

FATE OF SELECTED 1-, 2-, AND 3-RING COMPOUNDS
DURING RECYCLE COAL LIQUEFACTION OPERATION

D. C. Cronauer, R. I. McNeil, D. A. Danner

Gulf Research & Development Company
P.O. Drawer 2038, Pittsburgh, PA 15230

and J. H. Wieland, and J. S. Abichandani

Department of Petroleum & Chemical Engineering
University of Pittsburgh, Pittsburgh, PA 15261

INTRODUCTION

To observe the adduction, isomerization, and cracking of labeled solvent species, a series of coal liquefaction runs was undertaken using a bench-scale unit capable of continuous recycle operation. These experiments were made with ^{13}C -labeled solvents including octahydrophenanthrene, phenanthrene, methylphenanthrene, dimethyltetralin, and mesitylene. This work served as an extension of previously reported⁽¹⁻³⁾ laboratory-scale experiments using similar labeled model liquefaction solvents.

EXPERIMENTAL

The recycle runs with labeled compounds were performed using a continuous, bench-scale, coal liquefaction unit, a schematic of which is shown in Figure 1. In summary, the unit consisted of feed and product systems, a preheater of 8 min nominal space time, and a 1 L stirred autoclave of 60 min space time.

The operating procedure consisted of preparing a feed slurry in a heated, stirred tank separate to the unit. The feed was made up of Powhatan No. 5 Mine coal, a portion of recycle heavy product slurry from the previous period, and a process solvent generated during previous SRC-II runs in the GR&DC P-99 PDU⁽⁴⁾ feeding the same coal. The analyses of the solvent and coal are given in Table I. This feed blend was introduced into the bench-scale unit every 4 h.

The ^{13}C -labeled compounds were prepared under the direction of Professor E. J. Eisenbraun of Oklahoma State University with a portion of the analyses of intermediates and products being done at GR&DC. A detailed description of the techniques of synthesis and analyses of a portion of these compounds are reported by Seshadri et al.⁽⁵⁾ and in Reference 3.

In addition to sample distillation and routine elemental analyses, samples of heavy product slurry were Soxhlet extracted using, in sequence, the solvents: pentane, toluene, and tetrahydrofuran (THF). The Soxhlet extractions with pentane and toluene were typically of 48 h duration, and the THF of 24 h. The solvents were stripped on a steam table (80°C) with a stream of

nitrogen prior to analysis. Selected samples of separator liquids (combined No. 2, No. 3, and ice traps) and pentane solubles were separated by HPLC into saturates, aromatics, and resin (polar) fractions. An in-house HPLC was used with Bio-Sil A silica gel (20-44 micron); a description of the operating procedure was reported by Suatoni and Swab.⁽⁶⁾

The level of ^{13}C -labeling in the product fractions was determined by the standard technique of combustion to CO_2 followed by use of a Varian MAT 250 MS to determine the ratio of mass 45 to 44 (stated sensitivity of $<2 \times 10^{-6}$). Isotopic compositions are reported as δ values, the definition of which follows:

$$\delta^{13}\text{C} = \frac{R_S - R_R}{R_R} \times 1000\% \text{ (parts per thousand)}$$

where R_S and R_R refer to the $^{13}\text{C}/^{12}\text{C}$ ratio in the sample and reference, respectively. The reference is PDB (Peedee Formation carbonate [belemnite]) with a value of 0.0112372. Coal has a typical range of -20 to -30 parts per million (This analysis was done at GR&DC and at Global Geochemistry Corp.)

RESULTS

Overall Material Balance of Recycle Runs--Lined-out operation of the bench-scale unit was first established with a feed consisting of Powhatan No. 5 coal, process solvent (boiling point $400^\circ\text{-}800^\circ\text{F}$), heavy recycle product slurry, and hydrogen. The product streams primarily consisted of gases, No. 2 and 3 condensates, and heavy product slurry. The reactor was run at conditions of 455°C , 1.0 h space time, and 13.8 MPa (2000 psig). After lined-out operation was achieved (34 h), a small sample of labeled octahydrophenanthrene (HPh) was introduced to the feed tank at a level of 26 g/5000 g charge. After 26 h, the next labeled compound, dimethyltetralin (DMT), was similarly charged, and the product streams were analyzed. For this and the remaining three labeled solvents, a 24-h period was used. The runs with labeled solvent were done in the following order: (89-1) octahydrophenanthrene (HPh), (89-2) dimethyltetralin (DMT), (89-3) mesitylene (MST), (89-4) methylphenanthrene (MePh), and (89-5) phenanthrene.

In all of the runs, it was assumed that the addition of the labeled solvent at a level of about 0.5 wt% once every 24 h would not affect lined-out recycle operation. Based on a detailed material balance of the second and fourth periods, this assumption appeared valid as shown in the Tables II and III.

Extraction of Process Samples from the Recycle Runs--To isolate concentrates for GC/MS and $^{13}\text{C}/^{12}\text{C}$ -MS analyses, samples of both the combined condensates and heavy slurry products were separated into fractions using extraction and HPLC. The results for 89-1 and 89-5 are given in Table IV.

Calculated Material Balance of Labeled Species--To follow the course of the ^{13}C -labeled species during SRC-II type recycle runs, it was necessary to account for both slurry product withdrawal and losses due to vaporization. In the case of very volatile compounds, most of the ^{13}C -label was recovered in the light condensate collected in the traps. This material was not recycled, and, therefore, it was quickly lost from the system. In the case of essentially nonvolatile species, losses occurred by removal of a portion of the reactor effluent stream as heavy product. To account for vaporization losses, the reactor system was modeled using average material balances with a factor "XVAP" giving the fraction of ^{13}C -labeled compound that was lost during each reactor pass due to vaporization. Figure 2 is a plot of the calculated concentration of traced (^{13}C) of the slurry from the product tank as functions of time and losses due to vaporization.

Results of Analysis of Fluids for ^{13}C -Labeled Compounds--In addition to an analysis of the product slurries and condensate streams, individual samples of pentane solubles (oils), asphaltenes, and THF insolubles were analyzed for $^{13}\text{C}/^{12}\text{C}$ ratios to determine trends with time. Overall ^{13}C material balances were calculated to show how the labeled compounds were distributed between gases, condensates (Traps 1-3), heavy products (asphaltenes, etc.), and bulk product.

As shown in Figures 3 and 4 ($^{13}\text{C}/^{12}\text{C}$ ratios of slurries and condensates), the results show the trends predicted from Figure 2. Specifically, a concentration peak occurred at about 4-6 h into the cycle, and this went essentially to zero after 24 h. In addition, the curves for the phenanthrene (Ph) and octahydrophenanthrene (HPh) runs were similar, as would be expected from the closeness of their boiling points. The loss of labeled species into the condensates recovered in the various traps also followed expected trends. As indicated by ^{13}C analysis, about 11.8% of the highest boiling labeled compound, methylphenanthrene (MePh) was found in the condensates. However, the ^{13}C -labeled methyl group readily cracked as indicated by a high recovery (namely 46.9%) of labeled gases, primarily methane. The recovery of ^{13}C -labeled compounds in the condensates from the HPh and Ph runs was essentially identical at 32.9 and 34.2%, respectively. In the run with labeled dimethyltetralin, in excess of 80% of the label was observed in the condensate. Only a low recovery (about 10%) of the low boiling mesitylene was recovered in the condensates. From an analysis of the remaining streams, it appeared that this compound was lost from the heated feed tank.

The levels of labeled compounds in the heavy product fractions somewhat follow anticipated trends. The amount of HPh held in the asphaltene fraction, by chemical adduction, was 4.8% of that fed, while that in the THF insolubles was 0.5%. In the case of Ph, the respective levels were 1.5 and 0.7%. The level of adduction of MePh was intermediate between HPh and Ph at 2.9% in the asphaltenes and 0.3% in the THF insolubles. Considering the high level of MePh cracking, these latter values are consistent with those of HPh. Essentially no adduction of dimethyltetralin and mesitylene were observed in that the $^{13}\text{C}/^{12}\text{C}$ ratios of the heavy fractions from these runs were the same as those of the base case before label use.

Reaction Trends of Individual Phenanthrene Compounds--The aromatic cuts of condensates and slurry product streams were analyzed for Run 89-1 (HPh) and 89-5 (Ph). It is first noted that octahydrophenanthrene was present in the products at concentrations less than 0.03 wt%. This compound gave up at least a portion of its hydrogen very rapidly, and, therefore, it can be considered to be absent from a recycle system unless external catalytic hydrogenation is used. Within the accuracy of the GC/MS analysis, the concentrations of phenanthrene, dihydrophenanthrene (H₂Ph), and tetrahydrophenanthrene (H₄Ph) remained essentially constant through the run periods of Runs 89-1 and 89-5. The results are given in Table V.

It is first obvious that the results from Runs 89-1 and 89-5 are consistent. The total concentrations of phenanthrene plus hydrophenanthrenes averaged 2.9 and 2.8 wt% in the condensate and slurry, respectively. (Note that alkyl substituted phenanthrenes are not included.) Due to boiling points, the relative distributions of hydrophenanthrenes to phenanthrenes were greater in the condensates than in the slurry. From an overall material balance, the conversions of coal to Ph, H₂Ph, and H₄Ph were about 0.7, 0.2, and 0.2 g/100 g MAF coal, respectively.

By a GC/MS analysis of the product fraction of Runs 89-1 and 89-5, it was found with the introduction of labeled Ph in SRC-II type operation, little of this component is hydrogenated to dihydro and tetrahydro species. In addition, an observed presence of labeled compounds of C₃-naphthalene and isomerized derivatives of octahydrophenanthrene confirms that ring opening and isomerization of hydroaromatics occurs at coal liquefaction conditions.

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Table I

ANALYSIS OF COAL AND P-99 DERIVED PROCESS SOLVENT

<u>Sample Designation</u>	<u>Powhatan No. 5 Mine Coal</u>	<u>Process Solvent</u>
1. <u>Proximate Analysis</u>		
% Moisture	1.1	--
Ash	9.6	--
Volatile	39.6	--
Fixed Carbon	49.7	--
2. <u>Elemental Analysis</u> (Dry)		
% Carbon	72.3	87.2
Hydrogen	5.1	8.7
Nitrogen	1.5	0.9
Oxygen	7.8 (diff)	2.8
Sulfur	3.6	0.4
Ash	9.7	--
	<u>100.0</u>	<u>100.0</u>

Table II

OVERALL MATERIAL BALANCE
Recycle Run 89

<u>Feed (g/h)</u>			<u>Products (g/h)</u>		
<u>Run Period</u>	<u>89-2</u>	<u>89-4</u>	<u>Run Period</u>	<u>89-2</u>	<u>89-4</u>
Coal	367.6	367.8	Gases (and H ₂ O)	98.9	97.5
Process Solvent	196.0	202.3	No. 2 Condensate	96.9	69.6
Heavy Product Slurry	661.6	656.0	No. 3 Condensate (plus ice traps)	95.1	141.8
Hydrogen (Consumption)	13.9	13.7	Heavy Product Slurry	900.5	882.3
Total	<u>1239.1</u>	<u>1239.8</u>	Total	<u>1191.4</u>	<u>1190.2</u>
			Recovery	96.1%	96.0%

Table III

NET PRODUCT YIELDS (MAF BASIS)
Recycle Run 89

<u>Yield Component</u>	<u>89-2</u>	<u>89-4</u>	<u>Average</u>
H ₂ Consumption	-4.2	-4.2	-4.2
C ₁ -C ₄	16.5	15.7	16.1
Other Gases (CO, etc.)	2.3	2.3	2.3
Water	5.9	5.9	5.9
C ₅ -380°F	15.5	16.8	16.1
380-550°F	9.1	13.0	11.1
550-900°F	10.3	7.6	9.0
C ₅ -900°F	34.9	37.4	36.2
380-900°F	19.4	20.6	20.1
900°F ⁺ P.S.	35.3	34.2	34.7
IOM	9.3	8.7	9.0
900°F ⁺ Organic	44.6	42.9	43.7

Table IV

HPLC EXTRACTION SUMMARY

<u>Product Fraction</u>	<u>Saturates</u> <u>(wt%)</u>	<u>Aromatics</u> <u>(wt%)</u>	<u>Resins</u> <u>(wt%)</u>	<u>Hexane Ins.</u> <u>(wt%)</u>
<u>Run Period 89-1:</u>				
a. Condensates	5.5 ± 1.6	50.1 ± 3.8	44.0 ± 4.0	0.4 ± 0.2
b. Oils (Slurry)	2.8 ± 0.5	64.7 ± 4.1	32.5 ± 6.5	
<u>Run Period 89-5:</u>				
a. Condensates	4.8 ± 2.4	53.0 ± 5.0	41.9 ± 3.7	0.3 ± 0.2
b. Oils (Slurry)	3.3 ± 0.3	69.0 ± 3.8	27.7 ± 3.8	

Table v

SUMMARY OF PHENANTHRENE CONCENTRATIONS, WT%

<u>Component</u>	<u>89-1</u>		<u>89-5</u>	
	<u>Condensate</u>	<u>Slurry</u>	<u>Condensate</u>	<u>Slurry</u>
Phenanthrene	1.66	2.10	1.85	2.25
H ₂ Ph	0.47	0.24	0.61	0.32
H ₄ Ph	0.67	0.33	0.51	0.30
H ₈ Ph	<0.03	<0.03	<0.03	<0.03

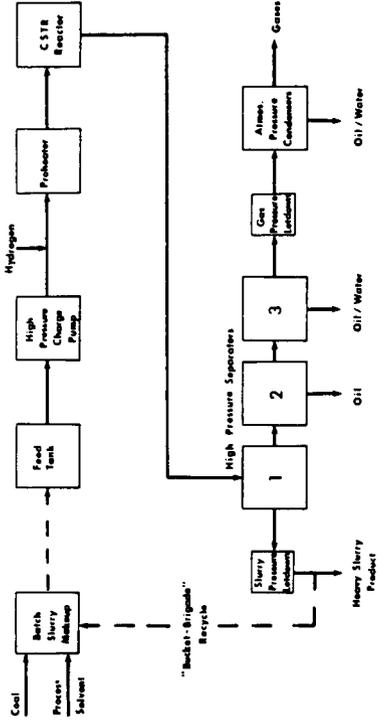


FIGURE 1: SCHEMATIC OF THE A1 RECYCLE COAL LIQUEFACTION UNIT

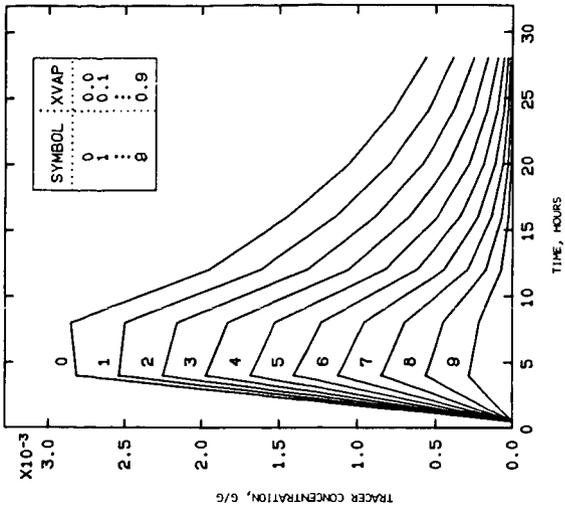


FIGURE 2: CONCENTRATION OF TRACER IN THE SLURRY PHASE AS A FUNCTION OF TIME AND FRACTION OF TRACER VAPORIZED: SLURRY DENSITY=1.00

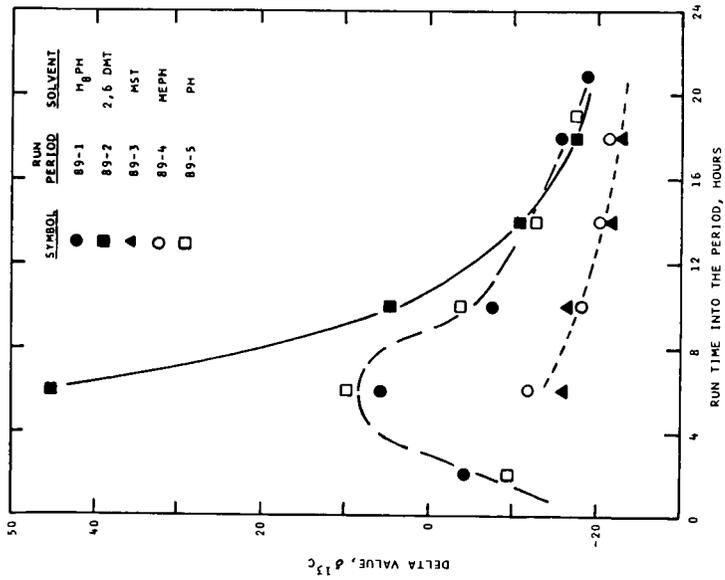


FIGURE 3: ^{13}C LEVELS IN THE CONDENSATE SAMPLES OF RUNS 89-1 THROUGH 89-5

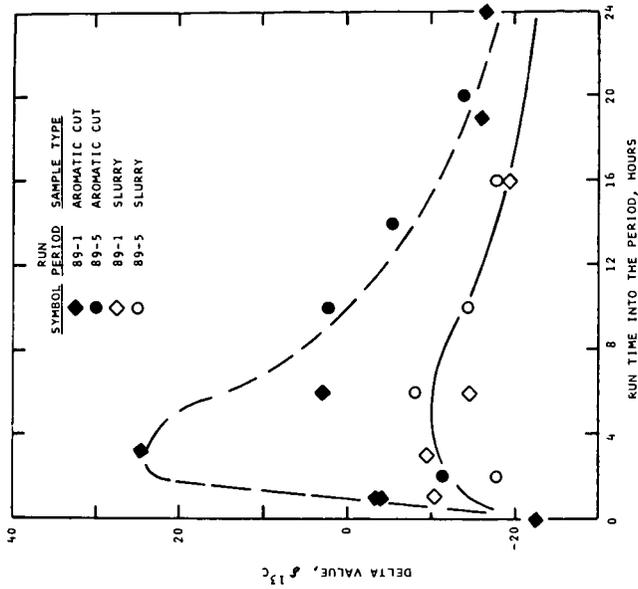


FIGURE 4: ^{13}C LEVELS IN SAMPLES OF PRODUCT SLURRY AND THE AROMATIC CUTS DERIVED FROM THE SLURRY