

THERMAL REACTIVITY STUDIES OF SOLVENT REFINED COAL

R. L. Miller and N. Shankar
Chemical Engineering Department

University of Wyoming, Laramie, Wyoming 82071

ABSTRACT

Four solvent refined coal (SRC) samples obtained from Kentucky 9/14 and Illinois 6 coals have been thermally hydrogenated in a stirred microautoclave reactor at short contact time coal liquefaction reaction conditions. No coal or catalyst was used in any of the runs. Reactivity of each SRC sample was monitored using C_4 -427°C distillate yield, hydrogen consumption, hydrogen-free gas make, and solvent solubility measurements.

Initial results indicated the existence of various interconversion reactions among the oil, asphaltene, preasphaltene, and pyridine insoluble organic matter (IOM) fractions of catalytically unhydrogenated Kentucky SRC at selected reaction conditions. The net result of this reaction sequence was a relatively high C_4 -427°C distillate yield with minimal hydrogen-free gas make and hydrogen consumption. Kentucky and Illinois SRC samples which had been catalytically hydrogenated prior to use in the present study did not undergo the same types of reactions. Hydrogen-free gas make and hydrogen consumption were higher and C_4 -427°C distillate yield was lower in runs using hydrogenated SRC samples.

INTRODUCTION

The primary reaction step in direct coal liquefaction is generally believed to involve thermal rupture of various labile bonds within the coal structure (1, 2, 3). If the reactive free radical coal fragments formed can be quickly capped with available hydrogen from a hydrogen-donor solvent or from portions of the coal itself (autostabilization), a complex mixture of stabilized products is obtained. For convenience, these mixtures have been operationally classified according to a series of solvent solubility tests summarized in Table I (4). Unfortunately, such a classification system does not produce fractions with simple chemical identities.

Preasphaltenes constitute the predominate primary liquefaction product with asphaltenes, oils (distillable and nondistillable), and gases formed in lesser amounts. Secondary reactions involving conversion of preasphaltenes and asphaltenes to produce additional quantities of oil and gas form an important part of coal conversion to distillable liquids. Furthermore, the use of residuum recycle has been shown to have a significant influence on liquefaction process performance. Silver reported that up to 50 wt% of the total distillate obtained in two-stage liquefaction of Wyodak coal could be attributed to conversion of mildly hydrogenated residuum (5). The need for a better understanding of residuum conversion to lighter products is necessary to further improve existing liquefaction processes.

The objective of the research described in this paper was to investigate the thermal conversion of coal-derived residuum in the absence of coal and catalyst at representative coal liquefaction conditions. Particular emphasis was placed on residuum behavior at short contact time reaction conditions similar to those employed in the Lummus ITSL process (6).

EXPERIMENTAL PROCEDURE

Solvent refined coal (SRC) produced from Kentucky 9/14 coal was used as feed residuum in the initial thermal reactivity experiments. This material, designated

F-51, boils above 427°C and was produced in the Pittsburg and Midway SRC-I pilot plant near Tacoma, Washington. To reduce SRC viscosity, blends of approximately 50 wt% F-51 and 50 wt% Kentucky 9/14 coal-derived distillate, designated F-7, were used as reactor feed. The F-7 distillate is a nominal 260-427°C boiling range fraction which was also produced at the Tacoma SRC-I pilot plant. Table II gives a brief description of F-51/F-7 properties.

Three other SRC-distillate mixtures were used in additional reactivity studies. Properties of these mixtures are also included in Table II. Sample F-102A was prepared by mildly hydrogenating a portion of F-51/F-7 at 370°C and 13.9 MPa initial cold hydrogen pressure for one hour over thermally activated Nalco 477 cobalt-molybdate catalyst in a batch reactor. Samples F-128 and F-129 are Illinois 6 coal-derived hydrotreated recycle residuum from Wilsonville, Alabama pilot plant runs 242 and 243, respectively. Run 242 was operated using a short contact time thermal reactor while run 243 utilized a long residence time dissolver. Both of these samples were obtained from essentially steady-state operations and represent residuum which had been recycled through the process many times. The C₄-427°C distillate content of both F-128 and F-129 was only about 30 wt%. Several reactivity runs were performed using F-128 or F-129 diluted with additional Illinois 6 coal-derived distillate to obtain feed mixtures containing about 50 wt% distillate. Results from these runs indicated that within experimental error, there was no effect on yields from the SRC when the feed distillate content was varied between 30 wt% and 50 wt%. Thus, yield data from the four SRC-distillate mixtures listed in Table II can be directly compared.

The thermal reactivity experiments were carried out in a 60 ml stirred microautoclave reactor system designed and constructed at the University of Wyoming. The reactor is similar to larger Autoclave batch reactors except that heating is accomplished with a high temperature sandbath. At the end of each run, the reactor and its contents are quenched with an icewater bath. This reactor system can provide the benefits of small tubing bomb reactors (quick heatup (~2 min.) and cool down (~30 sec.)) while at the same time insuring sufficient mechanical agitation of the reactants with an Autoclave MagneDrive II stirring assembly to minimize hydrogen mass transfer effects. Furthermore, the system is designed so that the reactor pressure is very nearly constant throughout an experiment.

The reactor runs were completed at 454°C and 6.9 MPa initial cold hydrogen pressure for reaction times in the range of 5 - 15 minutes. To simulate the slug flow behavior of commercial small diameter SCT reactors in which significant gas phase hydrogen mass transfer effects exist, the MagneDrive stirrer was turned off during these runs. These conditions are believed to simulate SCT operations reasonably closely.

Portions of the liquid products from each run were distilled to a 427°C endpoint using a microdistillation apparatus. Additional portions of the liquid product were sequentially extracted in a Soxhlet extractor using cyclohexane, toluene, and pyridine. Product gases were analyzed on an HP 5840A gas chromatograph.

RESULTS AND DISCUSSION

Using the experimental methods described, the product composition from each reactor run was measured. This data is summarized in Figures 1-4 in which weight fraction compositional changes as a function of reaction time are shown for each SRC-distillate sample. The weight fraction of hydrogen-free gas produced was always less than about 0.01 and is not shown on these figures. Results shown for F-51/F-7 are average values from duplicate runs, while data for the other three SRC-distillate samples were obtained in single runs. Based on previous experience with the reactor system and product analysis methods used, the weight fraction data presented has an experimental error of approximately ±10 relative percent.

Several interesting observations can be made from these results. First, a detailed examination of the material balance data indicates that the asphaltene fraction of F-51/F-7 formed both distillate and preasphaltenes particularly at reaction times greater than about 5 minutes. Several authors have previously noted this type of disproportionation behavior (7, 8, 9). In some cases these results have been interpreted as evidence of reaction "reversibility". However, as will be noted shortly, such reversibility does not really exist here, since the preasphaltenes formed by asphaltene disproportionation differ from the coal-derived preasphaltenes found in F-51/F-7. Figure 1 also shows a decline in the nondistillable oil content most likely caused by thermal cracking of oils to form additional distillate and gas. No significant amount of pyridine insoluble organic matter (IOM) was formed during the F-51/F-7 runs.

In contrast, results shown in Figures 2-4 for the hydrogenated SRC-distillate samples indicate somewhat different behavior. In each case, the asphaltene fraction apparently shows no propensity toward disproportionation. Rather, material balance data suggests that preasphaltenes and asphaltenes were slowly converted to nondistillable oils, and eventually cracked to distillate and gas in a series type mechanism. After about ten minutes reaction time, the conversion of nondistillable oils to distillate and gas was the only significant reaction taking place in the F-128 and F-129 samples. Once again, very little IOM was produced in any of the runs. This is not surprising since other researchers have noted the refractory nature of hydrogenated asphaltenes toward thermal or catalytic conversion to lower boiling products (10, 11).

The overall effect of differences in asphaltene and preasphaltene thermal reactivity between the unhydrogenated and hydrogenated SRC-distillate samples is summarized in Figure 5. In this plot, hydrogen utilization efficiency, defined as the mass of $C_{1-427}^{\circ}C$ distillate produced per unit mass of hydrogen consumed is plotted as a function of reaction time for each of the four SRC-distillate samples. The unhydrogenated F-51/F-7 sample obviously produces a significant amount of distillate with minimal hydrogen consumption when compared with yield data from the hydrogenated samples. Furthermore, Figure 6 shows that the hydrogen-free gas make was found to be 2 to 6 times less in the F-51/F-7 runs. It appears that asphaltene disproportionation is a more efficient method of distillate production than thermal cracking of nondistillable oils. However, it is apparent that even mild catalytic hydrotreatment of the SRC results in drastically reduced hydrogen utilization efficiency.

In an attempt to further study differences between the reaction pathways of unhydrogenated and hydrogenated asphaltenes and preasphaltenes, the preasphaltene fractions from the F-51/F-7 and F-102A thermal reactivity experiments were subdivided into chloroform soluble-toluene insoluble and pyridine soluble-chloroform insoluble subfractions, designated preasphaltene-1 and preasphaltene-2, respectively. Boduszynski has reported that preasphaltene-1 samples generally resemble asphaltenes in the number of function groups and degree of aromaticity (12). Preasphaltene-2 samples are more highly functional and are believed to fairly well represent coal-derived preasphaltene material. As shown in Figure 7, the increase in total preasphaltene content for the F-51/F-7 runs was due to an increase in preasphaltenes-1. At least a portion of the preasphaltenes-1 was obtained as a disproportionation product from the asphaltenes. The fact that the total preasphaltene content did not remain constant or decrease precludes the reaction sequence: preasphaltenes-2 to preasphaltenes-1 to asphaltenes as the only pathway involving these fractions. In contrast, as shown in Figure 8, the decrease in F-102A preasphaltenes occurred because of preasphaltenes-2 consumption. No significant buildup of preasphaltenes-1 was noted. Once again, this suggests that F-102A asphaltenes did not undergo disproportionation.

The exact mechanism responsible for the apparent change in asphaltene reactivity is not yet known. Painter (13) and Whitehurst (14) have indicated that retrogressive reactions of SRC fractions to ultimately form char involve the condensation of alkyl and phenolic functional groups rather than direct aromatic ring fusing. It is quite possible that the same functional groups are involved during asphaltene disproportionation. Catalytic hydrotreatment of the SRC would result in fewer available functional groups with which the disproportionation could occur. Efforts are currently underway to test this hypothesis by observing detailed structural changes of the F-51/F-7 and F-102A preasphaltene and asphaltene fractions during thermal hydrogenation.

CONCLUSIONS

The thermal reactivity behavior of one unhydrogenated and three hydrogenated SRC-distillate samples has been studied at simulated short contact time (SCT) reaction conditions. Unhydrogenated coal-derived asphaltenes were found to disproportionate into primarily C_7 -427°C distillate and preasphaltene-1 material resulting in high hydrogen utilization efficiency and low hydrogen-free gas make. Asphaltenes from the hydrogenated SRC-distillate samples did not disproportionate. As a result, hydrogen utilization efficiency was significantly lower and hydrogen-free gas make was higher in runs using the hydrogenated samples.

ACKNOWLEDGEMENTS

Financial support for this research was provided by the Electric Power Research Institute under Contract Number RP 1604-04. Mr. Norman Stewart of EPRI provided helpful comments.

LITERATURE CITED

1. Farcasiu, M., ACS Div. Fuel Chem. Preprints, 24, 1, 121, (1979).
2. Han, K.W., and Wen, C.Y., Fuel, 58, 779, (1979).
3. Neavel, R.C., Fuel, 55, 237, (1976).
4. Schweighardt, F.K., Retcofsky, H.L., and Raymond, R., ACS Div. Fuel Chem. Preprints, 21, 7, 27, (1976).
5. Silver, H.F., Corry, R.G., Miller, R.L., and Hurtubise, R.J., Fuel, 61, 111, (1982).
6. Schindler, H.D., Chen, J.M., and Peluso, M.; "Liquefaction of Eastern Bituminous Coals by the Integrated Two-Stage Liquefaction (ITSL) Process", Proceedings of the Seventh Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (May, 1982).
7. Thomas, M.G., "Catalyst Behavior in Direct Coal Liquefaction", Proceedings of the Sixth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (May, 1981).
8. Lee, W.C., Interconversion of Coal-Derived Products, Ph.D. Dissertation, University of Southern California, (1980).
9. Farcasiu, M., Mitchell, T.O., and Whitehurst, D.D., ACS Div. Fuel Chem. Preprints, 21, 7, 11, (1976).
10. Baldwin, R.M., Personal Communication, (1983).

11. Silver, H.F., Corry, R.G., and Miller, R.L., "Coal Liquefaction Studies", Final Report for EPRI Projects 779-23 and 2210-1, (December, 1982).
12. Boduszynski, M.M., Hurtubise, R.J., and Silver, H.F., *Anal. Chem.*, 54, 375, (1982).
13. Painter, P.C., Yamada, Y., Jenkins, R.G., Coleman, M.M., and Walker, P.L., Jr., *Fuel*, 58, 4, 293, (1979).
14. Whitehurst, D.D., Mitchell, T.O., Farcasiu, M., and Dickert, J.J., Jr., "The Nature and Origin of Asphaltenes in Processed Coal", Final Report for EPRI Project 410, vol. 2, (December, 1979).

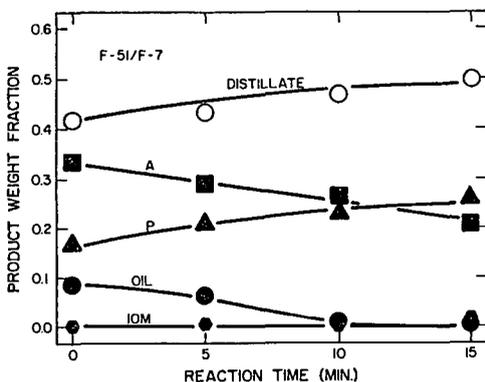


Figure 1 - Product Distribution for F-51/F-7 Runs

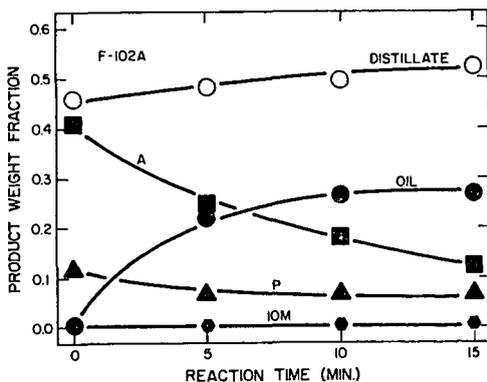


Figure 2 - Product Distribution for F-102A Runs

Table I
Classification of Coal Liquefaction Products

<u>Fraction</u>	<u>Definition</u>
Insoluble Organic Matter	Pyridine or THF insoluble
Preasphaltenes	Pyridine or THF soluble; benzene or toluene insoluble
Asphaltenes	Benzene or toluene soluble; pentane, hexane, or cyclohexane insoluble
Oils	Pentane, hexane, or cyclohexane soluble

Table II
SRC - Distillate Feed Mixture Properties

SAMPLE	F-51/F-7	F-102A	F-128	F-129
SOURCE COAL	KY 9/14	KY 9/14	ILLINOIS 6	ILLINOIS 6
WT.% BOILING ABOVE 427°C	58.0	54.8	68.5	69.2
HYDROGENATION LEVEL	NONE	MILD	SEVERE	SEVERE
ULTIMATE ANALYSIS (WT% DRY BASIS)				
CARBON	86.4	86.9	89.1	89.3
HYDROGEN	7.1	8.0	8.9	8.9
NITROGEN	1.9	1.5	0.4	0.6
SULFUR	0.8	0.6	0.1	0.1
OXYGEN (DIFFERENCE)	3.7	2.9	1.1	0.9
ASH	0.1	0.1	0.4	0.2

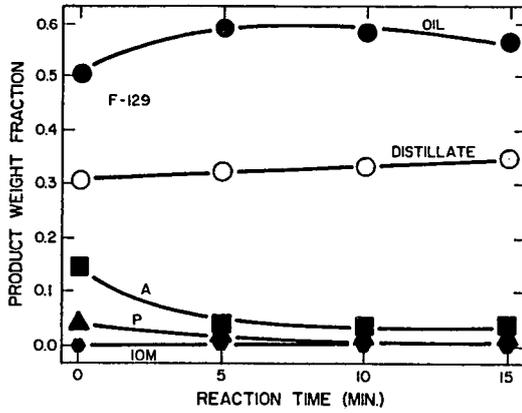


Figure 4 - Product Distribution for F-129 Runs

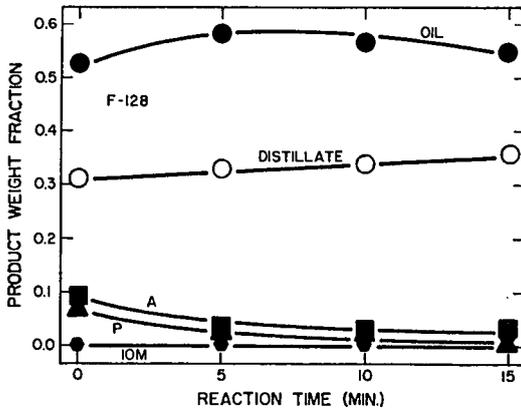


Figure 3 - Product Distribution for F-128 Runs

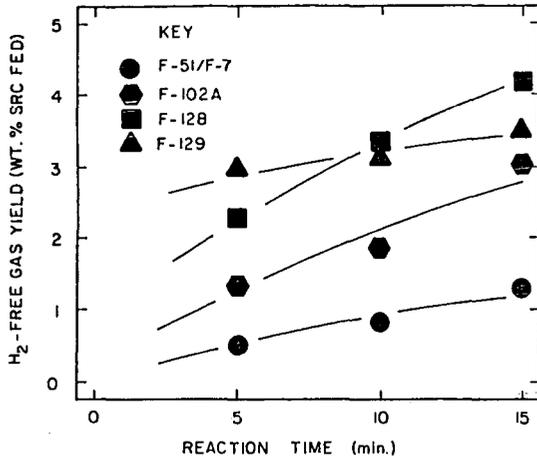


Figure 6 - Hydrogen-free Gas Yield as a Function of SRC Feedstock and Reaction Time

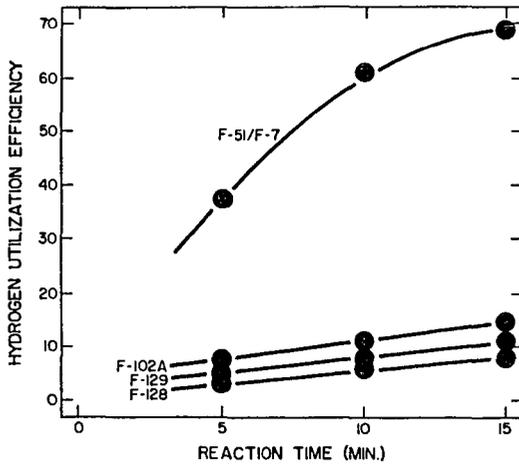


Figure 5 - Hydrogen Utilization Efficiency as a Function of SRC Feedstock and Reaction Time

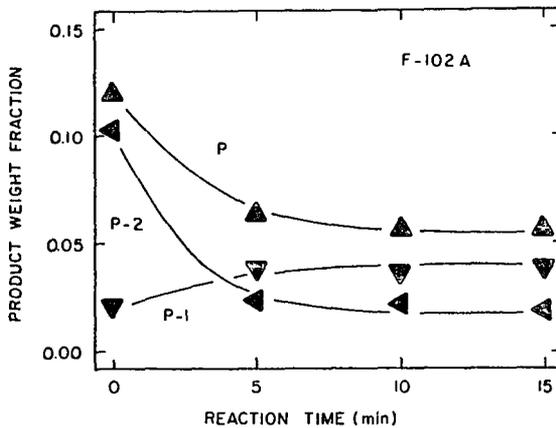


Figure 8 - Preasphaltene Composition for F-102A Runs

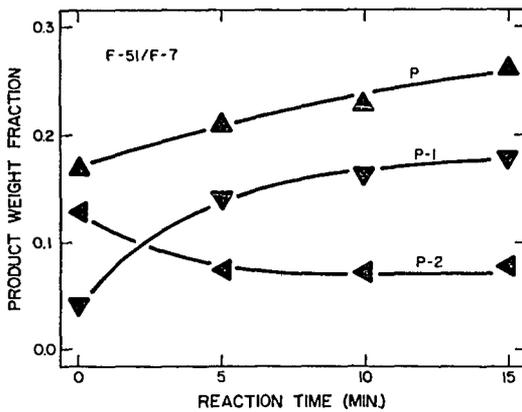


Figure 7 - Preasphaltene Composition for F-51/F-7 Runs