Handwritten initials "VJ" and "S" above a stamp box. The stamp box contains the text "DVORSCAK" and two lines of handwritten signatures, "M. P. Dvorscak" and "S. L. Lee".

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ADVANCED CONCEPTS IN COAL LIQUEFACTION -
OPTIMIZATION OF REACTOR CONFIGURATION IN COAL
LIQUEFACTION

V.R. Pradhan
A.G. Comolli
L.K. (Theo) Lee

FINAL

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Work Performed Under Contract

DE-AC22-91PC91052

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November 1994

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ABSTRACT

This final report covers the experimental work and findings thereof for the Optimization of Reactor Configuration Project as a part of the DOE's Advanced Coal Liquefaction Program conducted at Hydrocarbon Research, Inc. under DOE Contract No. DE-AC22-91PC91052 from October 1, 1991 until November 30, 1994. The overall objective of this Project was to find the ways to effectively reduce the cost of coal liquids to about \$ 25 per barrel of crude oil equivalent. The work described herein is primarily concerned with the testing at the laboratory scale of three reactor configuration concepts, namely (i) a fixed-bed plug-flow reactor as a "finishing reactor" in coal liquefaction, (ii) three-stage well-mixed reactors in series, and (iii) interstage stream concentration/product separation.

The three reactor configurations listed above were tested during this project using a 20 cc tubing microreactor, a fixed-bed plug flow reactor, and a two-stage modified Robinson-Mahoney reactor system. The reactor schemes were first evaluated based on theoretical modelling studies, then experimentally evaluated at the microautoclave level and laboratory scale continuous operations. The fixed-bed "finishing reactor" concept was evaluated in both the upflow and the downflow modes of operation using a partially converted coal-solvent slurry as feed. For most of the testing of concepts at the microautoclave level, simulated coal, recycle oil, and slurry feedstocks were either specially prepared (to represent a specific state of coal/resid conversion) and/or obtained from HRI's other ongoing bench-scale and PDU scale coal liquefaction experiments.

The three-stage continuous stirred tank reactors (CSTR) and interstage product stream separation/concentration concepts were tested using a simulated three-stage CSTR system by employing a laboratory-scale ebullated-bed system and a modified version of the HRI's existing Robinson-Mahoney fixed catalyst basket reactor system. This testing was conducted as a fourteen day long continuous run, divided into four Conditions to allow for a comparison of the new three-stage CSTR and interstage product concentration concepts with a two-stage CSTR baseline configuration.

EXECUTIVE SUMMARY

PROJECT DESCRIPTION

In October of 1991, HRI was granted a contract to test the proposed concepts in reactor configuration, namely the fixed-bed "finishing reactor", the three-stage backmixed CSTR in series, and the interstage product stream separation/concentration concepts. The primary objective of this project was:

To develop a new approach to coal liquefaction that generates an all distillate product slate at reduced cost of about \$ 25 per barrel of crude oil equivalent.

To accomplish this primary cost objective, the reactor configurations, named above, were evaluated to determine their individual impact on the kinetics of coal liquefaction.

The Statement of Work consisted of the following:

Task 1 - Project Work Plan

Task 2 - Laboratory Support: This Task provided the analytical support required for the experimental activities performed in Task 3, under Laboratory Scale Operations.

Sub-task 2.1 Feed and Product Characterization

Sub-task 2.2 General Support

Task 3 - Laboratory Scale Operations- Reactor Configuration: The goal of this Task was to obtain experimental data on coal and resid conversion kinetics to establish and to validate kinetic models.

Sub-task 3.1 Fixed-Bed Reactor Configuration

Sub-task 3.2 Three-Stage Close-Coupled Back-Mixed Reactor System

Sub-task 3.3 Interstage Product Stream Separation/Concentration for feed to Subsequent Stage Reactor/s.

Task 4 - Technical Assessment: The objective of this Task was to use the experimental data obtained in Task 3 to develop kinetic models and use these models to assess the performance in various reactor configurations.

MAJOR CONCLUSIONS

The following were the major findings based on the experimental work conducted during this Project:

1. Incorporation of a fixed bed plug-flow reactor as a "finishing" stage in coal conversion, indicated that at space velocity values greater than a certain (5000 Kg/hr/m²) minimum, fixed bed reactor can be used for coal liquids/slurries in

the downflow mode of operation to minimize solid settling and subsequent plugging of the bed. In general, the fixed bed plug-flow type of a reactor was found less forgiving for any pumping/feed problems than a completely backmixed CSTR system, even when used as a "finishing reactor" on a micronized coal slurry feed. Thus, in general, fixed-bed operation was found to have low probability of success, in comparison to an ebullated bed reactor, even with partially converted slurried due to solids plugging problems.

2. The three-stage backmixed system of CSTRs was found to be more effective kinetically and resulted in a superior yield structure than a conventional two-stage baseline. A three-stage close-coupled system of CSTRs can be further improved by optimizing the temperatures (or overall process severities) in individual reactor stages.
3. Interstage product stream separation/concentration was a very successful way of enhancing the overall liquefaction kinetics and therefore, the process performance. Higher coal and resid conversions, and higher distillate yields were obtained with an interstage light ends separator that removed mostly the material boiling below 343°C. It appeared from the experimental work in this Project that with such a process configuration, involving the interstage separation, improvements in the process performance could be obtained even at a reduced overall process severity.

RECOMMENDATIONS

Further studies and development are recommended as follows:

1. To investigate the impact of ashy recycle on products yields and quality.
2. To study the interstage product stream concentration/separation concept further to be able to effectively control the yields and product distribution in bench-scale and PDU operations..
3. To investigate the multi-stage CSTR in series configuration with a goal of looking for optimum temperatures for the individual reactor stages that will result not only in higher distillate yields but will give better product slate also.
4. To investigate the recycle of an intermediate process stream on CTSL process performance.

INTRODUCTION

HRI has conducted research on coal liquefaction for more than 25 years. During this time, HRI evaluated the single-stage and two-stage configurations, under both thermal and catalytic mode of operations at various process conditions. These research activities led to the development of the current catalytic two-stage configuration which significantly increased liquid yields, improved product quality, and process economics. The better performance is mainly due to the following process improvements:

- Staging coal liquefaction reactions
- Lower temperature and higher residence times
- Heavier (345°C+) boiling recycle solvents preferred
- Low-High temperature sequence mode of operations
- Coal concentration in feed slurries increased from ca. 30 W% to ca. 50 W%
- Deep coal cleaning improved feedstock quality for liquefaction
- Continuous sulfiding for low-rank, low-sulfur coals
- In-Line hydrotreating for product quality improvement
- Use of synthesis gas in first stage instead of pure H₂ improved net hydrogen utilization

With all these process improvements, HRI's CTSL Process (shown in *Figure 1*), in an extinction recycle mode of operation, has a much better overall performance with both bituminous and sub-bituminous coals than the H-Coal Process, developed in the early 1980's, as compared in *Table 1*.

HRI has been selected by the U.S. Department of Energy to study the optimization of reactor configurations with a goal of developing a feasible cost-effective processing scheme that will result in an increased overall yield of higher quality distillates. Since the high pressure-high temperature reactors and associated equipment for a coal liquefaction plant can comprise up to 20% of the capital costs of a grass roots plant, significant savings can result from optimized reactor configurations and an increased throughput. It is also expected that improved reactor configurations will lead to improvements in the product selectivity, product slate, and hydrogen utilization. The reactor configurations/concepts studied in this Project are:

- Incorporation of a fixed-bed plug flow reactor after partial conversion and micronization of coal in an upstream CSTR (or an ebullated bed reactor)
- Three-stage back-mixed reactor system
- Interstage concentration of unreacted materials for improved kinetics in the two (or three) stage back-mixed reactor system.

HRI's CTSL Process uses a relatively low first-stage temperature (400-415°C) and a higher second-stage temperature (435-450°C). The first stage with more favorable hydrogenation conditions, regenerates the hydrogen-donor capacity of the recycle solvent, while accomplishing a significant degree of coal conversion and production of

FIGURE 1

Simplified Schematic of the CTSL Process

TABLE 1.
CTSL PROCESS PERFORMANCE IMPROVEMENTS

Coal Process	<u>Illinois Bituminous</u>		<u>Wyoming Subbituminous</u>	
	H-Coal	CTSL	H-Coal	CTSL
Coal Conv., W% maf	94	97	91	93
524°C+ Conv., W% maf	73	94	75	89
C ₄ -524°C Liquid Yield				
W% maf Coal	51	78	48	66
Bbl/Ton Coal	3.3	5.0	3.1	4.3

TABLE 2.
CREDITS AND DEBITS OF AN EBULLATED-BED REACTOR SYSTEM

Credits	Debits
• Near Isothermal operation, fully utilizes the heat of reaction • Well-mixed system, intimate contact of gas, liquid and solids with constant catalyst activity • High solids-tolerance • Low pressure drop • Operates at catalyst equilibrium with constant activity for long periods	• CSTR kinetics, large reactor volume necessary • Catalyst volume is limited by the hydrodynamics • Catalyst attrition • Requires a customized pump • Overall high equipment cost

distillate liquids. The second stage with higher temperature, to promote cracking, completes the conversion of coal with production of additional distillable and low-heteroatom containing liquids. The CTSL Process employs two ebullated-bed reactors in which catalyst particles are in a fluidized state. The vigorous motion of the reactor fluids and catalyst particles permits un-restricted passage of finer particles (particles that are a few orders of magnitude smaller in size than the supported catalyst particles) and allows on-line replacement of catalyst.

The advantages and debits of an ebullated-bed reactor are compared in Table 2. Most of the advantages are based on it's well-mixed characteristics which result in uniformity in heat and mass distribution within the reactor. However, this same characteristic also acts as a severe kinetic debit. In a plug flow reactor the chemical potential (driving force for a reaction) is highest at the reactor inlet and declines progressively towards the reactor outlet. However, in a CSTR system the reactant concentrations in the reactor are identical to that of the outlet stream and results in a significant lower driving force for the reaction. As a result a larger reactor CSTR reactor is required to achieve a similar process performance as a plug flow reactor.

HRI has developed first order mathematical models, using CSTR kinetic equations and analysis of coal conversion results from the CTSL and various modes of coal liquefaction experience at the HRI's R&D Center. Application of such a model requires identification of species with different reactivity from coal, more or less corresponding to the maceral types identified by the petrographic analyses, although the actual correlating proportions of different reactive coal species have been developed from the two-stage CTSL or the single-stage H-Coal liquefaction results. Classification of coal as a reactant, into three species (one unreactive) has proven adequate to rationalize the CTSL experimental results giving coal conversions between 30 and 97 % maf coal.

Hydrogen transfer reactions from the donor-solvent in the liquid phase are a factor in coal conversion; however, in the correlation of CTSL results, where donor-solvent is generated *in situ*, inclusion of donor-solvent contribution is not deemed necessary in correlating the results. Although the quality of donor-solvent changes with the catalyst age, only small changes in conversions have been observed as a result of the catalyst age in CTSL Bench Experiments. These correlations were used in the current program to project and compare the performances of different reactor configurations or processing schemes under consideration. HRI's current mathematical model based on the first order kinetics of the CTSL Bench Scale data is shown in Figure 2.

Using the first order kinetic modelling, different reactor configurations can be compared relative to a two-stage CSTR performance, with either coal or residuum (524°C+) conversion as the basis for such comparison. Figure 3 compares reactor volumes necessary to achieve certain coal conversions with Illinois No. 6 coal. This comparison indicates that a system following first-order kinetics at 95 % conversion would require 130% greater reactor volume as a two-stage CSTR than as a plug-flow fixed bed system,

FIGURE 2
HRI's Kinetic Model

FIGURE 3

REACTOR CONFIGURATION AND REACTOR VOLUME

all other kinetic factors being equal. Based on the initial CTSL modelling projections, the optimum reactor configurations or processing schemes studied in this program (Figure 4) were as follows:

Fixed-Bed Finishing Reactor

The application of fixed-bed reactors for direct coal liquefaction was extensively tested in the first stage of the Synthoil process. Problems occurred with plugging, coking, and rapid deactivation of the catalyst. Since majority of the coal dissolution reactions occurs in the first stage, HRI's approach is to use a fixed-bed hydrocracker as a finishing reactor in the second or third stage where the solid concentration will be less than 20-30% of the moisture-ash-free coal fed to the first stage. Also, the coal particle will undergo a significant size reduction. The use of such a finishing reactor at relatively lower temperature will also reduce the rate of coking deposition on the catalyst thus prolonging the service life of the catalyst. Furthermore, with the use of appropriately shaped, low pressure drop catalysts and properly selected flow regime, the plugging problem can be brought under control. A simple first order model with identical rate constants and a conversion of 95% in two stages indicates that the CSTR-Fixed Bed combination would require only 55% of the reactor volume as the CSTR-CSTR configuration. In modelling the CSTR-Fixed Bed and CSTR-CSTR configurations on Black Thunder Mine Wyoming coal, the plug-flow option with an isothermal second stage could raise coal conversions by about 3.4%, lower the bottoms plus gas yield by 3.9%, and improve the distillate liquid yield by 4% with a 0.3% lower hydrogen consumption.

Three-Stage CSTR System

The addition of a third ebullated bed in series to the CTSL configuration would assuredly result in closer approach to plug-flow fixed-bed reaction potential and involves virtually no processing uncertainties. The ebullated bed configuration in series differs from the previous three stage concepts in control of stage temperatures to obtain an optimum interrelation of hydrogenation and cracking functions. It is recognized that three-stage ebullated CSTR system does not present a radical innovation, since from the inception of the ebullated bed development, it was recognized that the CSTR kinetic effect of the ebullated bed system can be overcome in part by staging the reactor systems, two, three or more reactors. This program involves three ebullated bed configuration largely as a reference for other essential innovations of this program such as the use of a fixed-bed as the third reactor stage, or the incorporation of a practical method of reconcentration of heavy reactants before entering the next reactor stage. A simple first-order kinetic model, with equal temperatures in the stages, indicates that a three-stage system would require 25% less total reactor volume than the two-stage system at a conversion level of 95%. The three-stage concept can be improved further through optimization of operating temperature for each of the three stages.

FIGURE 4

Interstage Stream Reconcentration

The concentration of primary reactants declines progressively in a plug-flow system and is lower stage-by-stage in a close-coupled, multistage CSTR system. More effective use of the reaction space for the conversion of liquid and solid phase reactants can be promoted if their concentration in the liquid phase could be maintained at higher levels and the hydrogen partial pressure increased. For example, in a three-stage CSTR system with simple first-order kinetics, attaining 95% conversion, the primary reactant concentration being fed to the third stage is about 15% of that in the feed to the first stage. Nominally, if the third stage feed concentration were raised to that of the original feed, the proportion of the reaction in the third stage could be correspondingly increased. Calculations based on simple first-order model indicate that a three-stage system of CSTRs with reconcentration of the second stage product going to the third stage (to obtain the same content of the reacting components as in the first stage feed) would require only 43% as much reactor volume to attain 95% conversion as would be needed in a conventional two-stage system with no interstage product concentration. Use of an interstage vapor/liquid separator offers an opportunity to increase the reactant (350°C+ slurry) concentration, increasing the subsequent hydrogen partial pressure and decreasing the production of by-product light hydrocarbon gases from further cracking of 350°C- liquids.

TASK 2. LABORATORY SUPPORT

The primary goal of the Laboratory Support was to provide a complete analytical coverage to the experimental work carried out in this Project. The laboratory support work conducted during this Project covered the screening of processing concepts at the microautoclave level, analytical work associated with it, and also the analytical support for the laboratory scale operations made using a fixed-bed reactor and a modified Robinson-Mahoney two-stage CSTR system.

Experimental:

A vertically-shaken microautoclave (Figure 5), 20 cc in volume, with rapid heating and cooling was used for most of the work related to screening of the proposed reactor configurations at a small scale. This reactor, used in a batch mode of operation, with or without catalysts, is in a kinetic regime similar to a fixed-bed plug-flow reactor (Figure 5).

In order to evaluate the advanced reactor configurations experimentally and therefore obtain the kinetic data on coal liquefaction at different stages of coal conversion, samples of partially converted coals (between 40-90% conversion) and coal-slurries were obtained from HRI's Bench and PDU scale operations. These partially converted (synthetic or simulated) feedstocks were processed further using either a batch microautoclave system or a continuous fixed-bed reactor system to shed some light on the possible merits of the fixed-bed processing concepts, three-stage testing and the interstage stream concentration concept. Efforts were made to study partially converted coal and slurry samples derived both from a bituminous Illinois No. 6 coal and a subbituminous Black Thunder Mine Wyoming coal.

The partially converted coal and slurry samples we have evaluated in this program consisted of:

(i) Atmospheric bottom slurry (Tank O-47) from the PDU Run 260-03 carried out on Black Thunder Mine coal, designated as L-772: This partially converted coal slurry was characterized in detail and used in the microautoclave screening tests. Its properties are summarized in Tables 3 and 4. As shown in these Tables, L-772 slurry consisted of 84.6 W% of quinoline soluble oils and 12.1 W% of the unconverted coal. The coal conversion during the PDU operations was 74.6 W% maf. The pressure filter liquid obtained from L-772 had an initial boiling point of 280°C and contained 11.1 W% hydrogen besides small amounts of nitrogen and sulfur.

(ii) Pressure filter liquid and pressure filter solid samples obtained from the Bench Run 227-76 (CC-16); these were mild reaction severity samples collected when the CTSL ebullated-bed reactors K-1 and K-2 were at 399 and 316°C respectively. The detailed

FIGURE 5

HRI's Microautoclave Reactor

MECHANICAL DESIGN

- 20cc INTERNAL VOLUME
- MAXIMUM INLET HYDROGEN PRESSURE 3000
- OPERATIONS TO LIQUEFACTION TEMPERATURE
- THERMAL AND GAS INLET COUPLING
- 347ss MATERIAL OF CONSTRUCTION
- EXTERNAL CAP THREADS
- REACTOR CAP REDESIGN
- COLD TRAPS
- CATALYST BASKET
- UTILIZES WHOLE EXTRUDATE CATALYST
- GAS COLLECTION
- SHAKEN VERTICALLY IN A SAND BATH

TESTING CAPABILITIES

- THERMAL TESTS VARYING CHARGE, FEED RATIOS, TEMPERATURE, TIME
- CATALYTIC TESTS VARYING CHARGE, FEED RATIOS, TEMPERATURE, TIME

TABLE 3

FEED SLURRY (L-772) INSPECTION PRESSURE FILTER LIQUID
Pressure Filter Liquid

Pressure Filtration, W%

Filter Liquid	74.73
Filter Cake	25.27

Filter Liquid

API Gravity	16.0

ASTM D-1160 Distillation

Cumulative Volume [V%]	Temperature [°C]
IBP	280
5	310
10	326
20	340
30	352
40	364
50	376
60	388
70	402
80	430
90	503
92	524

B.P. Distribution, W%

IBP-343°C	20.42
343-454°C	62.30
454-538°C	8.85
538°C+	8.44

Elemental Analysis, W%

Carbon	88.65
Hydrogen	11.14
Nitrogen	0.050
Sulfur	0.019
H/C Ratio	1.51

TABLE 4

**FEED SLURRY (L-772) INSPECTION
PRESSURE FILTER CAKE**

Quinoline Filtration, W%

Quinoline Solubles	39.03
Quinoline Insolubles (Ash-free)	47.71
Ash	15.21
Sulfur in Ash	5.14
SO ₃ -free Ash	13.21
Coal/ Ash (SO ₃ -free)	3.60
Coal Conversion, maf W%	74.6

**Mineral Analysis of Ash
(W% of Ignited Sample)**

Silica, SiO ₂	33.33
Alumina, Al ₂ O ₃	18.72
Titania, TiO ₂	1.40
Ferric Oxide, Fe ₂ O ₃	7.86
Lime, CaO	19.92
Magnesia, MgO	3.96
Potassium Oxide, K ₂ O	0.35
Sodium Oxide, NaO	0.50
Sulfur Trioxide, SO ₃	9.83
Phosphorous Pentoxide, P ₂ O ₅	0.65
Strontium Oxide, SrO	0.10
Barium Oxide, BaO	1.62
Manganese Oxide, Mn ₃ O ₄	0.07
Undetermined	1.63

TABLE 5**ANALYSIS OF PRESSURE FILTER CAKE
(RUN 227-76-PERIOD E3)****Distribution:**

W% of Whole Slurry Sample	29.42

Elemental Analysis, W%

Carbon	75.09
Hydrogen	6.25
Nitrogen	1.70
Sulfur	0.85
SO ₃ -Free Ash	13.48
ASTM Ash	13.91
S in Ash	1.20

Quinoline Filtration, W%

Insolubles (QI)	36.77
Ash in QI, W% PFC	14.60
S in QI Ash	1.03

Coal Conversion, W% (By quinoline filtration)	88.9

Coal Conversion, W% (By THF-filtration)	87.2

TABLE 6**ANALYSIS OF PRESSURE FILTER LIQUID
(RUN 227-76-PERIOD E3)**

Distribution, W% Whole Slurry Sample	70.58
API Gravity	1.3
Elemental Analysis, W%	
Carbon	89.51
Hydrogen	8.84
Nitrogen	0.54
Sulfur	0.22
Boiling Point Distribution, W%	
IBP	306°C
IBP-343°C	5.35
343-454°C	42.68
454-524°C	12.95
524°C+	38.27
Loss	0.75

TABLE 7A

PREPARATION CONDITIONS FOR SIMULATED FEEDSTOCKS)

Sample I.D.	HRI-6138	HRI-6139
Coal (100g)	Illinois No. 6	Illinois No.6
Solvent* (200g)	L-769	L-769
Catalyst* (100g)	Ni-Mo/ Alumina	Ni-Mo/ Alumina
Temperature, °C	370	350
Pressure, MPa (psig)	13.8 (2000)	13.8 (2000)
Reactant Gas	H ₂ /H ₂ S	H ₂ /H ₂ S
Flowrate [std liter/h]	2.36	2.36
Reaction time [min]	15	15
Material Balance, %	97.7	100.7
Coal Conversion**,maf%	57.4	35.9

* The solvent (pressure filter liquid) and the catalyst (recovered 2nd stage catalyst) used for preparing above samples in a batch mode (using 1 liter stirred autoclave reactor) were recovered from the HRI's PDU Run 260-03, carried out on a sub-bituminous coal.

** The coal conversions reported here are already corrected for the catalyst-fines contamination.

TABLE 7B

ANALYSIS OF SIMULATED FEEDSTOCKS)

Sample I.D.	HRI-6138	HRI-6139
ASTM Ash, W%	38.35	34.4
Molybdenum*, W%	1.65	2.03

* The amount of molybdenum in the catalyst employed for the above preparation reactions, was about 8.0 W%.

TABLE 8

**CATALYST PROPERTIES COMPARISON
PRESULFIDED SHELL S-317 1/20" TRILOBE
COMPARISON WITH CATALYSTS USED IN THE CTSL PROGRAM**

	Shell Trilobe Presulfided	Shell Extrudate	Criterion Extrudate
HRI NUMBER	6030	5394	5903
Nominal Diameter, inches	1/20	1/32	1/16
Chemical Analysis (W% mf)			
Molybdenum	7.91	11.4	10.11
Nickel	1.55	2.2	2.38
Mo/Ni Ratio, w/w	5.1	5.2	4.2
Carbon	3.03		
Hydrogen	0.85		
Nitrogen	0.07		
Sulfur	7.35		
Physical Properties			
Bulk Density, lb/ft ³	43.8	36.7	38.1
Particle Density, g/cc	1.090	0.966	0.938
Pore Volume, cc/g	0.490	0.652	0.645
Surface Area, M ² /g			
Hg Porosimetry	160	197	283
BET Method	166	N/A	314
Pore Size Distribution, cc/g			
> 30 Å	0.490	0.65	0.64
> 100 Å	0.276	0.39	0.30
> 250 Å	0.140	0.19	0.27
> 500 Å	0.122	0.16	0.24
> 1500 Å	0.084	0.11	0.18
> 4000 Å	0.018	0.02	0.08
Modal Diameter, Mesopores Å	90	95	46
Modal Diameter, Macropores, Å	3300	2800	4200

analyses of the pressure filter liquid and pressure filter cake from this sample are listed in Tables 5 and 6.

(iii) Two samples of partially converted Illinois No. 6 coal, one with low initial conversion and another with a higher initial conversion, were obtained from Dr. A. Cugini of the Pittsburgh Energy Technology Center: HRI-6138 and HRI-6139 were the two samples of partially converted coal for microautoclave studies. These samples had to be prepared because the partially converted coal samples in (ii) had a very high degree of conversion (87.2 W% maf) which rendered their further reactivity difficult. The detailed analyses of these simulated feedstock samples and their preparation conditions are given in Tables 7b and 7a, respectively.

Besides the detailed analysis of the simulated feedstock samples discussed above, the detailed characterization of the supported catalyst required for the fixed-bed testing was also carried out under the laboratory support. For the fixed-bed tests in this Project, a trilobe catalyst was chosen as it is known to give lower pressure drop than an extrudate or a beaded catalyst. A batch of Shell S-317 1/20" presulfided trilobe catalyst (HRI-6030) was obtained from Wilsonville for this purpose. Selected chemical and physical properties of this catalyst in comparison to a fresh Shell S-317 1/32" extrudate (HRI-5394) catalyst and a Criterion 1/16" extrudate (HRI-5903) catalyst are given in Table 8. The trilobe catalyst contained 7.35 W% of sulfur.

The other physical characterization of the trilobe catalyst such as pore properties evaluation was also carried out. The comparison of the pore size distributions for different supported catalysts and pore-size characteristic curve for the trilobe Shell S-317 catalyst are shown in Figures 6 and 7. The pore volume of the sulfided trilobe catalyst was about 25% lower than the fresh Shell 317 1/32" extrudate.

Laboratory support also covered the detailed analyses of the coal and solvent feed stocks for and reaction products from the continuous laboratory scale operations of the Robinson-Mahoney CSTR system (these are addressed in the later sections).

Results and Discussion from Microautoclave Testing:

Reactivity of Partially Converted Coal

A series of microautoclave tests (AC-01 through' AC-06) were carried out to assess the reactivity of partially converted coal samples to evaluate the kinetics of multi-stage coal liquefaction. The partially converted coal was the THF washed cake of the pressure filter solids recovered from Bench Run 227-76. In spite of the relatively low severity (1st stage: 399°C and 2nd stage: 399°C) at which this sample was recovered, the coal conversion was fairly high (87.2 % based on THF solubility). Following were the reaction conditions for the microautoclave tests that were performed and the data on conversions, material balances, and product characterization were obtained.

THF Washed Cake (Run 227-76 PFC):	2.0 g
Solvent (Run 227-76-13 PFL):	8.0 g
Catalyst (Recovered AO-60 Cat):	2.0 g
Pressure (at reaction temperature):	13.8 MPa (2000 psig) of H ₂
Temperature:	399-440°C
Time:	15-60 minutes

* THF washed, second stage catalyst recovered from Bench Run 227-76.

The results of coal conversion relative to the starting materials and percent improvements in conversion levels are listed in Table 9.

A fair improvement was obtained in overall coal conversion (between 3-8 wt%) of the partially converted coal, and more significantly it was the resid conversion that is enhanced considerably (as much as 32 wt%) by the additional processing of the partially converted coal. These results, therefore, seem to suggest that three-stage processing of coal definitely holds promise in improving the conversion levels, especially the resid conversion levels significantly. The partially converted coal sample used for these tests was originally 87.2 wt% soluble in THF. Considering this high dissolution, there was not much room in the improvement in this number even though coal conversion levels, based on THF-solubility, of 95 wt% were obtained in these tests. A further series of microautoclave tests to evaluate the same concept (three-stage reactors) with mildly converted coal samples (THF solubility of less than 80 wt%) was carried out and the results are discussed below:

The kinetic advantage offered by multistage CSTR processing in terms of achieving high coal and resid conversions through a kinetic approach to a plug-flow behavior was established in terms of coal conversion to lighter products at the microautoclave testing level (Tables 10 and 11) using the mildly converted samples of Illinois No. 6 coal obtained from Pittsburgh Energy Technology Center. The coal conversion of lower conversion sample was 35.9 W%, while that of the other was slightly higher at 57.4 W%.

As shown in Tables 10 and 11, multistage reactor configuration did not have a significant effect on the overall coal conversion, although, it is thought from the related bench-scale experience that the 524°C+ heavy resid conversion and light hydrocarbon gas formation would be favorably affected by the multi-stage processing where temperatures of individual reactor stages are optimized based upon the chemistry of resid conversion and gas formation during coal liquefaction.

Tables 10 and 11 list the coal conversion results obtained, both in the form of actual conversions of the partially converted coal samples, and the final total conversions with respect to the starting Illinois No. 6 coal. The starting coal, when reacted independently in one single-stage reactor, gave under identical reaction conditions, about 85, 91, and

TABLE 9

**REACTIVITY OF PARTIALLY CONVERTED ILLINOIS NO. 6 COAL -
THF Washed Solids from Run 227-76-E3**

Test No.	Temp. [°C]	Time Min.	STTU	% Increase in Coal Conversion	% Increase in Resid Conversion
AC-01	399	15	1.1	3.2	-1.0
AC-02	399	30	2.2	5.3	2.1
AC-03	427	15	9.7	5.8	7.6
AC-04	427	30	19.4	7.4	31.5
AC-07	427	60	29.1	7.8	28.2
AC-05	440	15	10.5	7.1	11.5
AC-06	440	30	21.0	7.6	23.2

TABLE 10

**REACTIVITY OF PARTIALLY CONVERTED COAL SAMPLE WITH HIGH INITIAL
COAL CONVERSION OF 57.4 W% MAF**

Test No.	Time [min]	Temperature [°C]	STTU*	Coal Conversion, % Overall	Incremental
AC-17L	15	399	1.11	76.7	19.3
AC-18L	30	399	2.21	80.1	22.7
AC-19L	60	399	4.42	81.9	24.5
AC-21L	30	427	9.71	84.3	26.9
AC-22L	60	427	19.42	90.0	32.6
AC-23L	90	427	29.14	91.1	33.7
AC-24L	15	440	10.50	82.5	25.1
AC-25L	30	440	21.0	88.1	30.7
AC-26L	60	440	42.0	90.9	33.5

*STTU is the process severity in terms of Standard Time and Temperature Units.

FIGURE 6

CATALYST PORE SIZE DISTRIBUTION

Criterion (HRI 5903) And Shell S-317 (HRI 5394, 6-30) Catalyst

FIGURE 7

Shell S-317 1/20" Trilobe Catalyst

$dV/d\log R$ vs Pore Diameter

92 W% conversions at 399, 427 and 440°C respectively, at a reaction time ranging from 15 to 90 minutes. The partially converted coal sample with low initial conversion (35.9 W%) was more reactive than the other sample with 57.4 W% initial conversion. This can be expected as the sample with low initial conversion had more of the reactive organic part of coal (about 65 W%) as compared to the high initial conversion sample (about 43 W%). Also, the highest coal conversions obtained in both the cases (88.8 and 91.1 W% maf) were not very different from the highest conversion obtained with the same coal in one single-stage conversion under similar severity conditions (92 W% maf). Comparing with the Run 227-76 sample, the mildly converted samples from PETC were 3.5 to 8.8 times more reactive:

Relative Reactivity Of Partially Converted Illinois Coal

Sample	227-76	PETC #1	PETC #2
Initial Coal Conv. W%	87.2	57.4	35.9
STTU*	Ratio of Incremental Coal Conversion at similar STTU		
1.1	1.0	6.03	8.84
2.2	1.0	4.28	8.04
9.7	1.0	4.64	7.05
10.5	1.0	3.54	6.15
19.4	1.0	4.41	6.84
21.0	1.0	4.04	6.39
29.1	1.0	4.32	6.54

*STTU is the process severity in terms of Standard Time and Temperature Units.

Effect of Residuum Concentration

The pressure filter liquids (PFL) obtained from Bench Run 227-76 contained 38.27 wt% of 524°C+ resid material. This resid content corresponded to a resid conversion level of 61.5 W%. The reactivity of this resid at different concentrations was tested to evaluate the interstage stream concentration concept. In order to alter the composition of the residuum fraction of this PFL, the following diluents were mixed with the PFL in different proportions for the microautoclave tests:

Diluent B: IBP-454°C material from PFL

Diluent C: 454°C+ material from PFL

Tests AC-08, 10, 11 & 16 were charged with the whole PFL, without any diluents. In tests 12 and 15 approximately 1/3 of the whole PFL (0.67 g) was replaced by Diluent B and C, respectively. As a result there were three levels of resid concentration (25.51, 38.27 and 50.42 W%) in these series of tests. The results obtained from the

FIGURE 8

FIGURE 9

microautoclave tests AC-8 through' AC-16 are presented in Table 12. The THF-washed recovered catalyst from the second stage of Run 227-76 was used in these tests.

Table 12 shows the effect of interstage stream concentration, in terms of the concentration of the 524°C+ residuum in pressure filter liquid feed charge for the microautoclave tests, on the percent resid conversion levels. Comparison of tests AC-08 and AC-12, both carried out at 427°C, indicates that AC-08 which has a higher concentration of resid in the feed charge, results in slightly better conversion levels (better resid conversion and lower char formation). Also, comparison of tests AC-10 and AC-15, both carried out at 440°C, indicates that AC-15 with higher concentration of residuum in the feed charge resulted in improved conversion levels. These results definitely indicates the merit in the interstage stream concentration concept for enhanced kinetics of direct coal liquefaction. The incremental resid conversion varied proportionally with the reaction severity, as shown in Figure 10.

In this way, this was by far the most successful processing concept tested at the laboratory scale during Phase I. In another DOE-sponsored Project (CMSL Program), the concept of interstage product separation or concentration was very successfully demonstrated at the 50 pounds per day bench scale of operations. The removal of 343°C-light ends and off-gases from stage I reactor exit stream before it enters the second stage reactor was found to enhance the overall coal and resid conversions significantly, the net light distillate yield was also increased by about 5 % maf coal. Interstage light ends separation, besides increasing the coal and resid concentration in the feed to the second stage reactor, helps to increase the effective partial pressure of hydrogen in that reactor stage. It also removes carbon oxides in off-gases before they have a chance to undergo further reforming reactions to yield methane, thereby consuming valuable hydrogen.

TABLE 11

**REACTIVITY OF PARTIALLY CONVERTED COAL SAMPLE WITH
LOW INITIAL COAL CONVERSION**

Test No.	Time [min]	Temperature [°C]	STTU*	Coal Conversion, %*	
				Overall	Incremental
AC-17R	15	399	1.11	64.2	28.3
AC-18R	30	399	2.21	78.5	42.6
AC-19R	60	399	4.42	77.9	42.0
AC-21R	30	427	9.71	76.8	40.9
AC-22R	60	427	19.42	86.5	50.6
AC-23R	90	427	29.14	86.9	51.0
AC-24R	15	440	10.50	79.6	43.7
AC-25R	30	440	21.0	84.5	48.6
AC-26R	60	440	42.0	88.8	52.9

*STTU is the process severity in terms of Standard Time and Temperature Units.

TABLE 12

**EFFECT OF FEED CONCENTRATION ON RESIDUUM CONVERSION
- Pressure Filter Liquid from Run 227-76-E3**

Test No.	Reactants (gm)	Temp./Time [°C]/min.	STTU	%524°C+ in Charge	%Resid Conversion
AC-08	PFL (3)	427/30	19.42	38.27	29.7
AC-12	PFL (2) & Dil B(1)	427/30	19.42	25.51	27.2
AC-10	PFL (3)	440/30	21.0	38.27	31.5
AC-15	PFL (2) & Dil. C(1)	427/30	21.0	50.42	34.3
AC-11	PFL (3)	427/60	29.14	38.27	37.0
AC-16*	PFL (3)	427/30	19.42	38.27	22.7

* This test was carried out without any catalyst, i.e., a thermal background.

FIGURE 10

TASK 3. LABORATORY SCALE OPERATIONS

The laboratory scale operations included two continuous fixed-bed plug-flow reactor tests carried out on a partially converted coal slurry and a seventeen day long continuous test carried out in a modified Robinson-Mahoney CSTR system for the investigation of the three-stage CSTR and interstage product stream separation concepts.

Fixed-Bed Reactor Tests

Two continuous flow tests were completed using a partially converted slurry (L - 772) generated from PDU Run 260-03 during this reporting period. Two different shaped and size, a 1/20" trilobe and a 1/16" extrudate, Ni/Mo supported catalysts were tested in both upflow and downflow mode of operations. Results from these tests are discussed in this report.

Objective

The main purpose of the these small scale flow tests were to evaluate the viability of using fixed bed reactor as a 'finishing' reactor in coal liquefaction.

Specifically, Run ACL-01 and ACL-02 was to determine the flow regimes at which solids in the feed slurry will not settle in the fixed-bed reactor.

Equipment and Operations

The test system consists of one or two 3/8" I.D. fixed bed reactors connected in either upflow or downflow mode, *Figure 11*. The detailed description of the reactor system is given in the Attachment 2.

The slurry feed to the reactor system was provided by a positive displacement metering pump. This pump was initially sized for the lower end of the range of space velocity tested and subsequently boosted to a higher flow range by increasing both the gear ratio and the plunger diameter. Due to the high stoke frequency at high flow rate, there were excessive leakages through the pump packing hence affected the actual flow through the reactor substantially.

Each run had a total slurry feed duration of approximately 60 hours. However, there were five to six interruptions during each run. These interruptions were mostly due to high pressure build-up as a result of solid deposition in the reactor or transfer lines. In

FIGURE 11
Experimental Set-up of Fixed-Bed Units

most cases the interruption were immediately preceded by a reduction in feedrate, or loss in slurry feed, due to excessive leakage at feed or low pressure circulating systems.

Run Summary

The run summaries for ACL-01 and ACL-02 are presented in *Tables 13 and 14*, respectively. In Run ACL-01, Shell S-317 1/20" trilobe catalyst was tested. This catalyst was obtained from Wilsonville in a presulfided form. Three test conditions were evaluated in 5 mass balance periods with run durations varying from 6.3 to 20.5 hours. The longest run duration was achieved in Period 5 when the reactor configuration consisted of one reactor connected in downflow mode. Periods 1 to 4 were in upflow mode with two reactors connected in series. The average reactor temperatures (sandbath mid-point temperature) ranged from 402-422°C in Periods 1 to 4 and at 369°C in Period 5. The space velocity was in the range of 2100 to 5050 Kg/h/M².

To simplify the operation only one reactor was used in Run ACL-02. Four test conditions were tested. Periods 1 to 4 were in downflow mode while Period 5 was in upflow mode. The space velocities investigated in this test were higher than those in ACL-01 ranging from 4900 to 8900 Kg/h/M². However, the temperature was around 370°C for majority of the Periods.

Feed Slurry

The feed slurry used in these tests was partially converted coal slurry (L-772) from PDU Run 260-03. The properties of L-772 are listed in *Table 3*. It contains 12.06 and 3.35 W% of unconverted coal and ash (SO₃-free basis).

Results and Discussion

With the exception of ACL-02 Periods 1 and 2, most mass balances were low varying from 82.0 to 92.9 W%, *Tables 13 and 14*. It is mainly due to the small scale of the operations as well as the relatively short duration of each Period.

The ash balance was low for ACL-01 Periods 1 to 3 with ash recovery of only 18.3 to 31.7 W%. These Periods were in upflow mode with a relatively low space velocity ranging from 2090 to 2500 Kg/h/M². At space velocities of greater than 4410 Kg/h/M², as in ACL-01 Period 5, ACL-02 Periods 2 and 3, the ash recovery were much higher and closer to complete recovery (100%). In ACL-01 Period 4 the initial product was contaminated by product from the start-up conditions in which a solid-free gas oil feed was used. As a result the ash recovery (35.4 W%) in ACL-01 Period 4 was not in the expected range of high recovery.

Normalized product distribution for selected mass balance periods are presented in *Table 15*. The normalization procedure used in this calculation assumed that the low

TABLE 13

FIXED-BED OPERATION: RUN 254-01
Shell S-317 1/20" Trilobe Catalyst (HRI-6030)

RUN SUMMARY

Condition	1	1	1	2	3
Period	1	2	3	4	5
No. of Reactor	2	2	2	2	1
Mode of Operation	Upflow	Upflow	Upflow	Upflow	Downflow
Duration, hours	9.4	6.3	12.8	11.5	20.5
Reactor Temperature (°C)*	402	417	416	404	369
Space Velocity Kg/h/M ²	2090	2650	2500	5040	4410
DMDS, W% Feed	2.8	2.8	2.8	2.8	2.8
Mass Recovery, W%	56.0	83.5	82.0	92.9	90.8
Ash Recovery, W%	n/a	18.3	31.7	35.4	93.8

---

* Mid-point temperature of the fluidized sandbath heater.

TABLE 14

FIXED-BED OPERATION: RUN 254-02
Shell S-317 1/16" Extrudate Catalyst (HRI-5903)

RUN SUMMARY

Condition	1	1	2	3	4
Period	1	2	3	4	5
No. of Reactor	1	1	1	1	1
Mode of Operation	Downflow	Downflow	Downflow	Downflow	Upflow
Duration, hours	9	21	11	4	9.4
Reactor Temperature (°C)*	372	371	396	372	407
Space Velocity Kg/h/M ²	5170	4890	5630	8870	8510
DMDS, W% Feed	2.8	2.8	2.8	5.0**	2.8
Mass Recovery, W%	95.5	110.0	92.4	88.0	88.8
Ash Recovery, W%	n/a	107.7	104.3	n/a	180

* Mid-point temperature of the fluidized sandbath heater.

TABLE 15

**FIXED-BED OPERATIONS (RUN ACL-01 & 2)
NORMALIZED PRODUCT DISTRIBUTION**

Run No. Period No.*	Normalized Product Distribution (Basis: 100 part of L-772)						L-772 Slurry
	1 2B	1 3B	1 4**	1 5B	2 2B	2 3B	
Gases							
C ₁ -C ₃	1.77	2.03	1.00	0.38	0.49	0.38	
C ₄ -C ₇	1.55	1.78	1.04	0.00	0.00	0.41	
H ₂ S	1.12	1.28	1.72	1.19	1.16	3.46	
Others	0.00	0.00	0.03	0.00	0.04	0.08	
Total	4.44	5.09	3.79	1.56	1.70	4.32	
Filtrate (PFL)							
IBP-343°C	24.24	31.12	24.07	14.03	16.37	19.34	15.26
343-454°C	48.69	41.62	46.00	44.24	42.67	40.70	46.55
454-524°C	19.00	9.54	13.41	7.10	5.83	7.67	6.61
524°C+	1.05	7.10	4.60	6.31	6.35	5.40	6.31
Total	92.98	89.37	88.08	73.15	72.21	73.10	74.73
Filter Cake (PFS)							
Quin.Solubles	2.11	3.11	4.58	11.91	13.13	10.36	9.86
Quin. Insolubles*	2.07	3.29	4.67	10.92	12.52	11.56	12.06
Ash (SO ₃ -free)	0.61	1.06	1.19	3.14	3.61	3.49	3.35
Total	4.79	7.45	10.44	25.97	29.26	25.42	25.27
Total Product**	102.2	101.9	102.3	100.7	102.2	102.8	100.0
Coal Conversion, W% maf Coal ***							
	76.0	78.2	72.3	75.4	75.4	76.6	74.6
Incremental Conv., W% change over L-772							
	1.9	4.8	-3.1	1.1	1.1	2.7	

* Each period was divided into two 12-hour sub-periods A and B.

** Averaged result using data from sub-periods A and B.

* Quinoline insolubles do not include ash.

** Total Product = 100 part of L-772 + 2.88 parts of DMDS + H₂ consumed.

*** In reference to the coal feed to the PDU Run 260-03.

mass balance was mainly due to the over estimation of the amount of feed slurry fed to the system. This is a reasonable assumption in view of the leakage or unaccountable loss at both the circulation and feed pumps.

Coal conversion of the feed slurry (L-772) was 74.6 W% in reference to the coal fed to the PDU. Due to the relatively low reactor temperature in all Periods the incremental conversion was minimum, less than 5 W%.

Based on the results of the first two fixed bed tests, it appears that the downflow mode of operation is more preferable in terms of minimizing solid settling in the bed. Also, a space velocity of greater than 5,000 kg/h/m² is needed to sustain continuous operation. Due to the presence of solid matter in the feed, the fixed-bed operation will be limited to a narrow range of operation parameters, e.g. a small turn-down ratio. Thus, in general, fixed-bed operation, with coal-slurry feed appears to have a low probability of success, especially because of the plugging problems due to coal solids.

Three-Stage CSTR & Interstage Product Separation

Two simulated 3-stage liquefaction tests were conducted using a dual-reactor CSTR system. An equilibrated (spent) Shell 317 catalyst (Ni-Mo/ Alumina), in the form of 1/16" extrudates, was placed inside a specially designed Lee-Faupel-Canas (LFC) fluidized-bed reactor system. The simulated tests were conducted in two parts. The first part involved two-stage operations, while the second part was single-stage operations (the simulated third stage in series). Products from Part I (worth 7 days of continuous operations) was split into two fractions (40/60 w/w%). The smaller fraction was fed "as is" to the single-stage (Part II) reactor, a simulated third stage reactor, while the larger fraction was topped off to remove material boiling below 343°C. This topped material was used as a feed (separately) for the third simulated stage reactor to evaluate the effect of interstage product concentration/separation. The data from these continuous experiments indicate a significant improvement in the light distillate yields as well as the overall process performance upon either three-stage processing or as a result of the interstage product separation, when compared to the data obtained from the two-stage baseline case of comparable process severity.

Details of the Run

As mentioned earlier, the existing Robinson-Mahoney dual-CSTR system was modified to handle the solids-containing streams and as a result the LFC fluidized catalyst cage was developed (please see the more detailed description in Attachment 3). Using this 150 CC catalyst volume cage in each reactor, a sixteen-day long continuous run was carried out to simulate the three-stage system and to meet the technical objectives of the Phase I of this Program.

The slurring oil, L-802, was a mix of pressure filter liquids obtained during some of the earlier bench runs (CMSL-02 and CMSL-03: with Illinois No. 6 and Black Thunder mine coals respectively). The analysis is shown in Table 16. The analysis of the feed coal, Illinois No. 6 Crown II mine is shown in Table 17. A 16-day long continuous test was carried out following the completion of the modifications of the reactor internals. The entire run was divided in four Conditions (and two Parts) that are explained below.

Part I:

Condition #1 (Periods 1 thru 8): This is the first condition of Part I, a non-integrated three-stage configuration. Two close-coupled CSTRs were employed. Temperatures of reactors 1 and 2 were set at 399° and 429°C, respectively, and with a space time velocity of 765 Kg/h/M³ (51 lb mf coal/h/ft³) catalyst per stage. A solvent/coal ratio of 1.0 was selected

to closely match that of the bench unit operations. The operating temperatures and space velocities for this Condition are shown in Table 18. This condition produced feedstock

TABLE 16

**ANALYSIS OF SLURRYING OIL, L-802
For Runs 245-29/31**

API	7.8
Weight Percents	
IBP-650 F	11.81
650-850 F	48.23
850-975 F	15.06
975 F+	24.02
LOSS	0.88
Elemental, W%	
C	87.95
H	9.57
S	0.206
N	0.36
CHX INSOLS	6.72
TOL. INSOLS	2.89

TABLE 17

ANALYSIS OF FEED ILLINOIS NO. 6 CROWN II MINE COAL

Moisture Content	3.98
Proximate Analysis, W% Dry	
Volatile Matter	41.48
Fixed Carbon	49.08
Ash	9.44
Ultimate Analysis, W% MAF	
Carbon	75.58
Hydrogen	5.01
Sulfur	4.39
Nitrogen	1.11
Oxygen (Diff.)	14.91
Catalytic Conv. @800F, 30 min	96 % maf

(PFL,PFC, SOH) for Conditions #3 and #4 (Part II) designed to evaluate the three-stage CSTR and interstage product separation concepts.

Condition #2 (Periods 14 thru 16 of a separately conducted run): This was a base case for evaluating the close-coupled two-stage configuration using the Robinson-Mahoney system.

Temperatures:	K-1 at 399° C
	K-2 at 440° C
Space Velocity:	510 Kg/h/M ³ (34 lb mf coal/h/ft ³)Catalyst
Solvent/coal:	1.0

Part II:

This was Part II of the simulated, three-stage operation. Only one stirred tank reactor is required. A new batch of the spent Shell S-317 catalyst (catalyst recovered from the Stage II reactor after the Bench run CMSL-05 or 227-82) was used.

Condition #3 (Periods 9 thru' 11): The feed for this condition was the whole slurry product, collected from Condition #1 of Part I. The simulated third stage was operated at the following conditions (Conditions for the simulated three-stage CSTR system were chosen such that total reaction severity remained the same as the close-coupled two-stage system as in Part I, Condition 2, i.e., the two-stage baseline):

Temperature:	440° C
Space Velocity:	765 Kg/h/M ³ (51 lb mf coal/h/ft ³) Catalyst

Condition #4 (Periods 12 to 13): The process conditions chosen for this condition were identical to Condition 3. However, the feed to this condition was topped separator bottoms from Condition #1 (to remove materials boiling below 343°C).

Operations Summary:

Condition 1 (Run 245-29):

The slurry feed was introduced to the two-stage configuration with very uniform temperature distribution across the catalyst bed (less than 3°C). The unit was operated for seven days continuously before encountering the feed pump outages that caused significant temperature gradients within the reactors. This prompted an early shut-down of the unit. Changing the agitation speed in the reactor had no apparent effects on the significant temperature gradients within them. The Condition 1 of the run 245-29, as per the original run-plan, was to serve to collect the feed materials for the part II (Conditions 3 and 4) of this continuous run. It is estimated at the end of Period 7B that adequate materials are collected (Separator Overhead Oil, Separator Bottoms-PFL and PFS) to last for the three days of continuous operations of Condition 3 and two additional days for the Condition 4. Period 5 normalized yields were worked out as a representation of the Condition 1, in terms of the process performance.

TABLE 18

SIMULATED THREE-STAGE AND STREAM RECONCENTRATION RUN
(Run Conditions: Condition 1)

Periods	1-8
Reactor Type	Two 1-litre CSTR
Mode	(Lee-Faupel-Canas Catalyst cage) Once-Through
Process Conditions:	
Coal Feed:	Illinois No. 6 Crown II Mine (L-811)
Catalyst:	Shell S-317 Ni/Mo 1/32" Extrudate (recovered from 2nd Stage of Run 227-82)
Solvent:	L-802
Solvent/Coal Ratio	1.0
Temperature, ° C	
Reactor #1	400
Reactor #2	429
Space Velocity	
[Kg mf coal/h/M ³ Cat per 1st stage]	765
Flowrates:	
Dry coal, g/h	123
Wet coal, g/h	
@ 3W% moisture	128
Solvent, g/h	128
Total Slurry, g/h	256
Hydrogen, scfh	11

TABLE 19

SIMULATED THREE-STAGE AND STREAM RECONCENTRATION RUN
(Run Conditions: Condition 2,3, and 4)

Lee-Faupel-Canas CSTR Reactor System
Illinois No. 6 Coal (L-811, Crown II Mine)
Spent Shell S-317 Ni/Mo 1/32" Catalyst (227-82-Stage II)

Condition	3	4	2
Run No.	245-30	245-30	245-31
Periods	1-3	4-5	1-3
No. of Reactor	1	1	2
Temperature, ° C			
Reactor #1	440	440	399
Reactor #2	n/a	n/a	440
Space Velocity			
[Kg/Hr/M ³ Cat.	765	510	510
per 1st stage]			
Feed Type	Cond. 1	Cond. 1	coal/L-802
	Whole	Topped	
	Product	Product	
Solvent/Coal Ratio	n/a	n/a	1.0
Flowrates:			
dry coal, g/h	n/a	n/a	82
wet coal (L-811), g/h			
@ 3W% moisture	n/a	n/a	85
solvent (L-802), g/h	n/a	n/a	85
Total Slurry, g/h	n/a	n/a	170
PFL, g/h	150	113	n/a
PFS**, g/h	30	30	n/a
SOH-Oil, g/h	30	0.0	n/a
TBA, g/h	7.0	0.0	n/a
MDS, g/h	8.0	0.0	n/a
Water, g/h	15.0	0.0	n/a
Hydrogen, scfh	8.0	8.0	8.0

* Topped Pressure Filter Liquid (343°C+)

** Toluene Extracted Pressure Filter Cake (Solids)

Shut-down Inspection :

Inspections of both the reactors K-1 and K-2 and the newly modified LFC catalyst baskets therein were made upon the shut-down. The reactor walls, catalyst baskets, and the other internals appeared to be clean and free of any carbonaceous deposits. No coke formation was observed. Some soft coal-oil slush was found accumulated on the top screen of the reactor K-1 basket; this material was confirmed to be unconverted coal in along with some supported catalyst from the reactors.

The average mass balance recovery (Figure 12) for the Condition 1 of the Run 245-29 was about 95 %. As indicated earlier, a loss of volatiles in the cooling system was the main reason for a slightly lower mass balance. The average cooling water temperature had been around 32°C, especially during sub-periods A of the run. In any case, it was expected that the products from Condition 1 collected by the end of Period 7 are adequate for its use as feedstocks for the three-stage and interstage separation testing during Conditions 3 and 4 (Part II) of the run. Coal conversion of between 94-96 W% maf were achieved during the first seven days of operations. The average temperatures of K-1 and K-2 are shown in Figure 13.

Condition 2 (Run 245-31)

The two-stage baseline condition was carried out in Run 245-31 over a period of three days. Similar to the start of Condition 1, the internal temperature distribution was very uniform for the first several hours of operation. At the end of the run, both reactors were inspected. The first stage reactor was clean as in Condition 1. However, solid deposits were found between the cage and the reactor wall in the second stage reactor. The operation conditions are detailed in Table 19. The average mass balance for this run was around 86 W%, probably due to solids accumulation in the second stage reactor.

Conditions 3 and 4 (Run 245-30):

These conditions were the second part (Part II) of the simulated three-stage operations evaluating the impact of interstage separator on the process performance. The feed for this single-stage run, simulating the third stage of a three-stage operation was slurry product collected from Condition 1 (Run 245-29) including the separator overhead oil, pressure filter liquids (full range or topped), and pressure filter cake. Dimethyl disulfide and tert-butyl amine were also added to simulate the vapor phase composition in the third stage reactor. The mass balance, in general, was lower than the norm with an average material recovery of 88 W% over the entire run.

FIGURE 12

RUN 245-29: ADVANCED COAL LIQUEFACTION DAILY MATERIAL RECOVERY BALANCES

FIGURE 13

RUN 245-29: ADVANCED COAL LIQUEFACTION K-1 AND K-2 INTERNAL TEMPERATURES, F

Process Performance

The normalized yields presented in Table 20 are mass and elementally balanced, and where applicable, the ash in the product has been adjusted to the feed ash value. The yields were expressed on the whole feed (coal+slurrying oil to the first stage reactor) weight basis. Since the feed coal to solvent ratio was held constant (in Conditions 1 and 2), and it was a once-through operation, the comparison on the total feed basis is a valid one.

The yield structure of direct coupled two-stage (Case A) and three-stage (Case B) configurations are compared with a three-stage with interstage separation (Case C) in Table 20. Coal conversions for all three cases were high (96% + maf). However, the light gas yields (13-15 W% of feed) were higher than that of the Bench and PDU scale operations under similar conditions. It is speculated that the high gas make were due to the hydrocracking of the slurrying oil. (L-802) and also due to a high relative severity for these tests. As much as 40W% of the total gases were generated from the third stage processing.

Comparing with the base case two-stage configuration (Case A), the three stage operations were of lower thermal severity. Case B, the direct coupled three-stage operation had a relative severity index of 0.64, while for Case C (three-stage with interstage separation), it was 0.87. Although similar coal conversions were obtained for all three cases, the three stage operations gave higher 524°C+ resid conversion (81.4 vs. 83-84.6 W% of feed) and higher C₄-524°C distillate yields (68.9 vs. 70.1-72.9 W% of feed). The main difference between the performances of Cases B and C was the higher degree of cracking observed in Case C. This is reflected by about 2 W% higher yield of light hydrocarbon gases and by a noticeable shift in the boiling range of the distillate products to lower temperatures (lighter distillates). This is illustrated in Figure 14. The yield of light naphtha (C₄-177°C) product, as shown in Figure 14, was 8.2, 14.7, and 35.1 W% for the Cases A, B, and C respectively. Thus, the kinetic advantage of the interstage product separation plus the three stage arrangement was clearly demonstrated.

The analysis of the results obtained during the continuous tests described in this paper shed some light on the merits of the three-stage CSTR processing and the interstage product separation/concentration. Kinetically, both these concepts lead to higher distillate yields and better product quality. The resid conversion and distillate yields were found improved in going from a base-line two-stage close-coupled CTSL operation to a three-stage close-coupled and also to a three-stage with interstage product stream separation configurations. In order to further investigate these processing concepts, it would be necessary to carry out continuous testing which would allow longer time for equilibration and data obtained from such tests will be more consistent and reliable.

TABLE 20

COMPARISON OF DIFFERENT REACTOR CONFIGURATIONS

Coal: Illinois No. 6 Crown II Mine
Solvent: L-802 (from Illinois No. 6 Coal)

Catalyst: Shell S-317 1/32" Extrudates
(Recovered from Bench Run 227-82)

	Case-A 2-Stage Baseline	Case-B 3-Stage Close Coupled	Case-C 3-Stage Inter- stage Separation
A. Conditions:			
Relative Severity	1.00	0.64	0.87
<u>Part I</u>			
First Stage Temp. (deg C)	402	399	399
Second Stage Temp. (deg C)	439	427	427
Coal Space Velocity (Kg/hr/m3 catalyst)	527	790	790
Solvent/Coal	1	1	1
<u>Part II</u>			
Third Stage Temp. (deg C)	N/A	440	440
Space Velocity (Kg/hr/ft3 catalyst)	N/A	790	480
B. Process Performance, W% (Coal plus L-802)			
C1-C3	13.40	13.60	15.10
Other Gases	3.83	4.60	5.03
Water	5.60	5.68	5.80
C4-C7	2.92	3.60	7.23
IBP-177 C	2.75	7.10	17.40
177-260 C	14.90	18.20	10.40
260-343 C	15.40	15.96	16.64
343-454 C	27.26	22.80	14.45
454-524 C	5.45	5.20	3.94
524 C+	11.53	7.12	7.77
Unreacted Coal	2.02	1.73	2.10
H2-Consumption	5.06	5.60	6.10
Coal Conversion, W% maf coal	95.8	96.5	95.8
524 C+ Resid Conversion, W% Feed	81.4	84.6	83.0
C4-524 C Distillate, W% Feed	68.9	72.9	70.1
Hydrodenitrogenation, W%	78.0	80.6	86.5
Hydrodesulfurization, W%	82.0	87.1	89.6

FIGURE 14

COMPARISON OF PROCESS PERFORMANCE:
FOR CASES A, B, AND C

TASK 4. TECHNICAL ASSESSMENT

Theoretical Comparison of Different Reactor Configurations/Processing Schemes

In order to compare the different reactor configurations and processing schemes theoretically, a first-order kinetic model, based on the Bench-scale data was used. Coal and 524°C+ residuum conversions were used as the basis of this comparison. Due to high proportion of the "reactive" fraction in the Illinois No. 6 bituminous coal, the simulated coal conversions for various reactor schemes under consideration were not much different. Due to this apparent insensitivity of the total coal conversion to the processing scheme, only 524°C+ residuum conversions simulated by the model are used as the comparison-basis between different reactor configurations.

The following is the generalized expression for simulating the performance (in terms of either coal or residuum conversion) of any reactor configuration under consideration:

$$F_{Ci} = 1.0 - \left[\frac{(1 - X_D - X_D * R) * (R + 1)^{N-1}}{((1 + R) * (1 - X_D) + k\tau)^N - R * (R + 1)^{N-1}} \right]$$

Where,

F_{Ci} is the fractional conversion of the species "i"

X_D is the fraction of product stream removed (by distillation) from the feed to the Nth reactor

R is the recycle ratio: Vol.flow rate of recycle stream/Vol.flow rate of feed stream

k is the rate constant for disappearance of species "i"

τ is the residence time of species "i" in the reactor system

N is the number of reactor stages (all equal volumes) in series.

[Constraint on simulation: Equal Reactor Stage Volumes and Equal Overall Systems' Volume.]

The results of simulation in terms of the 524°C+ resid conversions are shown in Table 21. These results use the values of kinetic parameters derived for Illinois No.6 coal using the kinetic models based on the bench-scale data. Care has been taken to include data for reactivity under similar process severity conditions. The relative process severity for each individual condition has been defined with respect to the STTUs at a reference condition of reactor temperatures of 399 and 440°C and space velocity of 320 Kg/hr/m³ reactor volume. As shown in Table 21, the three-stage reactor configuration (Case # C)

with almost similar overall reaction severity (the relative STTU is higher since part of the product leaving reactor 2 and entering reactor 3 has been fractionated.) as the two-stage configuration (Case # A), results in about 4-5 W% higher resid conversion. Similarly, Cases D and E clearly show the benefit of interstage separation or product stream concentration, i.e., Cases D and E with 30 W% of product stream from Reactor 2 topped by distillation, show about 6 and 4 W% higher resid conversions than Case C, respectively. Increasing the fraction of product stream that is distilled to remove lighter materials, increases the residuum conversions further.

The experimental evidence to the predictions made by the above simulation was obtained from the continuous scale two/three stage operations described earlier. During these operations also, the three close-coupled CSTR stages and the interstage product stream separation configurations had resulted in an improved kinetics/process performance, even at a slightly lower process severity.

Table 21

COMPARISON OF VARIOUS REACTOR CONFIGURATIONS

ASSUMPTIONS:

Recycle-to-fresh feed = 0.5

All Backmixed Stages

Activation energy = 32 kcal/gmol

Pre-exponential factor=2.86E11

(lb/hr/ft³)

Configuration	Study Case	Reactor Temperature, deg C			lb coal/hr/ft ³ reactor	Distillation Fraction	Relative STTU*	% 524 C+ Residuum Conv. (Predicted)
		Reactor 1	Reactor 2	Reactor 3	Space Velocity			
Two-Stage	A	399	440		20.6	0	1.00	77.4
Three-Stage	B	399	399	440	30.9	0	0.69	74.9
Three-Stage	C	399	429	440	30.9	0	1.18	81.9
Three-Stage with Interstage Sep.	D	399	429	440	30.9	0.3	1.35	88.0
		399	429	440	30.9	0.4	1.45	90.7
		399	429	440	30.9	0.5	1.58	93.7
Three-Stage with Interstage Sep.	E	399	429	432	30.9	0.3	1.15	86.0
		399	429	432	30.9	0.4	1.25	89.0
		399	429	432	30.9	0.5	1.37	92.5

*The relative STTU is based upon a severity index of 40.71 for the reference condition of temperatures of 399 and 440 C and space velocity of 20.6 lb coal/hr/ft³ reactor.

CONCLUSIONS AND RECOMMENDATIONS

The following were the major findings based on the experimental work conducted during this Project:

(I) Incorporation of a fixed bed plug-flow reactor as a "finishing" stage in coal conversion, indicated that at space velocity values greater than a certain (5000 Kg/hr/m²) minimum, fixed bed reactor can be used for coal liquids/slurries in the downflow mode of operation to minimize solid settling and subsequent plugging of the bed. In general, the fixed bed plug-flow type of a reactor was found less forgiving for any pumping/feed problems than a completely backmixed CSTR system, even when used as a "finishing reactor" on a micronized coal slurry feed. Thus, in general, fixed-bed operation was found to have low probability of success even with partially converted slurried due to solids plugging problems.

(II) Three-stage backmixed system of CSTRs was found to be more effective kinetically and resulted in a superior yield structure than a conventional two-stage baseline. A three-stage close-coupled system of CSTRs can be further improved by optimizing the temperatures (or overall process severities) in individual reactor stages.

(III) Interstage product stream separation/concentration was a very successful way of enhancing the overall liquefaction kinetics and therefore, the process performance. Higher coal and resid conversions, and higher distillate yields were obtained with an interstage light ends separator that removed mostly the material boiling below 343°C. It appeared from the experimental work in this Project that with such a process configuration, involving the interstage separation, improvements in the process performance could be obtained even at a reduced overall process severity.

RECOMMENDATIONS

Further studies and development are recommended as follows:

- (1) Investigate the ashy recycle mode of operation in a CTSL configuration.
- (2) Study the interstage product stream concentration/separation concept further to be able to effectively control the yields and product distribution.
- (3) Investigate the multi-stage CSTR in series configuration with a goal of looking for optimum temperatures for the individual reactor stages that will result not only in higher distillate yields but will give better product slate also.
- (4) Investigate the recycle of an intermediate process stream on CTSL process performance.

ATTACHMENT 1

DESCRIPTION OF MICROAUTOCLAVE UNIT

The microautoclave unit (Figure 5) used in this coal program is HRI's fourth generation microreactor. It is constructed of 347 ss and has a 20 cc internal volume, into which the catalyst-charge basket can be inserted. N_2 or H_2 at up to 3000 psig are added to this system through 1/8" O.D. Tubing, which serves both feed and vent lines. The entire assembly is shaken with approximately one-inch strokes at 460 rpms and lowered into a preheated, temperature-controlled sand bath. A cold trap is located in the gas outlet line to collect the material that escapes the reactor when pressure is released at the end of the run. Two identical microautoclave reactor systems are operated side-by-side. Two identical sand baths, which can be heated to different temperatures, can be used to simulate close-coupled two-stage reactions.

ATTACHMENT 2

DESCRIPTION OF THE FIXED-BED UNIT

The test system consists of one or two 3/8" I.D. fixed bed reactors connected in either upflow or downflow mode, *Figure 11*. The reactor(s) was uniformly heated by a fluidized sandbath heater. In the upflow mode of operation the feed slurry was preheated in an downcomer prior to entering the reactor at the bottom location. Contrarily, in the downflow mode the slurry entered the top of the reactor without any preheating. In the latter case the differential temperature between the reactor internal and sandbath heater may be considerable. The slurry feed to the reactor system was provided by a positive displacement metering pump. This pump was initially sized for the lower end of the range of space velocity tested and subsequently boosted to a higher flow range by increasing both the gear ratio and the plunger diameter. Due to the high stoke frequency at high flow rate, there were excessive leakages through the pump packing hence affected the actual flow through the reactor substantially.

ATTACHMENT 3

DESCRIPTION OF ROBINSON-MAHONEY UNIT

This Robinson-Mahoney reactor system at HRI (Figure 15) has two 1000 cc reactors in series, can handle feed rates in the range of 10 to 60 pounds per day. It can operate at temperatures up to 850°F and pressures up to 3000 psig. It is equipped with a catalyst-holding cylindrical basket and a magnetic drive agitator with speed control, a heater with temperature control and an internal thermocouple. This reactor system is frequently used for catalyst testing, feedstock screening, and evaluation of process improvement concepts. It can be used as a single-stage or two-stage system with coal slurry or oil feed stocks. The catalyst basket, that holds up to 150 cc of supported catalyst, and the position of agitators/impellers in the modified Robinson-Mahoney unit is capable of providing reactor hydrodynamics very similar to an ebullated bed reactor and therefore, providing better mixing, slurry circulation, and uniform temperature control. The instrumentation for this unit is designed to require minimal operator attention. The reactor section is preceded by feed preparation and pumping section and is followed by the product separation/recovery section. This unit is capable of giving very tight material recovery balances.

FIGURE 15

ATTACHMENT 4

TABLE OF NOMENCLATURE

ACL	Advanced Coal Liquefaction
CMSL	Catalytic Multi-Stage Liquefaction
CSTR	Continuous Stirred Tank Reactor
CTSL	Catalytic Two-Stage Liquefaction
LFC	Lee-Faupel-Cañas Reactor
PDU	Process Development Unit
PFL	Pressure Filter Liquid
PFS	Pressure Filter Solids
SOH	Separator Overheads