# THE EFFECTS OF PROCESS SEVERITY ON PHYSICOCHEMICAL PROPERTIES OF PREASPHALTENES*

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## Introduction

Coal is converted from a high molecular weight solid (M.W. < 2000) to a low molecular weight oil (M.W. < 300), when heated in the presence of a suitable solvent. Between these two extremes exists a continuum of intermediate molecular weight materials. The intermediates are divided into three major groups by solubility in THF, toluene and pentane. Preasphaltenes are soluble in THF but insoluble in toluene; asphaltenes are soluble in toluene but insoluble in pentane; and oils are soluble in pentane and, to a large extent distillable. If the coal conversion process proceeds from dissolved coal to oil through the intermediate products, then examining the reaction mechanisms of the intermediates will provide information about the upgradeability (1-3) of the dissolved coal and about the entire coal conversion process.

This paper describes the physical character and reactions of preasphaltenes made from a bituminous coal. The preasphaltenes were obtained by reacting Illinois #6 Burning Star coal in contact with SRC-II heavy distillate under hydrogen pressure in an Autoclave for various times (10 to 30 minutes) and temperatures (350 to 450°C). The preasphaltenes were separated by using conventional Soxhlet extraction techniques. The primary question addressed was: Are preasphaltenes produced under one set of reaction severities (i.e., 350°C for 10 minutes) different than those made at other severities (i.e., 400 or 450°C)? The extracted preasphaltenes were analyzed for molecular weight, solubility and elemental composition. The chemical reactivities (upgradeability) were studied by further reaction of the extracted preasphaltenes with SRC-II heavy distillate solvent in shaking microreactors at 400°C under hydrogen for 0 to 30 minutes.

The conversion of the preasphaltenes was followed using a gel permeation liquid chromatographic analytical method. The results indicated that preasphaltenes generated at lower severity were more soluble, more reactive and had a higher molecular weight than those generated at higher severity.

## Experimental

Starting materials for this study are Illinois No. 6 Burning Star coal and SRC-II heavy distillate. An analysis of these materials is presented in Table 1. Initial experiments were performed in a 1-liter Autoclave equipped with a magnedrive stirrer and operated at constant pressure (4). Three runs of varying severity were performed to provide large samples of coal derived materials for analysis and subsequent testing. The run conditions and analyses are provided in Table 2. Preparatory scale separations were performed by sequential precipitation and Soxhlet extraction in the order THF, toluene,

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TABLE 1. Selected Analytic Data for Solvent and Coal

| | | Illinois No. 6 Burning Star Coal | SRC-II Heavy Distillate |
|---|---|---|---|
| Ultimate Analysis % dmmf | Carbon | 71.5 | 89.8 |
| | Hydrogen | 4.8 | 7.6 |
| | Nitrogen | 1.5 | 1.4 |
| | Sulfur | 3.3 | 0.4 |
| | Oxygen (difference) | 8.4 | 1.8 |
| Ash % dry basis | | 10.0 | 0.05 |
| Distillate Yield Weight % | | -- | 86.5 @ 850°F |

and pentane. Throughout this study, actual analyses were performed using a quantitative gel permeation liquid chromatographic (GPC) asphaltene analysis (5). This method separates a coal derived product into high, intermediate and low molecular size fractions that may be quantified by using appropriate standards.

Secondary reactions of preasphaltenes and asphaltenes were performed in 20 $cm^3$ shaking microreactors (6). The preasphaltene was added to SRC-II HD at a ratio of 1/14 and reacted at 400°C under 1800 psi hydrogen. Fluidized sand baths were used for heating (∿2 minutes to reaction temperatures) and cooling (∿30 seconds for a 200°C quench).

The reaction time for the 10 and 30 minute experiments is exclusive of heat-up and cool-down. The experiments labeled zero-time were performed by heating empty microreactors to temperature, then rapidly injecting the preasphaltene/solvent slurry. The mixture attained reaction temperature within 15 seconds. The microreactor was quenched in a water bath (∿5 seconds to 200°C). Preasphaltenes and asphaltenes were obtained from the preparatory Autoclave runs described and were analyzed by Huffman Laboratories for elemental compositions and molecular weights (VPO in pyridine).

## Results

Selected physical properties of preasphaltenes from the three preparatory runs described in Table 2 are provided in Table 3. Preasphaltenes are defined as material that is soluble in THF but insoluble in

TABLE 2. Run Conditions and Analytical Data from Autoclave Prep Runs

| | | | Weight % Based Upon dmmf Coal | | | |
|---|---|---|---|---|---|---|
| Run* | Temperature | Time | IOM | PreA | Asph | Oil |
| A35030 | 350°C | 30 min. | 40.2 | 34.7 | 24.7 | 4.3 |
| A40020 | 400°C | 20 min. | 25.9 | 30.3 | 43.0 | 10.8 |
| A45010 | 450°C | 10 min. | 25.2 | 19.0 | 43.0 | 22.8 |

* All runs performed with Illinois No. 6 Burning Star coal and SRC-II heavy distillate solvent (Table 1) at 1/2 coal to solvent.

TABLE 3. Molecular Weight and Elemental Analysis of Preasphaltenes

| Sample | Molecular Weight | Elemental Analysis Wt % C | H | N | S | O(1) |
|---|---|---|---|---|---|---|
| A350030 | 2867 | 80.1 | 5.3 | 1.9 | 1.9 | 10.8 |
| A400020 | 2482 | 82.3 | 5.2 | 2.0 | 1.4 | 9.1 |
| A450010 | 1777 | 85.9 | 5.2 | 2.1 | 1.1 | 5.7 |

(1) Oxygen by difference.

toluene; however, after the THF is removed, a significant portion of the preasphaltenes will not redissolve in THF. These are pyridine soluble and are called post-preasphaltenes. The THF insolubility varies with reaction severity. The 100% THF soluble preasphaltenes obtained from the 350°, 30 minute preparation reaction became 61% THF soluble after evaporation of the original THF while the material from the 450°, 10 minute preparation reaction became only 35% soluble. After approximately six months, the same experiments were repeated with the same preasphaltenes to determine whether storage in glass jars and in air at room temperature had an effect on solubility and/or reactivity. After six months of storage, the solubility of the preasphaltenes decreased from 61 to 32% and from 35 to 24% for the 350° and 450° materials, respectively. One possible explanation for this phenomenon is the gradual loss of a solvating molecule with time. A second explanation may be that the material oxidizes (7).

The Autoclave prepared Soxhlet extracted preasphaltenes were upgraded with SRC-II heavy distillate under 1800 psi hydrogen at 400°C for 0 to 30 minutes. The reaction products were analyzed for three components. One was the post-preasphaltene component; the other two were from the THF soluble portion. The soluble preasphaltenes were further divided by a gel permeation separation into high (similar to preasphaltene) and intermediate (similar to asphaltene) molecular weight fractions. Figure 1 shows the interconversion of the three components during the reaction. The SRC-II HD represents ∿92% of the whole liquid product and is not plotted. Small differences in preasphaltene concentration are measurable using the liquid chromatographic analysis (reproducibility = ± 5%). Also plotted is a point obtained by adding the preasphaltene to SRC-II HD under ambient conditions for 16 hours. The reason for indicating this data point was to show differences in starting material and also to follow conversion as the reaction components were heated from 25° to 400°C. A large portion of the post-preasphaltenes redissolve during heat-up.

Figure 2 presents the results as first order rates of decomposition. These data are based upon the concentration of preasphaltenes in solution at 400°C (zero time). The first order rate constants that were calculated from the plots in Figure 2 show that the 350° material ($K = 2.9 \times 10^{-2}$/sec) is more than 5 times more reactive than the 450° material ($4.6 \times 10^{-3}$/sec) (6, 8-10). There are at least two explanations for this observation. 1) The low severity reaction produces a different, more reactive material; or 2) The reactive preasphaltenes made during the 450° run have already converted to lower molecular weight material. The second possibility is corroborated by the data in Table 2, which shows that at 450°-10 minutes, more coal was converted than at 350°, yet less preasphaltene was extracted. Table 3 indicates that the less reactive 450° preasphaltene had a lower molecular weight and contained fewer heteroatoms.

We will attempt to clarify these differences in future studies by reacting the coal under various severities but to the same conversion and product slate and then extracting and reacting the preasphaltenes.

The data plotted in Figure 1b are the results of reacting the preasphaltenes after 6 months of storage at room temperature. The results show both differences in absolute values, caused by the change in solubility, and similarities in the trends. The 350° preasphaltenes were still more reactive than the 450° material even with the change in solubility.

In summary, preasphaltenes have been isolated from liquefaction runs under reaction severities from 450°C for 10 minutes to 350°C for 30 minutes. The preasphaltenes were isolated and differed in molecular weights, ∿2900-1800 amu, and in elemental composition. The materials also were not stable upon standing at room temperature. Reactivities were greatest for the preasphaltenes prepared at the lowest severity ($K = 2.9 \times 10^{-2}$/sec) and least for those prepared at the highest severity ($K = 4.6 \times 10^{-3}$/sec).

These results have potential implications for coal liquefaction, especially two stage liquefaction. If reactive or upgradeable intermediates can be produced at low reaction severity (350° vs 450°), then it may be possible to prevent retrogressive reactions. However, we have no indication that any overall product enhancement will be obtained from strictly thermal process.

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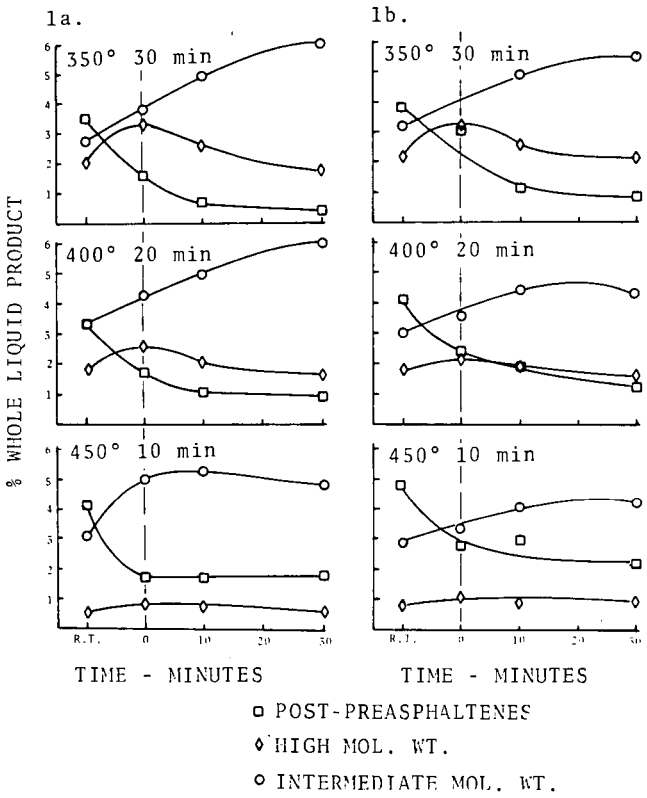


Figure 1a. Results of reacting preasphaltenes prepared at various reaction severities (350° - 30 minutes to 450° - 10 minutes) with SRC-II HD at 400°C for 0, 10 and 30 minutes.

1b. Results of reacting the same materials after 6 months of storage at room temperature.

Also included are the data obtained by contacting preasphaltene with SRC-II heavy distillate at room temperature for 16 hours (labeled R.T.).

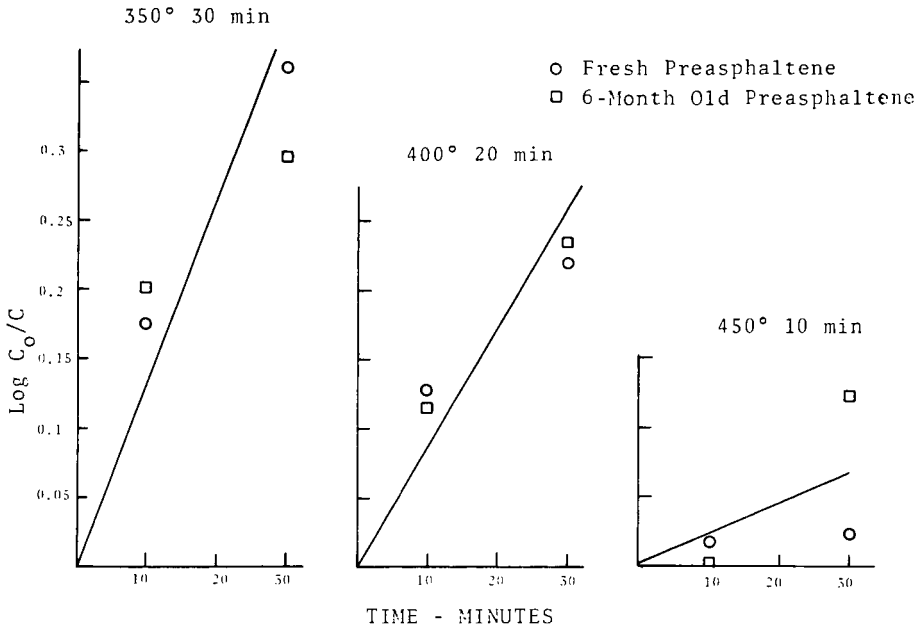


Figure 2. First order rates of decomposition of preasphaltenes based on $K = \frac{2.303}{t} \text{ Log } C_o/C$.