Energy

F
O
S
S
I
L

145
10-11-84 JS (2) DR-0477-4

DOE/OR/03054-35
(DE84015901)

EFFECTS OF STAGED VESSELS ON DISSOLVER
PERFORMANCE

Internal R&D Final Report

By
R. Sivasubramanian
E. N. Givens

Work Performed Under Contract No. AC05-78OR03054

International Coal Refining Company
Allentown, Pennsylvania

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A04
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

INTERNAL R&D FINAL REPORT:
EFFECTS OF STAGED VESSELS ON DISSOLVER PERFORMANCE

Prepared by
R. Sivasubramanian and E. N. Givens
INTERNATIONAL COAL REFINING COMPANY
P.O. Box 2752
Allentown, Pennsylvania 18001

for the
UNITED STATES DEPARTMENT OF ENERGY
Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR0-3054

MASTER

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
EXECUTIVE SUMMARY	1
INTRODUCTION	3
TASK 2: EFFECT OF SERIES VS. PARALLEL OPERATION	4
Experimental Plan	4
Materials	7
Operation	7
Feed and Product Analysis	10
Error Analysis	11
Analytical and Unit Reproducibility	12
Results and Discussion	19
TASK 3: INTERSTAGE CONVERSIONS FOR SERIES DISSOLVERS	24
Experimental Plan	24
Results and Discussion	29
Effect of Time and Temperature	28
Effect of Staged Temperatures	44
Segregation of Hydrogen Flow between Dissolvers	49
CONCLUSIONS	52
LITERATURE CITED	53
APPENDIX 1: LIQUEFACTION TEST FACILITIES	54

ABSTRACT

The process design for the SRC-I Demonstration Plant calls for two dissolvers operating in series. The objective of this study was to develop process data for operating the two dissolvers in the demonstration plant. Experiments were conducted in a 100-lb/day bench-scale unit using two different reactor configurations (series vs. parallel); series operation reduced the preasphaltenes yield. The effect of varying the temperatures in the two reactors was also studied.

EXECUTIVE SUMMARY

This report summarizes the work conducted under ICRC's Program Area 12.1.7, on the effects of staged vessels on dissolver performance. Program 12.1.7 consisted of three tasks: Task 1 on the effect of inert solids on liquefaction is discussed elsewhere (Skinner, 1983); Tasks 2 and 3, which are discussed here, examined the effects of series vs. parallel operation of the dissolvers, as well as the effect of staged temperatures on yield distribution.

Results from Task 2 showed that operating the dissolvers in series decreased the preasphaltenes yield. From a process viewpoint, this should increase the amount of recoverable product, because recovery from the plant's critical solvent deashing unit will increase when preasphaltene content decreases. Neither conversion nor oil, asphaltene, or gas yields were affected by reactor configuration.

Process data taken at residence times from 20 to 60 min and temperatures from 780 to 840°F showed that oil yields were directly affected by reaction time, but relatively insensitive to temperature. Hydrocarbon gas yield and hydrogen consumption paralleled each other, in that both increased with residence times, and also at temperatures above 800°F. Coal conversion levels, on the other hand, were not particularly affected by temperature or residence time in a regular manner. Preasphaltene yields decreased with an increase in temperature and residence time. Qualitatively, the data support a series reaction mechanism, but additional data are needed to confirm this.

Operating the dissolvers at staged temperatures may have some potential advantages. For Lafayette Kentucky #9 coal, operating the first dissolver at 810°F and the second at 840°F resulted in a higher yield of oils than several other temperature combinations that were tested. Other data on Mulford coal taken in series reactors under staged-temperature conditions, in which the first reactor was operated either at 780 or 810°F and the second at 840°F, agreed with the results observed under similar conditions on Lafayette coal. By operating the first reactor at a lower temperature, the oil yields were improved, compared to operating both reactors at the same temperature. The hydro-

carbon gas yields and hydrogen consumption were lower in the staged-temperature than in the isothermal mode.

An operation where fresh hydrogen flow would be split between the front end of the reaction train and the second dissolver was also simulated by examining 20-min reaction times at half the normal hydrogen feed rates. The oil yield after the first reactor dropped by 5%, and conversion also appeared to decrease by 2%. If this lower hydrogen feed rate and presumably lower hydrogen partial pressure allow the retrograde reactions to accelerate, significant problems may develop. This observation strongly supports the need for additional data to verify whether this effect will occur.

INTRODUCTION

Program 12.1.7 began in early 1981, following completion of another experimental program on the "Effects of Accumulated Solids and Solvent Initial Boiling Point (IBP) on Dissolver Performance" (Program Area 12.1.3). The program was designed to provide information required by the SRC-I Demonstration Plant team for the design of an optimized dissolver configuration. Specific objectives were as follows:

1. Determine how the addition of inert solids to the reaction slurry would affect conversion, yield structure, solvent rehydrogenation, and desulfurization.
2. Compare the effects of operating the dissolvers in series and in parallel.
3. Determine conversion, yield, and hydrogen consumption after the first dissolver in a simulated series operation.
4. Expand the data base to both 20- and 60-min residence times.
5. Show the effect of operating at low hydrogen feed rates.

In the early phase of the program, the statement of work consisted of two tasks. Task 1 was designed to address objective 1, in response to a request by ICRC, and Task 2 was designed to examine the effect of series vs. parallel operation of the dissolvers (addressing objective 2). Subsequently, a third task was added to develop data on the inter-stage conversion of staged dissolvers, to address objectives 3, 4, and 5. Only Tasks 2 and 3 are discussed here; Task 1 is detailed in a report by Skinner (1983). Tasks 2 and 3 have also been reported separately in greater detail (Sivasubramanian, 1982, 1983).

TASK 2: EFFECT OF SERIES VS. PARALLEL OPERATION

The objective of the second task was to develop process data needed to determine whether the two dissolvers specified for the demonstration plant should be operated in series or in parallel. Series operation, which is closer to plug-flow hydrodynamics than parallel operation, is expected to offer the following advantages:

- lower hydrocarbon gas yield
- improved solvent quality
- potentially lower sulfur in the products
- staged temperatures.

Parallel operation, on the other hand, is expected to offer the advantages of:

- more uniform temperature distribution across the reactor
- avoidance of quench between dissolvers
- reduced preheater outlet temperature.

Most of these factors indicate that series operation is advantageous, although parallel operation is the most conservative choice for temperature control. A major deciding factor, however, is the need to maintain an adequate level of catalytically active solids in the dissolver.

Run SCL-46 was conducted to study the differences in yield structure between series and parallel dissolver operations at three temperatures: 780, 810, and 840°F. In this run, the same temperature was maintained in the two reactors operated in series. Data on the parallel dissolver operation were obtained by operating a single component reactor at 30-min residence time at the same three temperature levels (see Table 1).

EXPERIMENTAL PLAN

At the start of the program, an attempt was made to predict the product yields resulting from two reactors operated in series using the

Table 1

Operating Conditions for Run SCL-46
 (Pressure, 2,000 psig; H₂ Flow, 28,000 scf/Ton of Coal;
 Feed Composition, 40% Lafayette Kentucky #9 Coal; 60% Recycle Solvent)

	Reactor I		Reactor II	
	Time (min)	Temp (°F)	Time (min)	Temp (°F)
I	12.1	780	13.7	780
II	12.8	810	14.5	810
III	12.8	840	14.1	840
IV	-	-	28.6	840
V	-	-	29.0	810
VI	-	-	28.1	780

following simplified version of the sequential kinetic model developed by Martin (1979):

Individual rate constants in the model were determined using experimental data from various runs on Kentucky #9 coal from the Pyro Mine. These rate constants were then used to predict product yields as a function of temperature for two reactors in series. A total space time of 40 min (20 min in each reactor) was used in the calculations.

The predictions indicated that the oil yields did not differ significantly, but asphaltene and preasphaltene yields were affected by the series reactor configuration. Details of the predictions can be found elsewhere (Sivasubramanian, 1982). However, the differences in yields of asphaltenes and preasphaltenes between the single reactor and two reactors in series were quite small and it was clear that multiple analyses might be necessary to distinguish the differences. Using the standard deviation calculated by Joshi (1981) for the analysis of asphaltenes and preasphaltenes, it was determined that four analyses would be necessary to distinguish any differences. Hence, in this program, it was decided to analyze each product liquid sample at least four times. In addition, the reproducibility of our coal process development unit (CPDU) was checked.

Although the original work statement for this program required a comparison only at design temperature (840°F), we felt that collecting data at several temperatures would be wise, since the expected dif-

ferences were small. Multiple data points can detect a definite trend far more easily than a single data point. Hence, three temperature levels (780, 810, and 840°F) were chosen for this task.

Because of limited work-up time, experiments were designed to be conducted at only one residence time (40 min). At the conclusion of the experimental run, however, we discovered that the volumes of the reactors were less than the 1-L volume anticipated. Therefore, the residence times were recalculated. Specific operating conditions for run SCL-46 are presented in Table 1. A description of the experimental facilities is included in Appendix 1.

Materials

Coal. Washed Lafayette Kentucky #9 coal was used in Task 2, since several other CPDU runs were planned simultaneously for this coal and also because the demonstration plant planned to use Kentucky #9 coal.

The coal sample, ground to 95% -200 mesh and air-dried, was screened through a 150-mesh sieve prior to use. Detailed analysis of the screened coal is reported in Table 2.

Solvent. The feed solvent was a recycle solvent produced at the Ft. Lewis pilot plant in Washington, while operating in the SRC-I mode (see Table 3 for the analysis). The solvent, when separated into individual fractions by solvent separation, contained 94.2 wt % oils, 4.8 wt % asphaltenes, and 8.3% hydrogen.

Operation

Extensive equipment modifications were completed in order to run two reactors in series: a second reactor and a preheater were installed and the unit was piped to allow bypass of either reactor. After modifications were completed, a shakedown run was conducted using creosote oil to check out the system.

The feed slurry (40 wt % Kentucky #9 coal and 60 wt % Ft. Lewis solvent) was prepared at room temperature, typically in 40- to 60-kg batches, immediately before use, and stored in a charge tank equipped with a turbine agitator and a recycle pump, to maintain uniform suspension of the solids.

Table 2

Analysis of Lafayette Kentucky #9 Coal

Proximate (%)	
Moisture	1.61
Volatile matter	34.48
Ash	9.40
Ultimate (moisture-free basis) (%)	
Carbon	72.93
Hydrogen	5.00
Oxygen	9.18
Nitrogen	1.54
Sulfur	2.94

Table 3

Analysis of Ft. Lewis Recycle Solvent

Solvent separation (wt %)	
Oils	94.2
Asphaltene	4.3
Preasphaltene	0.8
Residue	0.1
Elemental analysis (wt %)	
Carbon	87.9
Hydrogen	8.3
Nitrogen	1.0
Sulfur	0.4
Oxygen	3.1

The feed slurry was pumped to the continuous stirred-tank reactor (CSTR) from a feed tank maintained at ambient temperature. The feed tank, equipped with a recycle pump to mix the slurry, was refilled each hour from the charge tank. Whenever the feed slurry composition changed, the feed tank was drained and flushed several times with the new feed slurry. When reaction conditions were altered, at least 10 reactor volumes of slurry were processed through the reactor at the new conditions before collecting any product samples.

A continuous reactor was selected for these experiments so that its vapor composition, including the partial pressure of light solvent components, would match that of an SRC-I dissolver. The stirred autoclave design of the CSTR ensured that the solids were well-mixed and did not accumulate in the reactor. Cold-flow experiments, conducted in a Plexiglas model, have confirmed that the flat-bladed turbine agitator of the CSTR keeps the solids well distributed throughout the reactor volume, so that they do not accumulate (Ying, 1982).

Because of their tendency to promote coking, baffles were not used in the CSTR. However, a thermowell in the reactor reduced the size of the vortex so that the void fraction was about 0.18. Because all the sensible heat needed to bring the slurry to reaction temperature was provided by resistance heating of the reactor, the reactor wall was about 25°F hotter than the bulk slurry.

The product gas and slurry leaving the CSTR were quenched to 325°F before flowing to a gas/liquid separator kept at reactor pressure. The separator effluent slurry was throttled into the 40-psig product receiver at a rate that maintained a constant, small inventory in the separator.

Water, light hydrocarbons, and gases, which flashed from the product slurry in the 40-psig receiver, were combined with the product gas stream from the separator. The combined gas stream was cooled to about 60°F to condense the water and light organics prior to entering the gas chromatograph and dry test meter for measurement of product gas composition and volume.

Feed and Product Analysis

Two sets of product samples were withdrawn at each operating condition to ensure that the actual operating conditions during sampling were

sufficiently constant not to affect the product composition. Once the operation reached a steady state, only one set of product samples was analyzed further.

The feed and product slurries were solvent-separated into four fractions: pentane-soluble material (oils), pentane-insoluble and benzene-soluble material (asphaltenes), benzene-insoluble and pyridine-soluble material (preasphaltenes), and pyridine-insoluble material. The latter contains insoluble organic matter (IOM) and mineral residue. Note that the fractions from solvent separation were defined operationally, not chemically. The end points of each fraction often varied, depending on the nature of individual samples, as well as minute changes in detail in the procedures. Product slurries were analyzed twice. Each fraction was further subjected to detailed elemental analysis. Product gases were analyzed by on-line gas chromatography for hydrocarbon gases through C_4 , plus other nonhydrocarbon gases (H_2S , NH_3 , CO , CO_2 , etc.). Product water was determined indirectly by assuming that the water vapor exiting the process unit was in equilibrium with the condensed water.

Products sampled from the process unit included gases, light condensate, and main receiver product slurry. The light condensate was a mixture of water and oil, the water making up about 80% of the mixture. The quantity of oil was extremely small based on total main receiver product. Two of the organic condensate samples were subjected to elemental analysis, and the average of the two was used as the elemental analysis of the light oil condensate for this run.

Error Analysis

Multiple analyses of the product slurries clearly indicated good data reproducibility, reflecting a marked improvement in our solvent-separation technique. Because the differences in yield structure were small, determining the statistically permissible maximum differences between different analyses was extremely important. Consequently, an error analysis was conducted, using the multiple analysis data generated during this program.

As part of this program, five different samples were analyzed two or more times. By applying the pooled-variance statistical technique,

one can use the data generated to determine standard deviations for individual fractions measured by solvent separation (oil, asphaltene, preasphaltene, and residue). Tables 4-7 summarize the data gathered during this program for each fraction. The F-test for checking the homogeneity of the sum of square errors (SSE) was applied at a 95% confidence level to each of the data sets; nonhomogeneous samples are identified by an asterisk in the tables. Hence, the data are statistically homogeneous after the asterisked samples are omitted. Among all the data sets, only one set from Table 4 was omitted. The estimate of the variance is shown at the bottom of each table.

Using the values of these variances, ICRC calculated the statistically permissible maximum differences between two analyses of total product liquid. Table 8 lists these values for both duplicate and quadruplicate analyses performed on each product liquid. Note that the data in Table 8 are based on total product liquid analysis; these values will be magnified if based on moisture- and ash-free (MAF) yield. For experiments using 40 wt % Kentucky #9 coal, the statistically permissible maximum differences calculated on an MAF yield basis are presented in Table 9. These results will be used in the discussion below.

Analytical and Unit Reproducibility

Tables 10 and 11 list data that establish the reproducibility of the analytical experiments. Data in Table 10 represent duplicate analyses of the same sample performed by the same operator, whereas Table 11 data are from duplicate analyses of a sample performed by two different operators. Results indicate that both sets of data fall within the range of statistically permissible maximum differences established in Table 8. After the analytical precision of the data was established, we next checked the reproducibility of the CPDU. Yield distributions were calculated from two different samples taken 10 hr apart from the CPDU at the same operating conditions. The data (Table 12) clearly indicate that the unit is reproducible within the analytical precision established earlier.

Table 4

Statistical Analysis of Oil Fraction (Multiple Analyses)

Sample no.	wt %	df ^a	SSE ^b
46-119	64.8, 65.8, 65.2, 65.4	3	0.52
83	66.1, 65.3	1	0.34
93	66.3, 64.9	1	0.98
136	63.7, 62.0	1	1.45
32	67.4, 63.1	1	9.42*

$$s^2 = \text{SSE}/\text{df} = 3.29/6 = 0.548$$

$$S = 0.74$$

^adf, degrees of freedom.

^bSSE, sum of squared errors.

Table 5

Statistical Analysis of Asphaltenes Fraction (Multiple Analyses)

Sample no.	wt %	df	SSE
46-119	11.2, 11.3, 12.5, 12.8	3	2.01
83	11.0, 11.4	1	0.08
93	11.5, 12.3	1	0.32
136	11.5, 13.6	1	2.21
32	12.2, 14.0	1	1.62

$$s^2 = 6.24/7 = 0.891$$

$$S = 0.944$$

Table 6
Statistical Analysis of Preasphaltenes Fraction (Multiple Analyses)

Sample no.	wt %	df	SSE
46-119	13.2, 12.7, 13.4, 12.4	3	0.633
83	11.8, 11.9	1	0.005
93	11.8, 12.3	1	0.125
136	15.5, 15.7	1	0.020
32	13.6, 14.6	1	0.500
$S^2 = 1.283/7 = 0.183$ $S = 0.43$			

Table 7
Statistical Analysis of Residue (Multiple Analyses)

Sample no.	wt %	df	SSE
46-119	10.9, 10.3, 9.1, 9.5	3	1.95
83	11.0, 11.4	1	0.08
93	10.4, 10.0	1	0.08
136	9.3, 8.7	1	0.18
32	6.8, 8.3	1	1.13
$S^2 = 3.415/7 = 0.488$ $S = 0.698$			

Table 8
 Statistically Permissible Maximum Differences between
 Two Analyses of Total Product Liquid
 (95% Confidence Level; Based on Total Product Yield)

Fraction	Differences (wt %)		df
	2 analyses	4 analyses	
Oils	1.83	1.30	6
Asphaltenes	2.23	1.59	7
Preasphaltenes	1.02	0.72	7
Residue	1.65	1.17	7

Table 9
Statistically Permissible Maximum Differences
(95% Confidence Level; Based on MAF Yields)

Fraction	Difference (wt %)	
	2 analyses	4 analyses
Oils	5.14	3.65
Asphaltenes	6.27	4.47
Preasphaltenes	2.87	2.02
Residue	4.64	3.29

Table 10

Analytical Reproducibility: Duplicate Analysis of
 Sample SCL-46-83 by One Operator
 (Operating Conditions: 840/840°F, 2,000 psig, 29 min Total)

	Yield (wt %)	
Oils	66.12	65.3
Asphaltenes	11.0	11.4
Preasphaltenes	11.8	11.9
Residue	11.0	11.4
Operator	FG	FG

Table 11

Analytical Reproducibility: Duplicate Analysis of
 Sample SCL-46-93 by Two Different Operators
 (Operating Conditions: 840/840°F, 2,000 psig, 29 min Total)

	Yield (wt %)	
Oils	66.3	64.9
Asphaltenes	11.5	12.8
Preasphaltenes	11.8	12.3
Residue	10.4	10.0
Operator	CK	FG

Table 12
 CPDU Reproducibility: Yield Distributions
 (Operating Conditions: 840/840°F, 2,000 psig, 29 min)

	Yield (wt %)	
	SCL-46-83	SCL-46-93
Hydrocarbons	8.6	7.0
Other gases	2.6	2.5
H ₂ O	1.7	3.7
Oil	17.3	16.0
Asphaltenes	21.5	24.0
Preasphaltenes	31.3	31.4
IOM	18.4	17.0

RESULTS AND DISCUSSION

The composition of the solvent used in the material-balance calculations dramatically affected the yield distribution, especially oil yields. Although analysis of the solvent indicates that it contains only 94% oils, the asphaltenes in the solvent may have converted more easily to oils upon contact with coal than the coal-derived asphaltenes. Hence, one may argue that the solvent should be treated as containing 100% oils. For relative comparisons, that is, for comparisons of the two reactor configurations, the solvent composition is academic. In other words, the absolute numbers in either case will vary, but the effect will remain the same. To illustrate this observation, yield distributions were calculated assuming the solvent to be both 94 and 100% oils (see Tables 13 and 14, respectively).

Because differences in yields were expected to be small, these experiments were conducted at three temperature levels. Results in Tables 13 and 14 indicate that conversion decreased with increasing temperature. However, the reactor configuration did not seem to affect conversion at any temperature level.

Preasphaltene yields decreased at all temperature levels when the two reactors were operated in series. The decrease is outside the statistically permissible maximum differences established earlier (Table 9). At the highest temperature studied (840°F), the difference between the single reactor and two reactors in series was only 2.7% on an MAF coal basis. However, this decrease is statistically significant.

The reactor configuration does not change the sulfur contents of SRC significantly at 840°F. At 780 and 810°F, the series configuration results in a slight decrease in the SRC sulfur content.

The reactor configuration does not significantly influence asphaltene yields. At 780°F, the yield seemed to increase for two reactors operated in series, but at 810 and 840°F, the yield did not change with reactor configuration. At 810°F the oil yield seemed to increase when the series configuration was used, and this change is statistically significant. However, the oil and asphaltene yields do

Table 13
Effect of Reactor Configuration on Yield Distribution
(Calculated for Solvent Containing 94% Oils)

	Run no.	SCL-46				
	Pressure	2,000 psig				
	H ₂ feed rate	28,000 scf/ton of coal				
	Feed solvent	94% oils				
		Parallel			Series	
Temp. (°F)	780	810	840	780/780	810/810	840/840
Residence time (min)	28.6	29	28.1	12.1/13.7	12.8/14.5	12.4/14.1
Yield (% MAF coal)						
Hydrocarbons	2.2	4.0	6.9	2.9	5.6	7.0
Other gases	2.8	2.1	2.2	1.6	2.2	2.5
Oils	13.5	13.7	17.5	11.9	17.6	17.2
Asphaltenes	22.2	25.7	23.7	30.6	26.6	24.0
Preasphaltenes	46.7	40.6	32.9	42.3	35.3	30.2
Residue	11.9	13.6	16.8	10.0	11.1	16.7
Water	1.9	1.7	2.0	1.6	2.5	3.7
H ₂ consumption (total)	0.82	1.1	1.48	0.89	1.39	1.55
(% MAF coal)						
From gas	0.67	0.64	0.84	0.55	0.92	0.92
From solvent	0.15	0.46	0.64	0.34	0.47	0.63
S in SRC (%)	1.28	1.00	0.88	1.0	0.90	0.90
Solvent hydrogen (wt %)	8.21	8.02	7.92	8.10	8.02	7.92

Table 14
Effect of Reactor Configuration on Yield Distribution
(Calculated for Solvent Containing 100% Oils)

	Run no.	SCL-46				
	Pressure	2,000 psig				
	H ₂ feed rate	28,000 scf/ton of coal				
	Feed solvent	100% oils				
		Parallel			Series	
Temp. (°F)	780	810	840	780/780	810/810	840/840
Residence time (min)	28.6	29	28.1	12.1/13.7	12.8/14.5	12.4/14.1
Yield (% MAF coal)						
Hydrocarbons	2.2	4.0	6.9	2.9	5.6	7.0
Other gases	2.8	2.1	2.2	1.6	2.2	2.5
Oils	4.1	4.3	8.1	2.5	8.2	7.8
Asphaltenes	30.2	33.7	31.7	38.6	34.6	32.0
Preasphaltenes	48.1	41.9	34.3	43.6	36.6	31.6
Residue	11.9	13.6	16.8	10.0	11.1	16.7
Water	1.9	1.7	2.0	1.61	2.5	3.7
H ₂ consumption (total)	0.62	0.89	1.25	0.68	1.17	1.32
(% MAF coal)						
From gas	0.67	0.64	0.84	0.55	0.92	0.92
From solvent	-0.05	0.25	0.41	0.13	0.25	0.40
S in SRC (%)	1.28	1.00	0.88	1.01	0.90	0.90
Solvent hydrogen (wt %)	8.33	8.15	8.05	8.22	8.15	8.06

not change at all temperature levels--only the preasphaltene yields show the same trend at all temperature levels.

These results indicate that operating the dissolvers in series will decrease the preasphaltene yield. From a process viewpoint, this reduction should increase the amount of recoverable product, since recovery from the critical solvent deashing unit in the plant will increase when preasphaltene content decreases. Neither conversion nor oil, asphaltene, or gas yields are affected by reactor configuration.

The results presented above were obtained using Lafayette coal, a mildly reactive coal. In Task 3, a single data point was obtained using a highly reactive coal (Mulford) at 840°F and 40 min using two different reactor configurations (series and parallel). Additional data were to be obtained with Mulford coal in a fourth task, but the program was terminated before that work began.

Table 15 shows that no noticeable differences exist between the yield structures obtained from two different reactor configurations when a highly reactive coal (Mulford) was used as a feedstock. However, these data neither prove nor disprove the earlier conclusion. If anything, they support the conclusion that the yields of fractions other than preasphaltenes were unaffected by reactor configuration. Even in the earlier run, the data at 840°F showed that the decrease in preasphaltenes was barely outside the statistically permissible maximum differences. The earlier study was conducted at a residence time of 30 min, whereas this study was conducted at a residence time of 40 min. These data clearly show the importance of conducting these studies at multiple temperatures and residence times using different coals, so that a definite trend can be established.

Table 15
Effect of Series Dissolvers

Pressure: 2,000 psig
 H_2 Feed Rate: 28,000 scf/ton of Coal
 Coal: Mulford Kentucky #9
 Solvent: Ft. Lewis Recycle Solvent
 Temperature: 840°F

	1 reactor	2 reactors
Residence time (min)	40.3	41.9
Conversion (wt %)	87.4	88.6
H_2 consumption (wt %)	2.04	2.05
Yields (wt % MAF coal)		
Hydrocarbons	11.2	11.5
Other gases	4.1	3.8
Oils	21.1	20.0
Asphaltenes	20.8	25.2
Preasphaltenes	26.6	25.0
Residue	15.0	13.4
Water	3.7	3.2
S in SRC (wt %)	0.72	0.61

TASK 3: INTERSTAGE CONVERSIONS FOR SERIES DISSOLVERS

Data developed under Task 2 of this program showed that using dissolvers in series will favor high preasphaltene conversion, which will impact processes downstream of the dissolver. This will help ensure that the critical solvent deashing process achieves maximum SRC recovery. To use critical solvent deashing most effectively in the SRC-I Demonstration Plant, the preasphaltene content of the SRC feed to the CSD unit must be carefully controlled.

However, the earlier data were developed for a mildly reactive coal. No attempts were made to generate data for a more reactive coal, or to measure hydrogen consumption and yield structure after the first dissolver. In addition, sufficient data from operation for long residence times were unavailable. Hence, Task 3 (Interstage Conversions for Series Dissolvers) was conducted to provide some of the missing data. Specific objectives were to:

- ° Determine the conversion, yield, and hydrogen consumption after the first dissolver in a simulated series operation.
- ° Develop process data for operating two dissolvers in series at staged temperatures in a coal liquefaction plant.
- ° Generate data for both 20- and 60-min residence times.
- ° Show the effect of operating at low hydrogen feed rates.
- ° Use a more reactive coal.
- ° Distinguish between series and parallel models.

EXPERIMENTAL PLAN

In this task, data were developed to show the level of conversion and product distributions between the two series dissolvers with Mulford Kentucky #9 coal. Coal slurries of 40% Mulford coal in Ft. Lewis process solvent were processed through a single series dissolver at 780, 810, and 840°F, residence times of 20 and 40 min, hydrogen feed rates of 15,000 and 30,000 scf/ton of coal, and 2,000-psig total pressure.

Further runs were conducted at the same pressure and slurry concentration and at 30,000 scf of hydrogen/ton of coal in two series dissolvers, at the following conditions:

Time in each dissolver (min)	Temp (°F) in dissolver	
	1st	2nd
20	780	840
20	810	840
20	840	840
30	780	780
30	810	810
30	840	840

At each condition, conversion, hydrogen consumption, process yields, and sulfur in SRC were determined. The basic operation and the feed and slurry products analyses were essentially the same as described under Task 2.

The effect that two series reactors have on the yield distribution was taken into consideration in comparing the 60-min data to the 20- and 40-min data. Our results from Task 2 had already quantified the impact of operating this type of configuration; the only effect from operating two reactors in series was a decrease in preasphaltene concentration.

Washed Kentucky #9 Mulford coal was obtained directly from a coal preparation plant associated with the mine. The coal sample was ground to 95% minus 200-mesh particles, air-dried, and screened through a 150-mesh sieve prior to use. Proximate and ultimate analyses are provided in Table 16.

The feed solvent was a Ft. Lewis recycle solvent produced under SRC-I conditions. Table 17 lists analytical data for the specific batch used in this run. When fractionated into separate cuts by solvent separation, the solvent contained 96.2% oils, 3.8% asphaltenes, and 8.2% hydrogen.

Table 16

Proximate and Ultimate Analysis of
Kentucky #9 Mulford Coal

Proximate analysis (wt %)		
Moisture		2.15
Volatile matter		36.91
Fixed carbon		61.38
Ash		9.40
Ultimate analysis (wt %)		
	Moisture-free basis	Moisture- and ash-free basis
Carbon	72.32	81.26
Hydrogen	5.19	5.83
Oxygen	8.01	9.00
Nitrogen	1.77	1.99
Sulfur	2.85	1.92
Organic	1.71	1.92
Pyritic	1.14	
Ash	9.68	

Table 17
Process Solvent Data

Solvent fractionation (wt %)	
Oils	96.18
Asphaltenes	3.82
Preasphaltenes	Nil
Elemental analysis (wt %)	
Carbon	87.83
Hydrogen	8.21
Nitrogen	0.85
Sulfur	0.35
Oxygen	2.92

RESULTS AND DISCUSSION

Effect of Time and Temperature

The earlier work during Task 2 had shown that multiple analyses of product samples are needed to clearly distinguish the differences in yield structures at different operating conditions (Sivasubramanian, 1982). Therefore, to produce statistically significant data, the experimental design for this task called for at least duplicate analyses of each product sample. However, the reduced scope of the original program cut down the time available for duplicate analyses such that only five samples were duplicated. Those samples had been completed at the time of the reduction in scope. From that point on, samples were analyzed only once.

The duplicate or multiple analyses from Task 2 were used to calculate variances for each individual fraction measured by solvent separation (oil, asphaltene, preasphaltene, and residue) by using a statistical technique known as pooled variance. These variances can be used to determine the statistically permissible maximum differences between two analyses of total product liquid. By determining moisture and ash content of the feed coal, one can calculate the statistically permissible maximum differences in yield structure based on moisture-and-ash-free (MAF) coal yields. The maximum differences calculated during Task 2 for Lafayette coal are presented in Table 9.

Since duplicate analyses were available for five samples generated from Mulford coal, new values for the variances (s^2) for individual fractions in the product analysis were calculated. Results indicated that the variances for the individual fractions were essentially similar to the earlier analysis on Lafayette coal. Hence, the values of the variances from Task 2 were also used here; however, since Mulford coal has a different moisture and ash content compared to Lafayette coal, new values were calculated for statistically permissible maximum differences in yield structure based on MAF coal (see Table 18). The following discussion on yield structures is based on these adjusted values.

The data for 20-, 40-, and 60-min reaction periods are listed in Tables 19, 20, and 21, respectively. Generally, conversion of coal to pyridine-soluble product is insensitive to residence time or temper-

Table 18
Statistically Permissible Maximum Differences
(95% Confidence Level, Based on MAF Yields)

Fraction	Difference (wt %)	
	1 analysis	2 analyses
Oils	7.32	5.19
Asphaltenes	9.34	6.61
Preasphaltenes	4.25	3.01
Residue	6.91	4.89

Table 19
Yield Data

Pressure: 2,000 psig
H₂ Feed Rate: 28,000 scf/ton of Coal
Coal: Mulford Kentucky #9
Solvent: Ft. Lewis Recycle Solvent

	Temp (°F) and residence time (min)		
	780	810	840
	20.5	20.8	20.5
Conversion (wt %)	85.6	86.96	87.38
H ₂ consumption, total (wt %)	0.78	1.07	1.20
From gas	0.60	0.89	0.89
From solvent	0.18	0.18	0.32
Yields (wt % MAF coal)			
Hydrocarbons	2.18	4.57	6.68
Other gases	1.88	3.18	3.14
Lights	1.19	0.69	1.22
Oils	15.80	14.31	12.81
Asphaltenes	29.44	30.04	31.51
Preasphaltenes	34.81	31.03	29.74
Residue	15.47	14.23	14.09
Water	0.32	3.14	2.27
S in SRC (wt %)	1.04	0.93	0.77
Solvent hydrogen (wt %)			
Start	8.21	8.21	8.21
Finish	8.11	8.10	8.03

Table 20
Yield Data

Pressure: 2,000 psig
 H_2 Feed Rate: 28,000 scf/ton of Coal
 Coal: Mulford Kentucky #9
 Solvent: Ft. Lewis Recycle Solvent

	Temp (°F) and residence time (min)		
	780	810	840
	40.5	40.05	40.3
Conversion (wt %)	86.03	88.53	87.4
H_2 consumption, total (wt %)	0.73	1.59	2.04
From gas	0.88	1.37	1.39
From solvent	-0.15	0.23	0.65
Yields (wt % MAF coal)			
Hydrocarbons	3.82	7.27	11.17
Other gases	4.19	3.56	4.08
Lights	0.94	1.54	2.19
Oils	13.86	17.56	18.86
Asphaltenes	29.56	29.91	20.80
Preasphaltenes	31.56	24.63	26.62
Residue	15.00	13.04	15.06
Water	2.03	4.07	3.65
S in SRC (wt %)	1.09	0.81	0.72
Solvent hydrogen (wt %)			
Start	8.21	8.21	8.21
Finish	8.30	8.08	7.84

Table 21
Yield Data

Pressure: 2,000 psig
H₂ Feed Rate: 28,000 scf/ton of Coal
Coal: Mulford Kentucky #9
Solvent: Ft. Lewis Recycle Solvent

	Temp (°F) and residence time (min)		
	780/780	810/810	840/840
	61.56	61.25	62.40
Conversion (wt %)	90.63	91.00	87.11
H ₂ consumption, total (wt %)	1.15	1.88	2.73
From gas	1.13	1.66	2.19
From solvent	0.02	0.22	0.54
Yields (wt % MAF coal)			
Hydrocarbons	3.66	8.97	15.30
Other gases	3.34	3.99	4.38
Lights	1.23	1.07	3.28
Oils	23.59	25.44	18.82
Asphaltenes	30.11	25.99	23.56
Preasphaltenes	25.87	24.32	18.45
Residue	11.09	11.09	15.64
Water	2.85	1.22	3.32
S in SRC (wt %)	0.91	0.65	0.51
Solvent hydrogen (wt %)			
Start	8.21	8.21	8.21
Finish	8.20	8.08	7.90

ature, except at a residence time of 60 min. The data for 60-min residence indicate a slight increase in conversion at the lower temperatures (780 and 810°F), which could be due to the use of two reactors in series. This phenomenon was not, however, observed previously when series data were developed at a residence time of about 30 min.

Figures 1 and 2 show the effect of reaction time and temperature on oil yields. Figure 1 reveals that the data point at 780°F and 40 min is inconsistent with the rest of the data. If that data point is ignored, Figure 1 clearly shows that oil yield increases with an increase in residence time, and Figure 2 shows oil yield is insensitive to temperature changes from 780 to 840°F at all three residence times studied.

The data on hydrocarbon gas yield and hydrogen consumption are internally consistent. Figure 3 shows that both higher temperatures (810 and 840°F) and longer residence times favor higher hydrocarbon gas yields. The data at 780°F are so closely bunched that a clear temperature pattern is difficult to discern.

Hydrogen consumption behaves similarly. Both higher temperature and longer reaction times favor increased hydrogen consumption (Figure 4). The 20-min data may be a little less sensitive to temperature than the longer residence times, possibly because solvent supplies almost all of the hydrogen demand during the early reaction periods.

Figures 5 and 6 show the effect of time and temperature on the yield of asphaltenes and preasphaltenes, respectively. Figure 6 shows that the yield of preasphaltenes decreases with an increase in reaction time. Also, the yield seems to decrease with an increase in temperature. Quantitatively, the variations in asphaltene yield with time and temperature are within the statistically permissible maximum differences. Qualitatively, the following trends were observed. At 780°F, increasing residence time seems to have no effect on asphaltene yield, but at 810 and 840°F the yield appears to decrease. Figure 5 clearly shows that the yield of asphaltenes does not increase with an increase in residence time.

In addition to a study of the effect of time and temperature on process yields, another major objective of this task was to generate additional data needed to decide whether a series or parallel model represents the data better. Because the uncertainties associated with

Figure 1
Effect of Residence Time on Oil Yield

Figure 2
Effect of Temperature on Oil Yield

Figure 3
Effect of Temperature on HC Gas Yield

Figure 4
Effect of Temperature on Hydrogen Consumption

Figure 5
Effect of Time and Temperature on Asphaltene Yield

Figure 6
Effect of Time and Temperature on Preasphaltene Yield

the data are large due to the lack of multiple analyses, only a qualitative discussion can be presented here. Attempts were made to generate reaction rate constants and activation energies, but these were also dropped due to the absence of acceptable uncertainty analysis.

Figure 7 illustrates reaction pathway models for series and parallel operation. The different implications of the models can best be appreciated by considering the yield structures they predict. Figures 8 and 9 present the yield structure predictions as a function of residence time for the two models. The predictions are based upon kinetic constants regressed from other data sets and are not intended to be quantitatively applicable to the current runs or Mulford coal. However, these predictions are useful for qualitatively describing the different trends that the two models imply.

Both models predict the same behavior for unreacted coal (IOM) and preasphaltene yields. The unreacted coal decreases rapidly with residence time at shorter residence times and then approaches an asymptote, while preasphaltene decreases with time and approaches its asymptote only at long residence times. The series model predicts that both asphaltene and distillate (oil) yields will go through a maximum and then decrease. Distillate reaches its maximum as it cracks to form hydrocarbon gas, and the rate of distillate production decreases due to the reduced concentration of asphaltenes at extended residence times. Note, however, that the region of maximum distillate yield can be quite broad, as it is in this case. The series model also predicts that hydrocarbon gas will increase linearly with residence. In contrast, the parallel model predicts that asphaltene, distillate, and hydrocarbon gas yields will asymptotically approach a maximum at long residence times.

Thus, the main qualitative differences between the models are that (1) the series model predicts a linearly increasing hydrocarbon gas yield, while the parallel model predicts a relatively constant and much lower level of gas production, and (2) the series model indicates asphaltene yield reaches a maximum and then decreases, whereas the parallel model implies that asphaltene yield increases with residence time.

Figure 3 clearly shows that hydrocarbon gas yield increased almost linearly with time. While Figure 5 does not show that asphaltene passed

Figure 7
Comparison of Series and Parallel Models

Series Model

Parallel Model

Figure 8
CPDU--Series Model Predictions for 840°F

Figure 9

CPDU--Parallel Model Predictions for 840°F

through a maximum, nor even that asphaltene decreased, which would be predicted if the maximum asphaltene yield occurred before the 20-min residence time, the data clearly do not support a model that predicts increasing levels of asphaltene. Hence, the data seem to support the series model more than the parallel model. Additional data with multiple analyses are needed to confirm this trend.

Effect of Staged Temperatures

One advantage of operating with both dissolvers in series is that the temperatures in each of the two dissolvers can be varied. In a previous run (SCL-51) under Task 2 of this program, the temperatures of the two reactors in series were varied to study the effect of staged temperatures on yield distribution. The operating conditions for Run SCL-51 are shown in Table 22; the materials were the same as those used in Run SCL-46.

Once again, the yield distributions were calculated in two different ways--by assuming the feed solvent to be either 94 or 100% oils. Tables 23 and 24 show that the oil yield was at a maximum when the first reactor was operated at 810°F and the second reactor at 840°F, compared to several other temperature combinations. Yields of other fractions are not unusual; they followed the expected pattern. For example, with the increase in temperature of the first dissolver, hydrocarbon gas yields increased and preasphaltene yields decreased. Earlier results showed (Table 13) that, for Lafayette coal, increasing temperature resulted in a decrease in conversion. The same trend is observed here.

The results also indicate that operating the second dissolver at 810°F and the first at 840°F may result in lower gas and higher oil yields. However, from a process viewpoint, operating the second dissolver at a lower temperature than the first one will be impractical and will require a large amount of quenching between the two dissolvers.

We have reexamined the effect of staged temperatures in a run with Mulford coal at a 40-min total residence time, which was equally divided between the two reactors. In this run, we also lowered the first reactor temperature to 700°F to study whether any advantages exist in operating the first dissolver at a very low temperature. The results are presented in Table 25.

Table 22

Operating Conditions for
Run No. SCL-51
(Effect of Staged Temperatures on Yield Distribution)

Pressure: 2,000 psig
H₂ Flow: 28,000 scf/ton of Coal
Feed Composition: 40% Lafayette Kentucky #9 Coal,
60% Recycle Solvent

	Reactor I		Reactor II	
	Time (min)	Temp (°F)	Time (min)	Temp (°F)
I	13.3	780	15.1	840
II	12.1	810	13.7	840
III	12.5	840	14.2	810

Table 23

Effect of Staged Temperatures

Run: SCL-51

Coal: Lafayette Kentucky #9

Pressure: 2,000 psig

Feed Solvent: 94% Oils

	wt % yields at temp (°F) and time (min)			
	780/840	810/840	840/840	840/810
	13.3/15.1	12.1/13.7	12.4/14.1	12.5/14.2
Hydrocarbons	5.0	5.6	7.0	5.4
Other gases	1.7	2.2	2.5	2.0
Oils	12.1	22.7	17.2	19.6
Asphaltenes	23.3	23.0	24.0	22.3
Preasphaltenes	38.9	31.6	30.2	33.5
IOM	13.5	12.4	16.7	14.8
H ₂ consumption	1.42	1.74	1.55	1.37

Table 24

Effect of Staged Temperatures

Run: SCL-51
 Coal: Lafayette
 Pressure: 2,000 psig
 Feed Solvent: 100% Oils

	wt % yields at temp (°F) and time (min)			
	780/840	810/840	840/840	840/810
	13.1/15.1	12.1/13.7	12.4/14.1	12.5/14.2
Yields, MAF coal				
Hydrocarbons	5.0	5.6	7.0	5.4
Other gases	1.7	2.2	2.5	2.0
Oils	2.8	13.3	7.8	10.2
Asphaltenes	31.3	31.0	32.0	30.3
Preasphaltenes	40.3	32.9	31.6	34.9
IOM	13.5	12.4	16.7	14.8
H ₂ consumption	1.21	1.52	1.32	1.37

Table 25

Effect of Staged Temperatures

Pressure: 2,000 psig
 H_2 Feed Rate: 28,000 scf/Ton of Coal
 Coal: Mulford Kentucky #9
 Solvent: Ft. Lewis Recycle Solvent

	wt % yields at temp (°F) and time (min)			
	700/840	780/840	810/840	840/840
	41.12	41.07	41.37	41.09
Conversion (wt %)	89.18	89.6	89.4	88.6
H_2 consumption, total (wt %)	1.40	1.33	1.88	2.05
From gas	0.98	0.65	1.20	1.54
From solvent	0.42	0.68	0.67	0.52
Yields (wt % MAF coal)				
Hydrocarbons	7.25	7.82	9.55	11.48
Other gases	3.7	3.45	4.00	3.79
Lights	1.09	1.25	1.52	2.09
Oils	14.08	20.81	20.52	17.92
Asphaltenes	32.17	26.68	26.99	25.16
Preasphaltenes	27.39	28.71	23.24	24.98
Residue	12.49	12.10	12.76	13.44
Water	3.49	0.87	3.58	3.21
S in SRC (wt %)	0.84	0.73	0.67	0.61
Solvent hydrogen (wt %)				
Start	8.21	8.21	8.21	8.21
Finish	7.97	7.82	7.82	7.91

Clearly, lowering the temperature in the first reactor increases the oil yield. The 840/840°F oil yield is lower than the 780/840°F and 810/840°F data, although the difference is smaller than noted previously (see Table 24). This difference could be due to the more reactive coal or the differences in residence time (40 vs. 30 min). It could also be due to errors in the water yield. Table 25 indicates that the water yield at 780/840°F is 0.87 wt %, which is quite low. The yield of water at the other operating conditions (Table 25) is more than 3 wt %. Normally, water yield is higher than 0.87 wt % and an increase in water yield would result in a decrease in the yield of oils.

However, the data do show a definite advantage in staging the temperatures in the series dissolvers. The data also indicate that the optimum temperature for the first dissolver should be above 700°F. As can be seen from Table 24, operating the first dissolver at 700°F lowered the oil yield, even though hydrogen consumption and conversion were identical to the data at 780°F. Apparently, the conversion of asphaltene to oils is low at this temperature.

The hydrocarbon gas yields measured after 20- and 40-min residence times (Tables 19 and 25, respectively) are consistently additive. For example, 20 min at 780°F gives 2.18% hydrocarbon gases, while 20 min at 840°F gives 6.68%. The staged run of 780/840°F for a total of 40 min gave 7.82%, vs. an additive number of 8.86%. Similar comparisons can be made for the other combination. After 20 min at 810°F, 4.57% hydrocarbon gases were formed, vs. 6.68% at 840°F. The 810/840°F run gave 9.55% vs. the additive number of 11.25%.

The increased oil yields and reduced hydrocarbon gas yields noted with staged temperatures both here and in Run SCL-51 provide confidence that a definite advantage exists for operating with staged-temperature reactors that is not simply related to reactor mixing.

Segregation of Hydrogen Flow between Dissolvers

Data were also generated during Task 3 to show the effect of partitioning the hydrogen feed between the first and second dissolvers. The data at 840/840°F shown in Table 25 simulate the total result of feeding all of the hydrogen through both reactors. We also examined the effluent from the first reactor after only half of the hydrogen had been

fed (Table 26), which is consistent with the Baseline design for demonstration plant dissolver operation.

At a decreased hydrogen flow to the first reactor, namely, 14,700 scf/ton of coal, the total oil yield (lights and oils) dropped from 14.0 to 9.0%. Even though this may not be statistically significant based on a single analysis, the liquid oil yield alone dropped from 12.8 to 4.9 wt %, which is significant. Also, note that the statistical analysis on oil yields applied mainly to the liquid oil obtained from product analysis. The yields of lights reported here are generated from the light materials trapped in the condenser. The corresponding hydrocarbon gas yield did not change significantly (from 6.7 to 7.4%). The decrease in gas flow rate changed the hydrogen partial pressure from 1,770 to 1,430 psig. The flow rate change will also change the residence time, due to vaporization of light materials. Both of these changes may have affected the yield of oils. Generally, these data show that staging hydrogen addition is detrimental. How significant this would be after going through the second reactor at full hydrogen pressure is unknown at this time.

Table 26
Effect of Staged Hydrogen Addition

Pressure: 2,000 psig

Coal: Mulford Kentucky #9

Solvent: Ft. Lewis Recycle Solvent

	Gas rate (M scf/ton), temp (°F), and residence time (min)	
	29.4, 840, 20.5	14.7, 840, 20.62
Conversion (wt %)	87.38	85.46
H ₂ consumption, total (wt %)	1.20	1.19
From gas	0.89	1.00
From solvent	0.32	0.19
Yields (wt % MAF coal)		
Hydrocarbons	6.68	7.41
Other gases	3.14	3.54
Lights	1.22	4.15
Oils	12.81	4.89
Asphaltenes	31.51	27.52
Preasphaltenes	29.74	34.74
Residue	14.09	15.83
Water	2.27	3.21
S in SRC (wt %)	0.77	0.96
Solvent hydrogen (wt %)		
Start	8.21	8.21
Finish	8.03	8.10

CONCLUSIONS

Operating the dissolvers in series decreased the yield of pre-asphaltenes. From a process viewpoint, this reduction should increase the amount of recoverable product because recovery from the critical solvent deashing unit in the plant will increase when preasphaltene content decreases. Neither conversion nor oil, asphaltene, or gas yields are affected by reactor configuration.

Process data obtained at residence times from 20 to 60 min and temperatures from 780 to 840°F show that oil yields are directly affected by reaction time, but relatively insensitive to temperature. Hydrocarbon gas yield and hydrogen consumption parallel each other, in that both increase with temperature, especially above 800°F, and both also increase with residence times, also at temperatures above 800°F. Coal conversion levels, on the other hand, are not particularly affected by temperature or residence time in a regular manner. Preasphaltene yields decreased with an increase in temperature and residence time. Qualitatively, the data tend to support a series reaction mechanism. Additional data are needed to confirm this. Some additional data are being generated in other ICRC programs (Givens et al., 1983; Kang and Givens, 1983).

The results suggest that staged-temperature operation of the dissolvers may have some potential advantages. For Lafayette Kentucky #9 coal, operating the first dissolver at 810°F and the second at 840°F resulted in a higher yield of oils than several other temperature combinations that were tested. Essentially the same results were obtained when Mulford coal was used as a feedstock. The optimum temperature of the first dissolver may depend on the type of coal used.

An operation where fresh hydrogen flow would be split between the front end of the reaction train and the second dissolver was simulated by examining 20-min reaction times at half the normal hydrogen feed rates. The oil yield after the first reactor dropped by 5%, and conversion also appeared to decrease by 2%. If this lower hydrogen feed rate and presumably lower hydrogen partial pressure allow the retrograde

reaction to accelerate, significant problems may occur. This observation strongly supports the need for additional data to verify whether this effect will occur.

LITERATURE CITED

- Givens, E. N., C. F. Harris, S. V. Joshi, D. Kang, R. Sivasubramanian, R. W. Skinner, and D. H. S. Ying. 1983. Internal R&D Summary Report: Reactor Yields. DOE/OR/03054-47. International Coal Refining Co., Allentown, Pa.
- Kang, D., and E. N. Givens. 1983. Internal R&D Final Report: Effect of Asphaltene- and Preasphaltene-Rich Solvents upon Coal Liquefaction. DOE/OR/03054-64. International Coal Refining Co., Allentown, Pa.
- Joshi, S. V. 1981. Coal process development unit (CPDU) data analysis. Pages 405-467 in SRC-I quarterly technical report, April-June 1981. DOE/OR/03054-4 Vol. 2. International Coal Refining Co., Allentown, Pa.
- Martin, C. J. July 1979. Kinetic model for coal slurry reactors. Phase Zero SRC Report.
- Sivasubramanian, R. 1982. Effects of accumulated solids and staged vessels on dissolver performance. Pages 157-199 in SRC-I quarterly technical report, October-December 1982. DOE/OR/03054-11. International Coal Refining Company, Allentown, Pa.
- _____, and E. N. Givens. 1983. Effects of staged vessels on dissolver performance. Pages 1-32 in SRC-I quarterly technical report, supplement. April-June 1983. International Coal Refining Co., Allentown, Pa.
- Skinner, R. W. 1983. Final technical report: Effects of accumulated solids and solvent initial boiling point on dissolver performance. DOE/OR/03054-29. International Coal Refining Co., Allentown, Pa.
- Ying, D. H. S. 1982. Stirred reactor hydrodynamics. Pages 273-292 in SRC-I quarterly technical report, April-June 1982. DOE/OR/03054-8. International Coal Refining Co., Allentown, Pa.

Appendix 1

Liquefaction Test Facilities

The liquefaction testing was carried out in Air Products and Chemical's coal process development unit (CPDU) #1 (Figure A-1). This is a continuous process unit capable of simulating a wide range of thermal coal liquefaction process conditions, including:

Temperature	900°F (max)
Pressure	2,600 psi (max)
Residence time	10-180 min
Coal throughput	0.7 to 9.0 lb/hr
Reactor volume	0.5 to 7.5 L

In the process runs for these experiments, coal and process solvent were prepared at a solvent-to-coal ratio of 1.5 to 1. The slurry was fed to a 1-L continuous stirred-tank reactor at a nominal 1,630-g/hr feed rate. Pure hydrogen gas was fed to the reactor at a nominal 570-slph rate. These conditions resulted in a nominal 30-min reaction time at 840°F, with a hydrogen treatment rate of 28,000 scf/ton of feed coal. These are essentially SRC-I first-stage conditions with a somewhat shorter residence time. All experiments were started with a single batch of solvent blended in the solvent storage tank. The experiments were carried out on a once-through solvent basis with product solvent recovered in the batch still and stored for later runs.

DESCRIPTION OF THE EQUIPMENT

Slurry Feed

Three 65-gal charges tanks are used to contain the start-up solvent and slurry feedstocks for the coal liquefaction experiments. The tanks, constructed of stainless steel, can be operated at temperatures up to 300°F and pressures up to 100 psig. Provision is made to blanket the tanks with nitrogen. Each charge tank is equipped with a stirrer, and

Figure A-1

APCI COAL PROCESS DEVELOPMENT UNIT
(COAL LIQUEFACTION SYSTEM #1)

Tuthill pumps are employed to recycle the slurry feedstock in a closed loop to aid in maintaining a uniform dispersion of coal in the solvent. A spare Moyno pump is piped into the recycle loop.

The liquefaction reactor is fed from a 10-L slurry feed tank, constructed from 4-in. stainless steel pipe. This tank can be operated at ambient or elevated temperatures. A blanket of nitrogen is maintained over the slurry in the tank. Although the tank is not stirred, a 1.5-gpm Moyno pump circulates slurry around the tank to maintain a uniform solid suspension. A differential pressure transmitter mounted on the feed tanks measures the mass of slurry in the tank. The slurry feed tank is typically refilled every hour from one of the charge tanks by opening a pneumatically operated ball valve in the short length of tubing linking the feed tank to the charge tank recycle loop.

A separate 10-L solvent feed tank is also provided. This tank is equipped with a differential pressure transmitter and may be operated at temperatures up to 300°F.

The CPDU train has two high-pressure, positive-displacement slurry feed pumps. The Bran and Lubbe pump is typically used to pump coal slurries; the Milton Roy pump is used as a spare. These are both piston pumps with double ball-and-seat check valves at the inlet and discharge of the pump chamber. A tungsten carbide plunger and balls are used when pumping coal slurries. A variety of plunger sizes are available, permitting pump rates of about 250-10,000 cm³/hr. However, if minus 100-mesh coal particles are being processed, the minimum pump rate is about 800 cm³/hr. At lower rates, solids settle in the 9/16-in. transfer tubing and/or in the flow-through diaphragm isolators. The piping and valve arrangement at the inlet of the slurry pumps permits either or both of them to pump from either feed tank.

A high-pressure switch is installed at the discharge of each of the high-pressure pumps as a safety device. This switch will shut down the pump if the line pressure exceeds the designated operating pressure by 500 psi. A pressure gauge and rupture disc are also installed in this line. Flow-through isolators are associated with the pressure switch and pressure gauge. Nitrogen-purged priming lines are provided to facilitate pump start-up.

Inlet Gas Train

Hydrogen from an Air Products' tube trailer is compressed to 4,000 psig in a Carblin diaphragm compressor. Ballast tanks before and after the compressor stabilize the compressor operation and the hydrogen delivery pressure. Two forward pressure regulators in series are used to maintain a constant hydrogen pressure, typically 3,400 psig, in the hydrogen metering loop. A Hoke micrometering needle valve is used to control the hydrogen flow, and a Thermal Instrument mass flowmeter gives a relative measure of the flow. In addition, a glycol displacement system is used to provide a more accurate measure of the flow rate.

The purge nitrogen for the magnetic stirrer on the CSTR is supplied from 6,000-psig Air Products' cylinders. A forward pressure regulator is used to set the pressure on the stirrer at 100-200 psig above the system pressure. Almost all of this pressure drop occurs across a needle valve in the nitrogen line, which limits the flow to a few standard liters per hour. The nitrogen can also be used to purge the CSTR and the rest of the CPDU.

Continuous Stirred-Tank Reactors (CSTR)

The coal liquefaction reactors used in this program were either one 1-L CSTR or two 1-L CSTRs in series, both built by Pressure Products. These vessels are constructed of A-286 alloy steel and have pressure ratings of 5,000 psig at 1,000°F. The CSTRs have an inside diameter of 3 in. and an inside length of 9 in. Agitation is provided by 2-in.-diameter, six-bladed turbines, which are driven at speeds up to 2,000 rpm (typically 1,500 rpm) by sealed magnetic drives. The turbine blades are flat and 1/2-in. wide. The turbine is 1-1/4 in. above the bottom of the vessel.

Although the CSTRs are not baffled, a 3/8-in. thermowell effectively breaks the vortex at the typical impeller speed of 1,000 rpm. A cold-flow model of the vessel and agitator confirms that:

- ° solids are fully suspended
- ° the vortex is small

- ° the gas void fraction is about 18 vol % and
- ° most of the gas/liquid contact occurs in the immediate vicinity of the turbine.

A baffle was tested in the CSTR, but was discarded because it tended to collect solid particles, thus leading to coke formation.

Both the hydrogen gas and the feed slurry enter the CSTR at ambient temperature (or may be prewarmed) through a 9/16-in. inlet port centered in the base. The CSTR is operated in a flooded state in which both the product gas and slurry leave through a 9/16-in. port at the top of the body. A slow nitrogen purge must be maintained between the stirrer shaft and bearings to protect the graphite bearings from the slurry. The normal nitrogen concentration in the product streams is about 2 mol %.

The CSTRs are heated by stainless-steel-sheathed resistance heaters wrapped around the body and head. Temperature control is based on slurry temperature. Thermocouples placed at the bottom, middle, and top of the thermowell indicate that vertical temperature gradients in the CSTRs are small.

Gas/Liquid Separation

The product slurry is quenched to 325°F in a coiled heat exchanger, which is cooled with Mobiltherm on the shell side. The transfer tubing between the CSTR and the heat exchanger has a volume of slightly less than 100 cm³.

Like all of the transfer tubing and vessels downstream of the CSTR, this tubing is traced with electrical resistance heaters and insulated with fiberglass to avoid product freezing in the tubing during unplanned pump stoppages. The Mobiltherm heat-transfer fluid is heated or cooled, as required, to maintain the 325°F process fluid temperature.

The quenched product slurry and gases enter the gas/liquid separator through a dip tube, which directs the flow against the vessel wall, about an inch from the bottom. This 316 SS vessel has an outside diameter of 4 in. and an inside length of 22 in. A 3,200-psi rupture disc is mounted at the gas outlet from the gas/liquid separator. A dielectric conductivity probe senses the liquid level in the separator.

Although the mechanical seal (Teflon) on this device causes maintenance and reliability problems, the control signal is very stable and well-damped, facilitating control of the slurry dump valve.

A Masoneilan-Annin "Wee Willie" valve with size C tungsten carbide trim serves as the slurry dump valve. A manual bypass valve can be used to drain the separator if a plug develops in the Annin valve. The product slurry is let down to the 30-psig pressure of the low-pressure separator.

The low-pressure separator is a 4-in. by 22-in. I.L. 316 SS vessel. It is equipped with a differential pressure transmitter that measures the weight of product slurry held in the receiver. The separator is typically drained every hour, either to a sample receiver or a 55-gal. drum receiver. The product drum is placed on an electronic scale to provide a redundant determination of the product slurry rate.

Product Gas Train

The product gas is metered out of the gas/liquid separator through the system pressure valve (a Research Control Valve). The normal stellite trim set has a Cv of 0.0018. Larger or smaller trims are used, depending upon the product gas rate. This pneumatic valve is controlled based upon the system pressure, as measured by a pressure transmitter mounted between the gas/liquid separator and this valve. Because the system pressure valve may be blocked by heavy liquid drops elutriated from the gas/liquid separator, a redundant valve is provided. Block valves are also provided to permit one of the system pressure valves to be isolated for maintenance.

The dissolver gases and water that flash from the product slurry in the low-pressure separator are combined with the main product gas stream immediately downstream of the system pressure valve. The low-pressure product gas train is maintained at 30 psig by a back-pressure regulator. The combined product gas stream is routed to a water-cooled condenser to remove most of the water and the C₅+ hydrocarbons. Two condensers, each with its own condensate receiver, can be operated together in series or singly, with one held in reserve. Product in the condenser receiver is decanted to produce a water and light oils stream. The gases leaving the condensate receiver are further cooled in a packed vessel placed in

an ice bath. A single 1-gal vessel, packed with demister mesh, is currently used. A very small liquid volume is recovered from the ice trap every 2-8 hr.

The product gases are routed through a dryer tube to the Beckman process gas chromatograph, which is capable of analyzing two gas samples per hour for a total of 15 components (H_2 , N_2 , O_2 , CO , CO_2 , NH_3 , H_2S , C_1-C_4 , $i-C_4$, ethylene and propylene, and C_5+).

The product gas pressure is reduced to less than 1 psig in the back-pressure regulator before flowing to the dry test meter. A pressure transducer and thermocouple are mounted in the product gas line immediately upstream of the dry test meter to permit the flow rate to be converted from actual cubic feet per hour to standard liters per hour. A magnet is mounted on the sweep arm of the dry test meter to permit electronic data logging of the flow rate. The product gas is passed to a flare.

SAMPLING PROCEDURES AND PROCESS UNIT RAW DATA

Samples

Seven different types of samples are collected from the CPDU. Table A-1 lists the relevant information about each of the samples.

Raw Data

Each slurry batch is prepared by adding predetermined amounts of coal and solvent to the mix tanks. Typically, the amount of coal added is 20-30 kg and that of solvent is 30-40 kg. Both the weights are accurate within ± 0.1 kg. The slurry feed rate is measured with the help of the differential pressure transmitter on the slurry feed tank, and is accurate within ± 50 g/hr. The slurry feed rate can normally be controlled within ± 100 g/hr of the desired value. The density of the feed liquid sample is determined to ensure the uniformity of the slurry stream and also to be able to compute the nominal residence time of the coal in the CSTR from the slurry feed rate. The hydrogen feed rate is measured by both the thermal mass flow meter and the glycol displacement system. The flow rate determined from the glycol system is more reliable and is accurate to $\pm 2\%$.

Table A-1

CPDU Samples

Sample no.	Sample name	Type	Frequency
1	Coal	Solid	a
2	Solvent	Liquid	a
3	Additive (SRC/mineral matter/residue)	Solid	a
4	Feed liquid	Slurry	b
5	Product liquid	Slurry	c
6	Product gas	Gas	d
7	Condensate	Liquid	c

^aEvery time a new run is involved.

^bFew times for every batch involved.

^cEvery 4 to 6 hr after lineout.

^dEvery hour.

A differential pressure transmitter is used to compute the rate at which the liquid product is collected in the low-pressure separator. This measurement is unsatisfactory due to the fluctuating liquid level in the separator. Fortunately, however, the weight of the 55-gal drum receiver can be used to compute the liquid product rate within ± 60 g/hr. The condensate is drained from the condensate receivers and the demister, and is separated into aqueous and organic layers with the help of a separating funnel. The condensate rate is normally within ± 5 g/hr. The product gas rate, measured by the dry test meter, is accurate to $\pm 2\%$.

For all the gas components, the on-line GC output is converted to corresponding mole percent values and these are recorded periodically. The GC output and all the strip charts are saved and are available for inspection at a later date.