toluene insolubles (g)})}{\text{coal injected (g)}} \quad 2)$$

All weights are on a moisture and ash free basis.

Discussion

Experiments were carried out with Bruceton coal and toluene at supercritical toluene densities in the range of 0.157-0.601 g/cc. The temperature range studied was 647-698 K and the reaction time was varied from two minutes to 60 minutes.

The results of experiments at 647K and reduced densities of 0.5 to 2.0 (toluene densities of 0.157 g/cc and 0.601 g/cc) are given in Figures 2a and 2b. The experimental results show that toluene solubles (oils, asphaltenes, and gases) are produced during the reaction. They also show that the amount of toluene solubles formed at low reaction times increases with both temperature and density. In addition, solubility studies have shown that the amount of a solid which can dissolve in a supercritical fluid increases with density and, generally, with temperature. Hence, we concluded that the conversion of coal to oils + asphaltenes + gases is in some sense limited by the dissolution of the coal in the solvent.

We hypothesize that the only part of the coal which undergoes reaction to gas, oils and asphaltenes is the dissolved fraction, which increases with temperature and density. Increases in the dissolved fraction thus lead to higher conversions and faster reaction rates. These conversion products then participate in retrogressive reactions (Amestica and Wolf⁽¹²⁾) forming char, so that at longer times (15 minutes or more) the yield of gases + oils + asphaltenes decreases. At lower temperatures (647 K), the retrogressive reactions are insignificant and conversion does not decrease with time.

The above hypothesis is well explained by the results given in Figures 2a and 2b. At a lower density of 0.157 g/cc the fraction of coal dissolved in the supercritical fluid is much lower than when the density of the supercritical fluid is 0.601 g/cc. Hence, the fraction of coal, which is converted to asphaltenes, oils and gases, is also lower.

The results of experiments at 673 K and reduced density of 1.0 and 1.5 (supercritical toluene density of 0.301 g/cc and 0.444 g/cc) are given in Figure 3a. As observed at 647 K, the coal conversion to gases + oils + asphaltenes (toluene solubles) increase with reaction time and with the density of the

supercritical fluid. The retrogressive reactions are more significant now and hence, the toluene solubles show a maxima in conversion with time.

The results of experiments at 698 K and reduced density of 1.0 and 1.5 (supercritical toluene density of 0.301 g/cc and 0.444 g/cc) are given in Figure 3b. As observed at 647 K and 673 K, the coal conversion to gases + oils + asphaltenes (toluene solubles) increases with reaction time and density of the supercritical fluid. The retrogressive reactions are more pronounced than that at 673 K but we still observe a maxima in the toluene solubles as a function of reaction time. The initial rate of formation of toluene solubles (as seen from the steepness of the curves of toluene solubles versus reaction time) is higher at higher density and higher temperature. Also note that the amount of toluene solubles at the maxima is higher when the temperature and density of the supercritical fluid is higher. This is consistent with the hypothesis that the soluble fraction of the coal increases with temperature and density of the supercritical fluid.

Because coal is heterogeneous in nature, as the density is increased, heavier and heavier coal fractions (as opposed to more and more of the same fraction) are dissolved in the supercritical fluid. These would not dissolve if the density of the supercritical fluid were lower, and the supercritical fluid is, in general, unlikely to be saturated with any given fraction that is substantially dissolved (i.e. either zero or 100% of a fraction is dissolved). For example, if coal is considered to be composed of 100 fractions characterized by increasing molecular weight, more and more of these fractions dissolve as density is increased, but the solubility of a given fraction goes from (approximately) zero to 100% over a small change in density. If a given fraction, number 46 for example, is dissolved, then more of that molecular weight group would dissolve at that density if it were present, but none of the undissolved fractions would dissolve regardless of the amount of coal present. Hence, the fraction of the coal and not the amount of coal which dissolves in the supercritical fluid is a strong function of density and temperature of the supercritical fluid. In other words, if the amount of coal injected into the supercritical fluid at given temperatures and density was reduced to its half value, the absolute amount dissolved will fall by 50%.

If the amount of coal injected was increased indefinitely, then a point might be reached where the supercritical fluid is saturated with dissolved coal. If the amount of coal injected is increased beyond this value, the fraction of dissolved coal and the fractional coal conversion will start decreasing. The amount of dissolved coal in the supercritical fluid will be independent of the amount of coal injected in such a case.

Conclusions

When coal is contacted with a non-donor supercritical fluid a part of the coal instantaneously dissolves in the supercritical fluid. The dissolved coal undergoes liquefaction reactions which are thermal in nature resulting in toluene soluble products being formed from coal. These products can subsequently undergo retrogressive reactions yielding insoluble material. Hence the toluene solubles show a maxima in conversion with time.

The fraction of coal which dissolves instantaneously in the supercritical fluid increases with an increase in the density and temperature of the supercritical fluid. This effect is similar to that generally observed for the solubility of a solid in a supercritical fluid. With an increase in density and temperature higher molecular compounds present in coal go into solution, resulting in an undersaturated solvent with the fraction, not the amount, of the coal which is being dissolved.

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TABLE 1

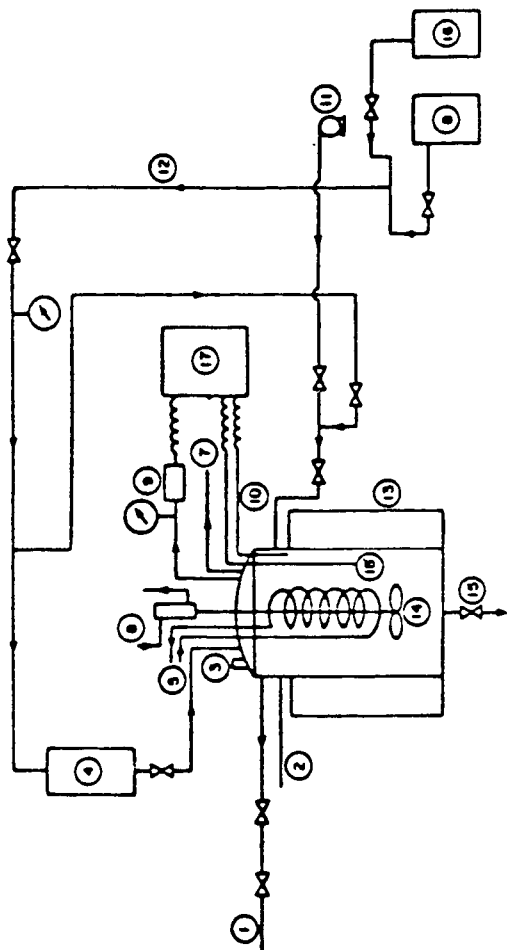
Analysis of Bruceton Bituminous Coal

ASH	3.93 ^a
Carbon	82.69 ^b
Hydrogen	5.56 ^b
Sulfur	1.46 ^b
Nitrogen	1.72 ^b

^a - moisture free basis

^b - moisture and ash free basis

FIGURE 1: EXPERIMENTAL SETUP FOR SUPERCRITICAL EXTRACTION



- | | |
|----------------------------------|--------------------|
| ① GAS SAMPLE LINE | ⑥ THERMOCOUPLE |
| ② RUPTURE DISC TO HOOD | ⑦ PUMP |
| ③ LIQUID SAMPLE PORT | ⑧ GAS LINE |
| ④ COIL BOMB | ⑨ FURNACE |
| ⑤ COLD WATER (FOR STIRRER) | ⑩ AGITATOR |
| ⑥ COLD WATER (FOR MAGNETIC HEAD) | ⑪ DRAIN VALVE |
| ⑦ VENT LINE TO HOOD | ⑫ ARGON CYLINDER |
| ⑧ HELIUM CYLINDER | ⑬ DATA LOGGER |
| ⑨ PRESSURE TRANSDUCER | ⑭ H ₂ O |

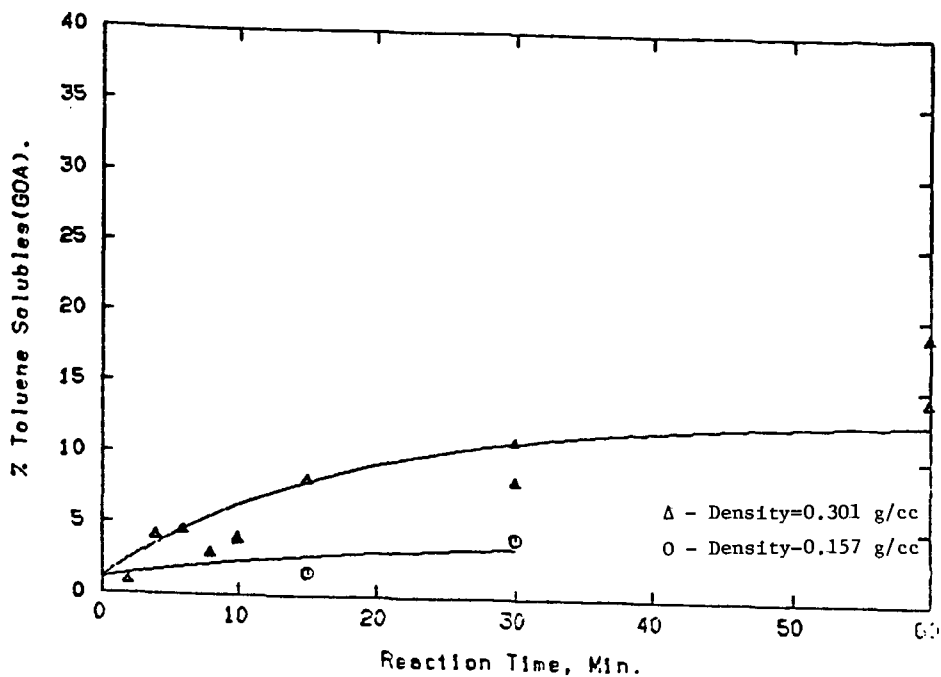


Figure 2a Effect of Reaction Time & Density on % GOA @ 647 K

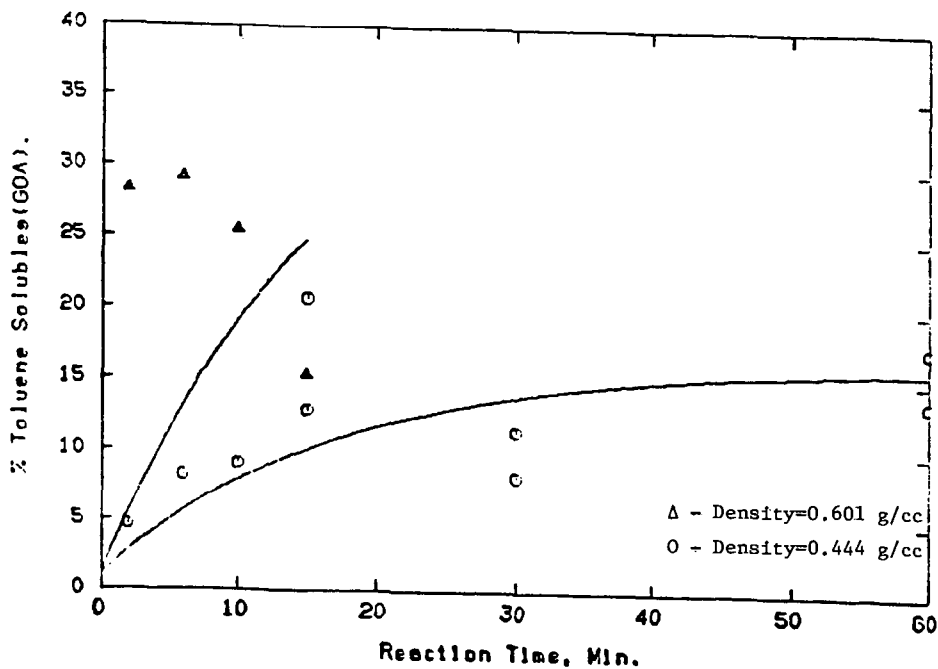


Figure 2b Effect of Reaction Time & Density on % GOA @ 647 K

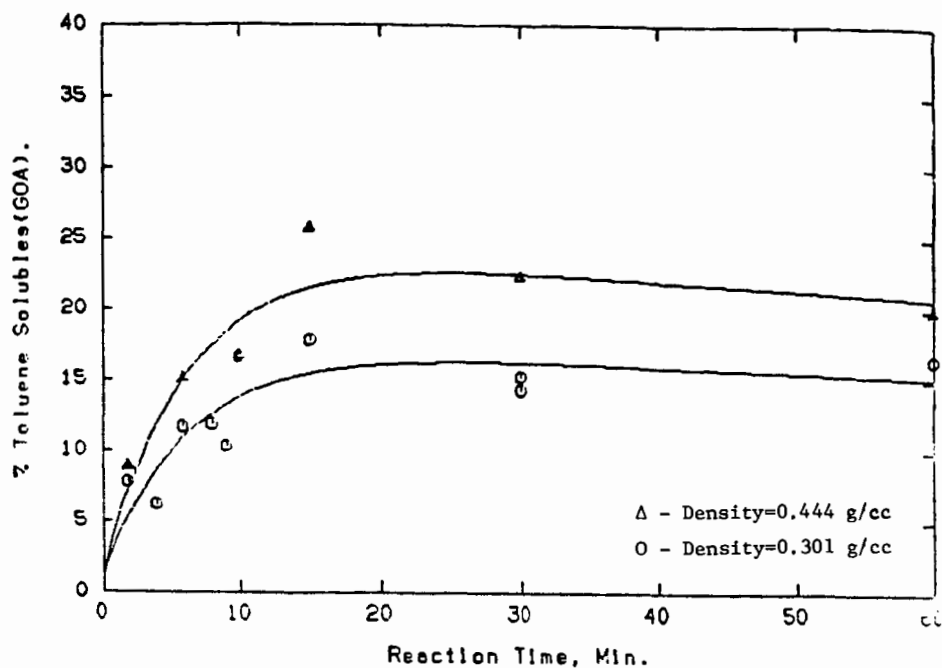


Figure 3a Effect of Reaction Time & Density on % GOA @ 673 K

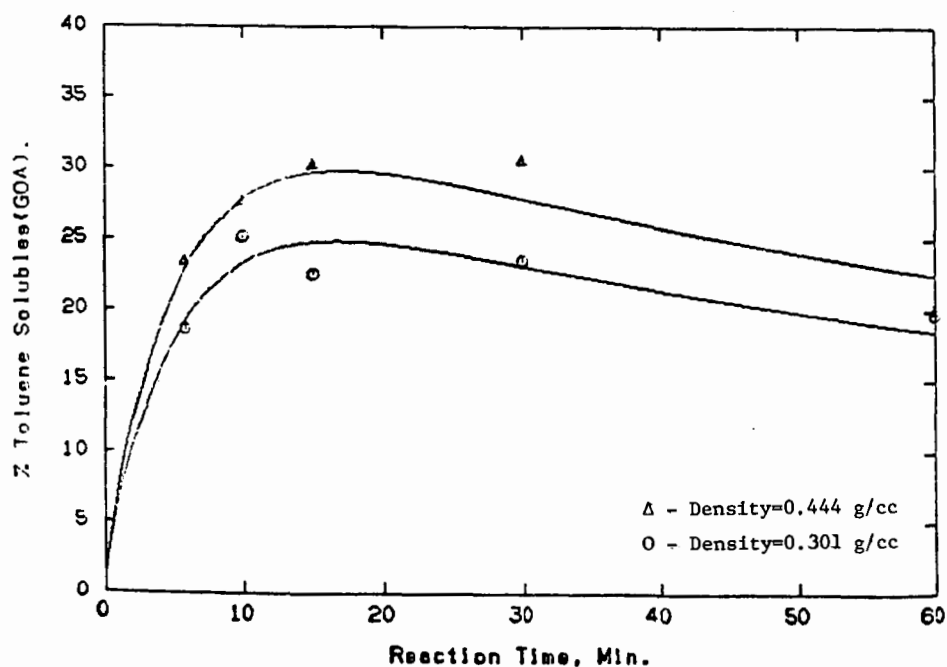


Figure 3b Effect of Reaction Time & Density on % GOA @ 698 K