

A LOW TEMPERATURE REACTION PATH FOR COAL LIQUEFACTION*

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Introduction

The interaction of coal and solvent to form a gel in the 250-350°C range has significant implications in the efficiency of short residence time or two-stage liquefaction processes and the operation of preheaters in existing coal liquefaction processes. This interaction has been noted (1,2) during the heating of coal slurries in autoclaves where an apparent "endotherm" appears in the time-temperature curve--the "endotherm" is currently believed to be due to a high viscosity gel reducing heat transfer to the thermowell in the autoclave. Evaluation of these transitions leads to the following qualitative results.

1. Coal Effects - As the reactivity (to benzene solubles) toward liquefaction of the coal increases, the temperature of the transition increases;
 - Lignites do not exhibit a measurable transition.
2. Solvent - Transitions are not noted with pure hydrogen donor solvents as tetralin;
 - Magnitude of the transition increases as dissolving ability of the solvent increases.

Work by Cronauer (3) and Whitehurst (4) suggests initial solvent coal reactions which form adducts.

This paper summarizes the results of initial experiments on coal-solvent interactions. Results of low temperature (300°C) batch studies are compared to results obtained from 400-450°C, short residence time continuous reactor studies.

Materials

Three coals of varying reactivity were reacted with pure and coal-derived solvents; analyses are shown in Table 1 (5).

Table 1. Analyses of Coals and Solvents

| Ultimate | Illinois #6 Burning Star | West Va. Ireland | Bruceton | SRC II Heavy Distillate | Creosote #4 Cut |
|----------|-----------------------------|---------------------|----------|-------------------------------|--------------------|
| Carbon | 71.5 | 73.0 | 81.3 | 89.9 | 90.8 |
| Hydrogen | 4.8 | 5.2 | 5.3 | 7.6 | 5.8 |
| Nitrogen | 1.5 | 1.2 | 1.6 | 1.4 | 1.1 |
| Sulfur | 3.3 | 4.5 | 1.2 | 0.4 | 0.4 |
| Ash | 10.0 | 10.0 | 3.7 | .05 | < .05 |

Three non-coal-derived solvents used were hexadecane, phenanthrene--both C.P. grade--and tetralin, technical grade.

Table 2 summarized results of autoclave liquefaction studies on the three coals.

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Table 2. Coals

| Coal | Autoclave Results(5) | | | Transition Temp.(2) in Creosote Oil, #4 Cut (°C) |
|-------------------------------|----------------------|--------------|---------------------|--|
| | Time | Temp (°C) | % Conv to ØH Sol | |
| Illinois #6 Burning Star | 30 | 430 | - | 300 |
| West Virginia Ireland Mine | 30 | 430 | 64 | 240 |
| Bruceton | 30 | 430 | 44 | 200 |

Experimental

Two systems were used. The first was a glass system constructed with Schlenk apparatus. A 100 ml flask was topped with an adiabatic (silvered) reflux column. A thermocouple was inserted directly into the slurry and the system was continuously flushed with argon at 1 atmosphere. Slurries contained approximately 9g coal and 22g solvent. The system was stirred with a teflon-coated stir bar in the slurry. (When high viscosities were reached, this method was ineffective.) This apparatus was also employed for heating the dry coals to 300°C. In these cases, a thin layer of coal covered the bottom of the flask and the thermocouple was in direct contact with the flask.

The second system was a four-stage continuous flow reactor. Slurries of 30% coal/70% solvent were employed. Procedures and results are given in reference 6.

Analysis

Products have been analyzed by exhaustive Soxhlet extraction with benzene, followed by a THF extraction of the benzene insols (7) and a separation of benzene sols into pentane sols and insols (7). Some samples were filtered using a pressure filter fitted with #50 Waltman filter paper. Viscosities were measured with a Brookfield LVT viscometer.

Stability of Coal and Solvents

Experiments on the coal and solvent individually were carried out to determine if reactions observed were due to the individual components. Results shown in Table 3 indicate no significant chemical reaction occurs below 370°C and heating to 300°C does not result in THF solubility. However, softening is noted in the 300-330°C range.

Table 3. Thermal Response of Coals and Solvent

| Coal | DSC (Broad Endotherm) | Maximum Rate of Wt Loss TGA | Temperature of Maximum Expansion by Dilatometry | Changes in Solubility Observed After Heating to 300°C |
|----------------------|-----------------------------|---|--|--|
| Ill #6 BS | ~ 370°C | ~ 450°C | 300°C | None |
| W. Va. | ~ 370°C | ~ 450°C | - | None |
| Bruceton | ~ 370°C | ~ 450°C | 330°C | None |
| SRC II Heavy Dist | Boiling | Range 290-550°C; no change noted in heating to 450°C. | | |

Solvent-Coal Studies at Low Pressures

Results of studies made under inert gas at one atmosphere are shown in Table 4.

Table 4. Low Temperature Liquefaction Results

| Coal | Solvent | Temp °C | Time Min. | % Soluble Based on MAF Coal | |
|----------------------------|---------------------------|------------|--------------|--------------------------------|-------|
| | | | | % Benzene | % THF |
| Solvent Effects | | | | | |
| Bruceton | Hexadecane | 200 | 15 | 0 | 0 |
| | Tetralin/ Phenanthrene | 200 | 15 | -0.4 | 11 |
| | SRC II H.D. | 200 | 15 | -6.0 | 25 |
| Coal Effects | | | | | |
| Bruceton | SRC II | 200 | 15 | -6 | 25 |
| W. Va. | | 260 | 15 | -12 | 22 |
| Ill #6 | | 300 | 15 | -4 | 19 |
| Ill #6 | | 300 | 300 | -6 | 23 |
| Temperature Effects | | | | | |
| Bruceton | SRC II | 25 | 0 | 0 | 0 |
| | | 25 | 15 | 4 | 12 |
| | | 50 | 15 | 8 | 13 |
| | | 93 | 15 | 7 | 12 |
| | | 120 | 15 | 6 | 13 |
| | | 130 | 15 | 4 | 11 |
| | | 170 | 15 | 3 | 13 |
| 200 | 15 | -6 | 25 | | |

The data from the low temperature experiments show the following:

1. Solvent: (a) A non-reactive solvent as hexadecane does not dissolve the coal. Tetralin/phenanthrene mix is a good hydrogen donor but does not give as large a THF conversion as the SRC II heavy distillate.
(b) Increased THF conversion is accompanied by increasing solvent loss (benzene solubles).
2. Coal: The least reactive coal (Bruceton) toward liquefaction at higher temperatures is dissolved more readily at lower temperatures. This agrees with the transition temperatures noted in autoclave heatup curves.
3. Temperature: Approximately 13% of the coal can be extracted in 15 minutes with THF and this solubility does not increase with temperature until the autoclave transition temperature is reached; THF solubility increases and solvent is lost.

High viscosity products were noted when the THF solubility exceeded 20%; the products contain a high preasphaltene/oil ratio. This condition was only observed when the temperatures equaled or surpassed temperatures where endotherms had been observed in autoclave experiments with the respective coal/solvent systems.

Continuous Reactor Data

If the reactions are thermally activated and no significant mechanism changes occur between 300 and 400°C, short time 400°C effects should be similar to the 15 minute low temperature data just described. Product distributions from the reactor runs with Ill. #6 coal, Figure 1, show that preasphaltenes are produced at short times, apparently at the expense of solvent. These distributions result in high viscosities.

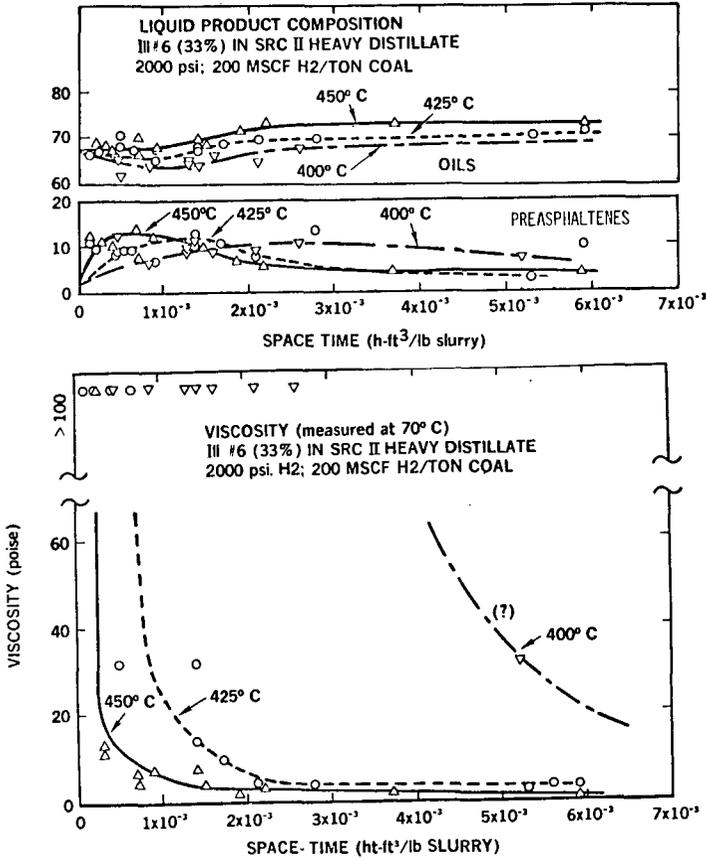


Figure 1

Thus, these continuous reactor data, at short reaction times, agree qualitatively with the low temperature, batch data. Initial regressive reactions have been noted in solvent imbalance during pilot plant short residence time preheater studies (8).

Evaluation of conversion data from the continuous reactor indicate the asphaltene concentration in the slurry product is independent of temperature and dependent on conversion at short times (benzene conversions of 0-55%). These data (Figure 2) suggest a series reaction sequence from coal to asphaltenes.

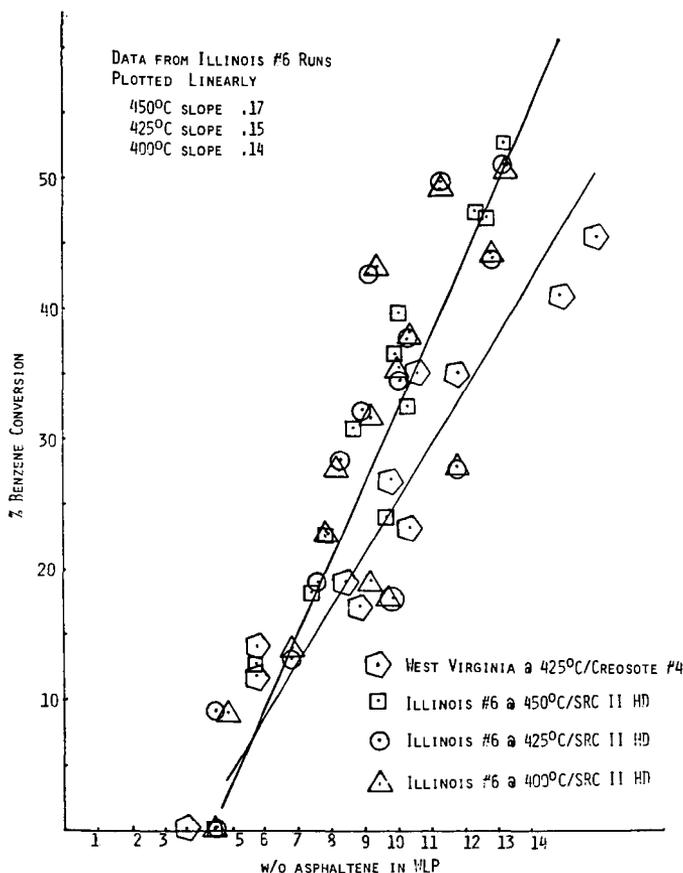
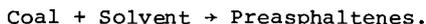


Figure 2

Discussion

Onset of a solvent-coal reaction occurs in the 200-300°C temperature range. The temperature and extent of this reaction are dependent on the coal and solvent. In this initial reaction, THF soluble products increase but solvent is lost indicating formation of a THF soluble, coal-solvent reaction product. This reaction product, defined in the preasphaltene or asphaltol compounds, results in high viscosity products--possibly gels.

A number of kinetic studies of coal liquefaction (Cronauer) processes made at long reaction times (< 10 min) show the liquefaction mechanisms can be represented by parallel reactions of coal to pre-asphaltenes, asphaltenes, oils and gases. However, these data show coal itself does not undergo thermosolvolytic at temperatures to 300°C and free radical processes need not be invoked to explain the reactions observed in the 200-300°C range. The data do suggest an initial series reaction of



The hydrogen donating capability of the solvent does not appear to be critical at this stage, but functional groups that can interact with the coal and cause swelling are important.

This initial series reaction is also indicated in the short time, continuous reactor results, Figure 2, where the preasphaltene content rises along with a solvent loss early in the reaction; subsequent decrease in preasphaltene content is accompanied by an increase in oil and asphaltene concentrations. The asphaltene content (and similarly the oil) is defined by the benzene conversion at 400, 425, and 450°C. The dependence of asphaltene and oil on conversion and not on temperature further suggests that the reaction of coal to preasphaltene goes to completion. Product distributions derived from two sources--coal and preasphaltene--would almost certainly be dependent upon temperature.

Preasphaltene chemistry needs further clarification. The extent, and possibly type, of coal-solvent interaction changes with temperature. Only about 30% THF conversion occurs at low temperatures with 80-95% conversion occurring over 400°C.

Conclusions

Coal liquefaction is initiated at 200-300°C by the reaction of solvent and coal to form preasphaltenes. The temperature of the reaction is a function of the coal type and the solvent. This reaction product imparts high viscosity to the slurry and its chemistry may influence subsequent liquefaction reactions. Understanding of this initial reaction is important to evaluate the applicability of advanced, two-stage liquefaction processes and could lead to the development of new, low temperature and pressure liquefaction schemes.

References

1. C. H. Wright and D. K. Schnalzer, "Short Residence Time SRC-I: Background and Recent Work," Proceedings of the DOE Project Review Meeting on Coal Liquefaction Preheater Studies, Oak Ridge, TN, March 21, 1979.
2. B. Granoff, unpublished data, Sandia Laboratories.
3. D. C. Cronauer, R. G. Ruberto, Y. T. Shah, "Reaction Mechanism Studies of Liquefying of Belle Ayr and Burning Star Coals," Proceedings of EPRI's Conference on Coal Liquefaction, Palo Alto, CA, May 1978.
4. D. D. Whitehurst, "Relationships Between the Composition of Recycle Solvents and Coal Liquefaction Behavior," Proceedings of EPRI's Conference on Coal Liquefaction, Palo Alto, CA, May 1978.

5. B. Granoff, P. M. Baca, M. G. Thomas, and G. T. Noles, "Chemical Studies on the Synthoil Process: Mineral Matter Effects," Sandia Laboratories Report SAND-78-1113, June 1978; R. K. Traeger and R. M. Curlee, "Preheater Effects in Coal Liquefaction Processes," Sandia Laboratories Report SAND-78-0312, March 1978.
6. R. K. Traeger and R. M. Curlee, "Preheater Studies in Coal Liquefaction," Sandia Laboratories Report SAND-78-1124, June 1978.
7. M. G. Thomas and G. T. Noles, "Sandia Fossil Fuel Analytical Laboratory Procedures Used in Coal Liquefaction Analyses," Sandia Laboratories Report SAND-78-0098, April 1978.
8. G. A. Styles and W. H. Weber, "Short Residence Time Studies Utilizing the Dissolver Preheater at the Wilsonville SRC Pilot Plant," Proceedings of the EPRI Contractor's Conference on Coal Liquefaction, Palo Alto, CA, May 1978.