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EDS COAL LIQUEFACTION PROCESS DEVELOPMENT, PHASE V
Final Technical Progress Report—Volume 1

February 1984
Date Submitted

Work Performed Under Contract No. FC05-77ET10069

Exxon Research and Engineering Company
Florham Park, New Jersey

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EDS COAL LIQUEFACTION PROCESS DEVELOPMENT

PHASE V

FINAL TECHNICAL PROGRESS REPORT - VOLUME I

LABORATORY RESEARCH AND DEVELOPMENT
AND
ECLP PROJECT MANAGEMENT, DETAILED ENGINEERING,
PROCUREMENT, CONSTRUCTION, AND OPERATIONS

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Submitted - February 1984

PREPARED FOR
UNITED STATES DEPARTMENT OF ENERGY
UNDER COOPERATIVE AGREEMENT NO. DE-FC05-77ET10069

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United States Department of Energy
Exxon Company, U.S.A.
Electric Power Research Institute
Japan Coal Liquefaction Development Company
Phillips Coal Company
Anaconda Minerals Company
Ruhrkohle AG
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EDS COAL LIQUEFACTION PROCESS DEVELOPMENT - PHASE V
FINAL TECHNICAL PROGRESS REPORT - VOLUME 1
LABORATORY PROCESS RESEARCH AND DEVELOPMENT AND
ECLP PROJECT MANAGEMENT, DETAILED ENGINEERING, PROCUREMENT,
CONSTRUCTION AND OPERATIONS

ABSTRACT

This report is the first volume of the Final Technical Progress Report for U.S. Department of Energy Cooperative Agreement No. DE-FC05-77ET10069 for EDS Coal Liquefaction Process Development in the areas of Laboratory Research and Development and ECLP Project Management, Detailed Engineering, Procurement, Construction, and Operations. Volume II of the Final Report will cover Engineering Research and Development and the Hybrid Boiler Development Program, and Volume III will cover the Toxicology Program and the Bottoms Gasification Program. Funding for the program is shared by the U.S. Department of Energy, Exxon Company, U.S.A. (a division of Exxon Corporation), Electric Power Research Institute, Japan Coal Liquefaction Development Company, Phillips Coal Company, Anaconda Minerals Company, Ruhrkohle AG and ENI. The agreement covers the period January 1, 1977 through December 31, 1985. The Laboratory Process Research and Development studies were conducted at various Exxon Research and Engineering Co. (ER&E) facilities: Research and Development Division at Baytown, Texas; Products Research Division at Linden, New Jersey; and the Exxon Research and Development Laboratories at Baton Rouge, Louisiana. The Engineering Research and Development studies were performed at the Exxon Engineering Petroleum and Synthetic Fuels and Exxon Engineering Technology Departments of ER&E at Florham Park, New Jersey. The information dealing with operation of the 250 T/D Exxon Coal Liquefaction Pilot Plant (ECLP) was generated at Exxon Company, U.S.A., Houston, Texas.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT
LIQUEFACTION PROCESS RESEARCH

1. OPERATION OF THE RECYCLE COAL LIQUEFACTION UNIT (RCLU)

All objectives as described in the EDS Cooperative Agreement for Phases III-B through V have been achieved for the RCLU pilot plants. EDS operations have been successfully demonstrated in both the once-through and bottoms recycle modes for coals of rank ranging from bituminous to lignitic. The bituminous coals studies include Illinois No. 6 from the Monterey No. 1 and Burning Star No. 2 mines, and Pittsburgh No. 8 seam coal from the Ireland and Arkwright mines. Subbituminous coals investigated include Wyoming coal from the Wyodak mine and Australian Black coal from the Wandoan mine. Lignitic coals examined were from the East Texas lignitic deposits, the Big Brown and Martin Lake mines. An extensive data base detailing the effects of process variable changes on yields, conversions and product qualities for each coal has been established. Continuous bottoms recycle operations demonstrated increased overall conversion and improved product slate flexibility over once-through operations. The liquefaction reactor hydrodynamics in RCLU were characterized through tests using radioactive tracers in the gas and slurry phases. RCLU was shown to have longer liquid residence times than ECLP.

Support work during ECLP operations contributed to resolving differences between ECLP conversions and product yields and those of the small pilot plants.

2. OPERATION OF THE ONE TON-PER-DAY COAL LIQUEFACTION PILOT PLANT (CLPP)

All objectives set out in Phases IIIB-V in the EDS Development Program for CLPP were achieved. Integrated EDS operations have been successfully demonstrated for bituminous, subbituminous, and lignitic coals. CLPP product yields confirmed yields from the smaller pilot plants (RCLU's) and verified yields at economically preferred conditions. Naphtha, solvent, vacuum gas oil and vacuum bottoms were generated for product quality testing. A continuous bottoms recycle system was developed for CLPP and used to demonstrate conversion and operability improvements. Recycle conversion of vacuum gas oil into lighter products was demonstrated. The liquefaction reactor hydrodynamics were determined through tests using radioactive tracers in the gas and slurry phases. The overall EDS liquefaction reaction was determined to be exothermic, causing an estimated adiabatic temperature rise in the reacting fluid of 60 to 110°F depending upon the conditions. Examination of reactor solids revealed that significant growth of reactor solids did not occur during bottoms recycle operation. However, calcium carbonate accumulation was observed and was greatest during lignite operations.

3. SOLVENT HYDROGENATION STUDIES

Solvent hydrogenation studies during Phases IIIB-V of the EDS program focused on long term activity maintenance of the Ni-MO-10 catalyst. Process variable studies for solvents from various coals (bituminous, subbituminous, and lignitic), catalyst screening evaluations, and support of ECLP solvent hydrogenation operations.

4. BENCH UNITS, MODELING AND CORRELATION STUDIES

Batch tubing bomb autoclaves and continuous flow reactors were used to provide yield and operability data for a variety of coals. The yield data from the bench scale hydrotreaters and the liquefaction pilot units were correlated to provide models for recycle solvent hydrogenation and liquefaction which were used for process simulation.

5. PRODUCT QUALITY STUDIES

Highly cyclic EDS naphthas represent unique and outstanding catalytic reforming feedstocks. High volumes of high octane motor gasoline blendstock are produced while liberating a considerable quantity of high purity hydrogen. Without external upgrading, EDS distillates satisfy most of the performance characteristics for application as home heating oil and as a stationary gas turbine fuel. The properties of EDS distillates can be enhanced through hydrotreating. While EDS derived fuel oils vary considerably in properties depending on the actual blend components used, they have demonstrated acceptable combustion characteristics. However, several technical concerns with EDS fuel oils have been identified, including relatively high nitrogen content (NO_x emissions), incompatibility with many petroleum products, and handling concerns.

The product quality studies suggest that a product slate consisting of naphtha and distillates is the most desirable, long-range product objective. Properties of EDS naphtha and distillates are essentially independent of liquefaction operating conditions for a given coal, and, with the exception of heterocyclic content, very nearly independent of the coal from which they are derived.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT
BOTTOMS PROCESS RESEARCH

6. COKING AND GASIFICATION STUDIES

Extensive data on coking yields, feed bottoms properties and gasification kinetics were obtained to support the study design of a FLEXICOKING unit and the planning of the prototype pilot plant demonstration.

A study was undertaken to determine the effect of slag chemical corrosion on refractories under conditions expected in a partial oxidation gasifier. Two commercially available refractories were identified which showed good chemical resistance to slag degradation. Slag viscosity and refractory porosity were identified as major factors in determining the rate of refractory decomposition.

Laboratory bench studies were carried out to identify the causes and important process variables responsible for coke formation in the ECLP slurry preheater. A continuous flow unit was developed to simulate ECLP slurry preheater operation. Operation of the unit allowed identification of operating conditions for various feed coals which are conducive to coke formation in the slurry preheater.

The physical and chemical properties of EDS bottoms were characterized in order to provide a basis for bottoms utilization. Bottoms properties were related to processing conditions, feed coal properties and chemical composition of the bottoms.

Studies to determine the feasibility of burning vacuum bottoms to provide process heat or steam showed that bottoms had a higher ignition temperature and burned at a slower rate than the parent coal. The difficulty in burning bottoms is proportional to the extent of conversion and the resulting high percentages of asphaltenes in the bottoms. Fouling rates were close to those of the parent coals.

ECLP PROJECT MANAGEMENT, DETAILED ENGINEERING,
PROCUREMENT, CONSTRUCTION, AND OPERATIONS

1. PROJECT MANAGEMENT
2. ENGINEERING AND PROCUREMENT
3. CONSTRUCTION
4. PREPARATION FOR OPERATIONS

These tasks were completed in 1980 and were reported in the Technical Progress Report entitled, "Construction of Exxon Coal Liquefaction Pilot Plant Final Report, FE-2893-66."

5. OPERATIONS

ECLP was operated on Illinois No. 6 bituminous coal (Monterey No. 1 mine) in both the once-through and bottoms recycle modes, and on Wyoming subbituminous coal (Wyodak mine) and Texas lignite (Martin Lake mine). Data were obtained for a design point for a commercial-sized plant on each of these coal and operating modes. A total of 90,000 tons of coal was processed in 10,692 hours of operation.

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EDS COAL LIQUEFACTION PROCESS DEVELOPMENT - PHASE V
FINAL TECHNICAL PROGRESS REPORT -- VOLUME I
LABORATORY RESEARCH AND DEVELOPMENT,
AND ECLP PROJECT MANAGEMENT, DETAILED ENGINEERING,
PROCUREMENT, CONSTRUCTION AND OPERATIONS

INTRODUCTION

This report is the first volume of the Final Technical Progress Report for the U.S. Department of Energy Cooperative Agreement No. DE-FC05-77ET10069 for the EDS Coal Liquefaction Process Development. This agreement covers the period January 1, 1977 to December 31, 1985, and is a continuation of DOE Contract No. E(49-18)-2353-Phase IIIA covering the period January 1, 1976 to June 30, 1977. The six-month overlap in funding in the first part of 1977 applies to activities related to the 250 T/D Exxon Coal Liquefaction Pilot Plant (ECLP), constructed during Phase IV of the project.

Prior development of the EDS Process was conducted during the ten-year period 1966 through 1975. During this period, the EDS process was selected over several other options as the preferred route to the production of coal liquids. This work was funded entirely by Exxon and was divided into Phase I, the Predevelopment Phase, and Phase II, the Planning and Design Phase. A summary of this work is given in the report, FE-2896-16 "Summary of EDS Predevelopment (1966-1975)." Phase IIIA was a continuation of the Phase I and II programs, and was divided into the following two tasks:

- Laboratory Process Research and Development, and
- Engineering Research and Development

A description of the work performed in Phase IIIA can be found in the EDS Annual Technical Progress Report for January-December 1976 (FE-2353-9) and the EDS Final Technical Progress Report, January 1976 to June 1977 (FE-2353-20). Phase IIIB, which began on July 1, 1977, and Phase IV, which began on January 1, 1978, include the above two tasks as well as tasks relating to project management, detailed engineering, procurement, and construction of ECLP. A final Phase IV report covering the project management, engineering/procurement, construction, and preparation for operations of the large EDS pilot plant (ECLP) at Baytown, Texas, has been issued (Construction of Exxon Coal Liquefaction Pilot Plant, Final Report, March 1981 (FE-2893-66)).

Because the several tasks constituting the EDS program will be completed at different times, the Final Technical Progress Report is being issued in three volumes. This volume, Volume I, covers the tasks of Laboratory Research and Development and ECLP Project Management, Detailed Engineering, Procurement, Construction and Operations. Volume II will cover the Engineering Research and Development and the Hybrid Boiler Development Program. Volume III will cover the EDS Toxicology Program, and the Bottoms Gasification Program.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

LIQUEFACTION PROCESS RESEARCH

1. Operation of Recycle Coal Liquefaction Units (RCLU)

1.1 Introduction and Summary

The Recycle Coal Liquefaction Units are continuous integrated liquefaction units with nominal coal feed rates of 75 pounds-per-day. Each unit consists of a hydrogen feed system, coal slurry feed system, liquefaction reactor, solvent hydrogenation reactor, and product recovery and solvent recycle systems. The flow plan for both units is shown schematically in Figure 1-1. A detailed flow diagram and process description is given in Appendix A of the July 1980-June 1981, EDS Annual Technical Progress Report (FE-2893-74).

The RCLUs are used for feed coal evaluations, process variable studies, and process improvement experiments. During Phases III-B to V of the EDS development program, process variable screening studies with eight different coals were conducted in the RCLUs. Table 1-1 lists the major studies completed during this time, the location of the detailed presentation of results, yield periods completed, and highlights of the results. Four bituminous coals, two subbituminous and two lignitic coals were processed on the RCLUs. Once-through and continuous bottoms recycle experiments were conducted with Illinois No. 6 bituminous coal from Monterey mine No. 1 and Burning Star mine No. 2, Pittsburgh No. 8 bituminous coal from the Ireland mine, Wyoming subbituminous coal from the Wyodak mine, Australian black coal (subbituminous rank) from the Wandooan region, and Texas lignite from the Big Brown and Martin Lake mines. Pittsburgh No. 8 coal from the Arkwright mine was investigated only in the once-through mode.

A total of 176 experimental conditions representing 775 individual yield periods were completed during this time period. ECLP support operations were conducted with Monterey No. 1, Wyodak, and Martin Lake mine coals. Liquefaction reactor hydrodynamics were studied using radioactive tracer tests during Wyodak and Ireland operations. Liquefaction reactor solids characterizations were conducted throughout the program with each coal.

1.2 Sponsor Coal Evaluations

1.2.1 Illinois No. 6 Bituminous Coal (Monterey No. 1 Mine)

Experiments with Illinois No. 6 coal from the Monterey No. 1 mine were conducted on the RCLUs in the once-through and bottoms recycle modes. Coal conversions, yield distributions, and product quality

FIGURE 1-1

RECYCLE COAL LIQUEFACTION UNIT

Table I-1

SUMMARY OF ILLINOIS NO. 6 (MONTEREY NO. 1 MINE) STUDIES

Coal: Illinois No. 6
 Rank: Bituminous
 Mine: Monterey No. 1

Quarterly	Year	Report No.	Study Title	ECLU No.	Series Designation	Yield Periods Reported	Results
2nd	1978	FE-2893-17	Solvent hydrogenation catalyst study	1	CD	489-509	• Results showed that the yield structure and solvent quality with Ni/Mo-10 catalyst were comparable to those obtained using Co/Mo-10 catalyst.
3rd	1978	FE-2893-21	Staged temperature liquefaction study	2	CE	94-97	• Long predissolver (1st reactor) residence times and low temperatures (120 minutes, 700°F) increase total liquid yield.
				2	CH	98-100	
				2	CI	101-102	
4th	1978	FE-2893-25	Liquefaction bottoms recycle study with Illinois No. 6 coal	1	CU	550-554	• Simulated bottoms recycle produced conversions of up to 17 wt % DAF coal higher than coal-only operations with once-through bottoms.
				1	CV	555-556	
				1	CW	557-558	
				1	CX	559-560	• Liquid yield improvements of up to 14 wt % DAF coal were noted with once-through bottoms.
				1	CY	561-563	
				1	CZ	564-568	
				1	C	564-566	• Second pass bottoms yielded lower gains in conversion and liquid yield than once-through bottoms.
3rd	1979	FE-2893-41	Bottoms recycle study in support of CLPP	1	DY	673-674	• CLPP continuous bottoms recycle conversions were lower than expected based on ECLU results.
				1	CV	678-680	
				1	CW	689-701	
				1	V	675-677	• ECLU screening of CLPP coal and bottoms showed no quality problems.
				1	V	681-682	
				1	EC	687-698	• CLPP bottoms recycle contacting facilities were modified to provide better contact between solvent and bottoms.
2nd	1980	FE-2893-53	Illinois (Monterey mine) coal bottoms recycle studies	1	BI	713-736	• Continuous bottoms recycle on ECLU continued to exhibit increased yields, economic incentive defined.
				1	EJ	717-743	
				1	BE	744-746	
				2	BN	106-110	• High pressure bottoms recycle operations improved yield structure.
				2	BO	111-114	
3rd	1980	FE-2893-57	Illinois (Monterey) coal bottoms recycle studies	2	BW	124-139	• Studies at high pressure, high bottoms-to-coal ratio provide understanding of bottoms composition relative to conversion.
				2	BX	140-144	
				2	BY	145-149	
				2	BA	150-156	• Continued process variables studies define economically preferred conditions.
				2	BC	157-161	
4th	1980	FE-2893-64	Illinois (Monterey) coal bottoms recycle studies	2	BH	169-172	• Lowering solvent-to-solids ratio had little effect on total liquid yield. Shifts product slate toward heavier liquids.
				2	BJ	173-176	
				2	BD	162-165	
				2	BE	166-168	• High pressure coal-only experiments define the effect of pressure on coal conversion.
3rd	1981	FE-2893-78	ECLP support studies ECLP support for HVGO feed	1	GN	863-866	• ECLP support studies indicated conversion was lower than ECLU data base for SQL #3.5.
				1	GK	860-862	
				1	GN	868-869	
				1	GH	852-854	• Experiments demonstrated that solvent composition was a function of both liquefaction and hydrotreater conditions.
				1	GE	859	
				1	GR	885-890	
3rd	1981	FE-2893-78	ECLP support studies ECLP support for HVGO feed	1	GT	891-892	• HVGO recycle experiments showed no detrimental effect of HVGO on coal conversion or solvent quality.
				1	GN	867	
				1	GP	870-884	
				1	GE	855-858	
				1	GN	898	
				1	GH	899-901	
				1	GN	893-897	
				1	GN	902-904	
				1	GZ	905-909	
				1	HE	910-914	
				1	HD	915-917	
				1	HE	918-930	

Table 1-1 (Continued)

SUMMARY OF ILLINOIS NO. 6 (BURNING STAR NO. 2) MINE STUDIES

Coal: Illinois No. 6
 Rank: Bituminous
 Mine: Burning Star No. 2

Quarterly	Year	Report No.	Study Title	RCLU No.	Series Designation	Yield Periods Reported	Results
3rd	1979	FE-2893-29	Burning Star coal screening study	1	DA	580-583	<ul style="list-style-type: none"> Burning Star coal conversion and total hydrocarbon yield was considerably lower than Monterey No. 1 coal at similar conditions. Conversion showed very little response to liquefaction residence time in the coal-only mode. Reactor solids accumulations were comparable to other high rank coals.
				1	DB	584-586	
				1	DC	587-589	
				1	DD	590-592	
				1	DE	593-595	
				1	DF	596-598	
				1	DG	599-602	
4th	1981	FE-2893-83	Burning Star mine coal bottoms recycle studies	1	HG	936-940	<ul style="list-style-type: none"> Conversions in the continuous bottoms recycle mode were approximately 5 wt % DAF'less for Burning Star coal than Monterey coal at all conditions. In contrast to coal-only operations, conversion increased significantly with increasing residence time in the bottoms recycle mode. Process variable studies for bottoms recycle operations completed.
				1	HI	941-945	
				1	HK	946-950	
				1	HL	951-955	
				1	HN	959-963	
				1	HR	964	
				1	DA	931-935	
				1	HM	956-958	
4th	1982		Burning Star mine coal Solvent Quality Index study	2	KJ	430-432	<ul style="list-style-type: none"> Coal conversions were constant for a range of solvent quality index from 2.5 to 3.5.
				2	KL	433-436	
				2	KO	437-440	

Table J-1 (Continued)

SUMMARY OF PITTSBURGH NO. 8 (IRELAND AND ARKWRIGHT) MINE STUDIES

Coal: Pittsburgh No. 8
 Rank: Bituminous
 Mine: Ireland

Quarterly	Year	Report No.	Study Title	RCLU No.	Series Designation	Yield Periods Reported	Results
2nd	1978	FE-2893-17	Pittsburgh No. 8 bituminous coal screening study	1	DX	511-515	● Initial studies with Ireland coal showed conversion levels and response trends to liquefaction residence time similar to Illinois No. 6 Monterey coal.
				1	CG	516-517	
				1	CK	518-521	
				1	DT	522-524	
3rd	1979	FE-2893-41	Pittsburgh No. 8 coal process variable studies	1	DT	648-650	● Thorough examination of liquefaction temperature/residence times combination revealed conversion trends similar to those found with Monterey coal.
				1	CK	651-652	
				1	DU	653-654	● Unlike Monterey coal, total liquid yields increased monotonically with increasing residence time.
				1	DV	655-657	
				1	CG	658-660	
				1	DW	661-663	
				1	CN	664-667	
				1	CL	668-671	
				1	DI	672	
				1	CE	683-685	
				1	CK	686-687	
				1	DY	688-689	
				1	DZ	690-692	
4th	1979	FE-2893-45	Pittsburgh No. 8 coal process variable studies	1		693COC	● Liquefaction pressure significantly increased conversion over the range 150-2500 psig.
				1	EA	693-695	
				1	EB	696, 702-704	● Changing hydrogen treat rate from 2 wt % on dry coal to 6 wt % did not affect conversion or total liquid yields; however, yield structure shifted toward lighter products with increasing treat rate.
				1	ED	705-707	
				1	EE	708-710	
				1	EF	711-713	
				1	EF	714-717	● Significant increases in conversion and yields similar to the effects previously demonstrated for Monterey and Wyodak coals were noted over the range of SGL 2 to 4.
				1	EF	718-719	
				1	CL	720-721	
1st	1980	FE-2893-49	Pittsburgh No. 8 coal process variable studies	1	EC	722-726	● Continuous bottoms recycle greatly improved conversion and liquid yields at high pressure compared to coal-only operations.
				1	CL	727-729	
				1	EB	730-732	
4th	1982		Pittsburgh No. 8 bituminous coal bottoms recycle study	1	JO	1048-1051	● Bottoms-recycle at 1500 psig pressure significantly increased conversion over coal-only experiments.
				1	JP	1052-1054	
				1	JQ	1055-1056	● Hydrodynamic studies established the effect of gas velocity on gas phase holdup.
				1	JA	1057-1059	
				1	JS	1060-1061	
				1	JT	1062-1065	
				1	KB	1066-1069	
				1	KD	1070-1073	
				1	KE	1074-1077	● Process variable studies with bottoms recycle completed.
Mine: Arkwright							
3rd	1978	FE-2893-21	Pittsburgh No. 8 bituminous screening study	1	CN	525-528	● Coal conversion during coal-only operations was 5-8 wt % DAF coal less than Ireland coal.
				1	CO	529-531	

Table I-1 (Continued)

SUMMARY OF WYOMING (WYODAK NINE) STUDIES

Coal: Wyoming
Rank: Subbituminous
Mine: Wyodak

Quarterly	Year	Report No.	Study Title	ECLU No.	Series Designation	Yield Periods Reported	Results
3rd	1977	FE-2893-3	Wyoming coal conversions and yields	1	BA	432-434	• More severe liquefaction conditions are required for Wyodak coal than Illinois Monterey coal to achieve the same liquid yields.
4th	1977	FE-2893-7	Liquefaction space time effect on Wyoming coal yields	1	BT	442-447	• Wyoming coal liquid yields at 840°F increases continually with increasing residence time.
			Liquefaction temperature effect on Wyoming coal yields	1	BV	448-451	• Optimum liquefaction residence time for Wyodak coal-only operations was 40-60 minutes.
							• Increasing liquefaction temperature provided the same liquid yield as lower temperatures but with less reactor volume.
1st	1978	FE-2893-12	Wyoming coal solvent quality	1	BN	456-459	• With coal-only operations, conversion and liquid yield are independent of solvent quality above an SGL of 4.0.
			Wyoming coal hydrogen treat rate study	1	BN	460-463	
			Sulfur dioxide pretreatment of Wyoming coal	1	BN	464-467	
				1	BN	468-472	• Reducing hydrogen treat rate from 4 wt % on dry coal to 2 wt % has no significant effect on products.
				1	BZ	473-476	
				1	BZ	477-480	
				1	BV	481-484	• Sulfur dioxide pretreatment of Wyodak coal was unsuccessful in reducing reactor solids accumulation.
				1	BZ	485-488	
				2	BT	79-82	
				2	CC	83-88	
				2	CA	89-90	
				2	CB	94	
				2	SV	91-93	
2nd	1978	FE-2893-17	Wyoming coal process variable study	1	CP	510	• Increasing hydrogen treat rate from 4 wt % on dry coal to 6 wt % has no significant effect upon yields and conversion.
3rd	1978	FE-2893-21	Staged temperature liquefaction study	2	CJ	103-105	• Long predissolver (1st reactor) residence time and low temperatures (110 minutes, 690°F) did not significantly increase total liquid yield.
4th	1978	FE-2893-25	Sulfur dioxide pretreatment of Wyoming coal	1	CE	569-574	• Pretreatment of Wyodak coal with sulfur dioxide followed by mild oxidation with air significantly reduced reactor solids formation with no detrimental effect on yields.
				1	BU	575-579	
2nd	1979	FE-2893-33	Liquefaction bottoms recycle studies	1	DM	603-605	• Simulated bottoms recycle experiment indicated increased conversion and liquid yields with subbituminous Wyodak coal.
				1	DI	610-613	
				1	DJ	617-620	
				1	DL	623-624	• More solvent required for Wyodak bottoms to convert to lighter liquids than required for Illinois Monterey bottoms.
				1	DU	604-608	
				1	DS	609	
				1	DS	614-616	
				1	DE	621-622	
3rd	1980	FE-2893-37	Wyoming (Wyodak) coal bottoms recycle studies	1	EL	747-753	• Continuous bottoms recycle experiments exhibited greatly improved operability and reduced reactor solids accumulation with Wyodak.
				1	EQ	759-764	
				1	EU	770-772	
				1	EZ	773-777	• Conversion and liquid yields were increased significantly with the use of bottoms recycle.
				1	EW	754-758	
				1	ES	765-769	• Higher solvent-to-coal ratio had little effect on conversions. Higher pressure accounted for approximately 5 wt % DAF increase in conversion.
4th	1980	FE-2893-64	Wyoming (Wyodak) coal bottoms recycle studies	2	FE	177-180	• For Wyodak coal during bottoms recycle operations liquefaction temperature affected conversion more than bottoms recycle rates.
				2	FW	181-183	
2nd	1981	FE-2893-74	Wyoming (Wyodak) coal solvent studies	2	FW	206-210	• With bottoms recycle operations conversion was approximately constant over the SGL range of 3-8.
				2	FE	211-215	
				2	FE	216-219	
				2	QC	220-222	
				2	FW	245-249	
				2	GU	250-254	
				2	QC	255-260	
				2	FE	261-263	
				1	FE	845-848	
				1	CP	849-851	
4th	1981	FE-2893-83	ECLP support studies for Wyodak bottoms recycle operations	2	HF	278-282	• Gas Supt Mill processing of Wyodak coal reduced liquefaction conversion 4 wt % DAF.
				2	HN	283-286	
				2	HJ	289-290	
				1	HV	965-968	• Hydrodynamic tests showed that ECLP actual liquid residence time was approximately 55% that of ECLU.
				1	HX	969-972	
				1	HZ	975-976	
				1	IO	973-974	

Table 1-1 (Continued)

SUMMARY OF AUSTRALIAN (WANDOO MINE) STUDIES

Coal: Australian
 Rank: Subbituminous
 Mine: Wandoo

Quarterly	Year	Report No.	Study Title	RCLU No.	Series Designation	Yield Periods Reported	Results
2nd	1979	FE-2893-35	EDS sponsor coal screening	1	DM	625-628	<ul style="list-style-type: none"> Liquid yield at 840°F peaked at a relatively short residence time of 40 minutes with Wandoo coal in the Once-through mode. Solvent balance problems were encountered at high severity temperature-residence time combinations such as 840°F/100 minutes and 880°F/25 minutes. Unit operability was comparable to other subbituminous coals such as Wyodak.
				1	DN	629-631	
				1	DC	632-634	
				1	DE	635-637	
				1	DO	638-640	
				1	DE	641-642	
1st	1981	FE-2893-70	Wandoo coal studies	1	DS	643-647	
				2	FM	184-188	<ul style="list-style-type: none"> Bottoms recycle resulted in increased total liquid yields of up to 9 wt % on a DAF coal basis. High pressure studies showed improved unit operability due to lower bottoms viscosities.
				2	FP	189-193	
				2	FL	198-201	
				2	FS	202-225	
				2	FQ	194-197	

Table 1-1 (Continued)

SUMMARY OF TEXAS (BIG BROWN MINE) STUDIES

Coal: Texas
 Rank: Lignite
 Mine: Big Brown

Quarterly	Year	Report No.	Study Title	ECLU No.	Series Designation	Yield Periods Reported	Results
3rd	1978	FE-2893-21	Texas lignite study	1	CP	532-536	<ul style="list-style-type: none"> • Big Brown solvent yield at 840°F was reduced due to solvent cracking at residence times greater than 40 minutes. • Hydrogen treat rate had little effect on conversion over the range of 4-6 wt % on coal.
				1	CQ	537-539	
				1	CR	540-543	
				1	CS	544-546	
				1	CT	547-549	
2nd	1981	FE-2893-74	Big Brown lignite studies	1	FB	778-784	<ul style="list-style-type: none"> • Increases in C₆-1000°F liquid yields of 10 wt % (DAF coal basis) were obtained with bottoms recycle operations as compared to once-through operations. • An BQI study showed that solvent quality had little effect on conversion with Big Brown coal. • Bottoms recycle operations reduced the total reactor solids accumulation rate significantly, improving operability.
				1	FF	785-790	
				1	FI	792-793	
				1	FL	794-798	
				1	FO	799-805	
				1	FT	806-810	
				1	FV	816-820	
				1	FY	821-825	
				1	GA	826-832	
				1	GB	833-836	
				1	GD	837-840	
				1	GE	841-844	
				1	GC	791	
				1	FU	811-815	

Table 1-1 (Continued)

SUMMARY OF TEXAS (MARTIN LAKE MINE) STUDIES

Coal: Texas
 Rank: Lignite
 Mine: Martin Lake

Quarterly	Year	Report No.	Study Title	RCLA No.	Series Designation	Yield Periods Reported	Results
1st	1982	FE-2893-89	Texas lignite (Martin Lake mine) bottoms recycle studies	1	IF	979-982	<ul style="list-style-type: none"> Product yields and conversion observed for Martin Lake coal were comparable to those observed with Texas lignite from the Big Brown mine at similar conditions. High bottoms ash content resulted in high viscosities.
				1	IH	983-936	
				1	II	987-990	
				1	IJ	991-994	
				1	IE	995-996	
3rd	1982	FE-2893-99	Martin Lake lignite screening study	1	IK	997-998	<ul style="list-style-type: none"> Experiments demonstrated that changes in hydrogen pressure over the range of 1500-2500 psig had an insignificant effect on conversion with Martin Lake. Increasing bottoms-to-coal ratio from 0.5 to 1.0 at 820°F/40 minutes resulted in a large increase in conversion (10 wt % DAP). Solvent quality experiments showed that Martin Lake was insensitive to SQI in the range of SQI from 2.6 to 4.8. Lower ash feed coal resulted in lower viscosity bottoms.
				1	IK	1012-1014	
				1	JD	1015-1018	
				1	JF	1019-1022	
				1	JG	1023-1027	
				1	JH	1028-1032	
				1	JJ	1033-1037	
				1	JL	1038-1040	
				1	JM	1041-1044	
				1	JN	1045-1047	

information were reported for 210 individual yield periods representing a total of 43 different experimental operating conditions. Table 1-1 details the highlights of the experiments conducted.

The initial operations with Monterey coal during Phase III-B of the EDS Cooperative Agreement were conducted during the 2nd quarter of 1978. The experiments addressed the effects of using a Ni/Mo-10 hydrogenation catalyst, rather than Co/Mo-10 hydrogenation catalyst, on solvent quality and liquefaction yield structure. The data indicated that the catalysts were comparable in both solvent quality maintenance and effect upon yield structure.

Additional studies during the 3rd quarter of 1978 focused on the use of staged temperature liquefaction. The use of a low temperature reactor stage to enhance the dissolution of the coal by the recycle solvent was believed to favor production of additional coal liquids in the second reactor stage. Early staged temperature liquefaction studies with Monterey No. 1 mine coal showed no increase in liquid yields at short predissolver residence times. Bench scale studies demonstrated that longer residence times were needed in the low temperature first reactor to obtain measurable liquid yield improvement. Predissolver conditions of 700°F and 120 minutes nominal residence time were selected and resulted in a 4 wt% dry, ash-free coal (DAF) increase in total liquid yield. Additionally, hydrogen consumption per barrel of liquid product was less for staged temperature liquefaction at low predissolver temperature compared to single stage liquefaction hydrogen consumption.

Successive studies with Monterey No. 1 coal from the 4th quarter of 1978 through the 4th quarter of 1980 investigated the effects of liquefaction bottoms recycle on yields and product quality. Initial scoping studies conducted on RCLU simulated bottoms recycle using once-through liquefaction bottoms from CLPP rather than continuous recycle. The objective of this study was to obtain yield data as rapidly as possible without significant unit modifications and to establish an economic incentive for bottoms recycle. Increases in conversion of up to 17 wt% DAF coal were observed, along with an increase in C₄-1000°F total liquids of 14 wt% DAF coal for once-through liquefaction bottoms. Second pass recycle bottoms exhibited decreased yields based on 1000°F+ bottoms fed. These encouraging results prompted some slight modifications to the RCLU's operational procedures to permit continuous bottoms recycle.

During the 3rd quarter of 1979, yield data obtained on the CLPP with continuous recycle of vacuum tower bottoms indicated lower than expected conversions with Monterey Mine coal. In support of the CLPP bottoms recycle operations, simulated bottoms recycle experiments were conducted in RCLU. The objective of these studies was to address whether the low CLPP conversions were due to the quality of the feed coal, quality of the CLPP bottoms, or CLPP unit problems. This study eliminated feed coal quality and CLPP recycle bottoms quality as being significant factors in the lower than expected conversion experienced on CLPP. As a result, the CLPP bottoms recycle system was modified to insure better contacting between vacuum bottoms and solvent.

Following recommissioning and unit validation during the second quarter of 1980, RCLU-2 was used to study continuous bottoms recycle with Monterey coal at low temperature and long nominal slurry residence time (800°F, 120 minutes). RCLU-1 was used for a similar study, but at higher temperature and shorter residence time (840°F, 60 minutes). Conversion and liquid yield were found to increase substantially for bottoms recycle operation at higher pressure (2000 and 2500 psig), when compared to lower pressure coal-only operations. Experiments also demonstrated that gas make could be controlled by operating at lower temperature/longer residence time combinations. Higher pressure operations produced bottoms with lower viscosity and increased asphaltene content, resulting in improved unit operability.

Experiments during the third quarter of 1980 investigated continuous bottoms recycle at high pressure (2000-2500 psig) and high bottoms-to-coal ratios of 1.0-1.5. Nominal residence time and solvent-to-coal ratios were varied between 60 and 100 minutes and 1.8/1 to 3/1, respectively. The results indicated significant increases in coal conversion and liquid yields with bottoms recycle over once-through operations. Increases in conversion with bottoms recycle were due to the net transformation of pyridine soluble portions of the bottoms to lighter products.

Continuous bottoms recycle operations with Monterey No. 1 coal were concluded in RCLU during the second quarter of 1980. The final experiment examined the effect of low solvent-to-solids ratio (1.2/1/0.5 solvent-to-coal-to-bottoms proportions). The primary result of the lower solvent-to-solids ratio was to shift the product slate toward heavier liquids. High pressure coal-only experiments were also conducted to determine the portion of the increased yield associated with bottoms recycle that is due to the higher pressures utilized during bottoms recycle experiments. Overall conversion and liquid yields were found to be ~3 wt% DAF higher due to the higher pressure (2000-2500 psig) relative to 1500 psig hydrogen pressure.

Experiments in support of Illinois No. 6 Monterey mine coal operations in the 250 ton-per-day EDS Coal Liquefaction Plant (ECLP) were conducted during the third quarter of 1981 in RCLU. These experiments were conducted to aid in assessing differences between ECLP yields, conversions and solvent quality from the historical small pilot plant data base. Additional details on the scope and results of ECLP studies with Monterey No. 1 coal can be found in Section 1.5.1.

Figure 1-2 shows hydrocarbon yield distributions for selected Monterey coal operations and illustrates the product slate flexibility of the EDS process. High naphtha selectivity was realized at high liquefaction reactor temperatures with bottoms recycle. High distillate selectivity was demonstrated at low liquefaction reactor temperature/long residence time combinations.

FIGURE 1-2
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED
RCLU MONTEREY COAL EXPERIMENTS

700 - 1000°F 400 - 700°F C4 - 400°F C1 - C3
 GAS OIL DISTILLATE NAPHTHA GAS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, °F 840
 H2 PRESSURE, PSIG 1500
 NRT, MINUTES 40
 S/C/B, BY WT. 1.6/1/0
 H2 TREAT, WT% ON COAL 4
 RCLU NO. 1
 YIELD PERIODS 863-866

64
 800
 2000
 100
 1.2/1/0.5
 6
 2
 173-176

72
 840
 2000
 60
 2.5/1/1
 6
 2
 150-156

1.2.2 Illinois No. 6 Bituminous Coal (Burning Star No. 2 Mine)

Operations with Illinois No. 6 coal from the Burning Star No. 2 mine were conducted on the RCLU in both once-through and bottoms recycle modes. Yield and product quality information at 14 different operating conditions for a total of 57 yield periods was obtained.

During the first quarter of 1979 a limited screening study was conducted to determine the response of Burning Star mine coal to the EDS process in the once-through mode. Liquefaction yields and unit operability were investigated as a function of liquefaction temperature (800, 840, and 880°F), nominal slurry residence time (25, 40, and 100 minutes), and solvent-to-coal ratio (1.6, 2.0). Over the range of conditions studied, the conversion and total C₄-1000°F, liquid yield for Burning Star coal were considerably lower than for Illinois No. 6 coal from the Monterey No. 1 mine. Also, in contrast to Monterey coal at 840°F, conversion showed very little response to increased liquefaction residence time. Consequently, as residence time was increased, C₄-1000°F total liquid yield decreased due to increased product cracking to C₁-C₃ gas.

Operability with Burning Star No. 2 coal was very smooth and comparable to previous RCLU experience with higher rank coals. No plugging problems were experienced in the liquefaction reactor or the residual bottoms accumulator.

Continuous bottoms recycle experiments with Burning Star coal were conducted in the fourth quarter of 1981 on RCLU. The response of Burning Star to changes in process variables such as liquefaction temperature, residence time, pressure, and bottoms-to-coal ratio paralleled responses observed with Monterey No. 1 coal. However, coal conversion in all cases was about 5-6 wt% less on a DAF coal basis for Burning Star coal when compared to Monterey coal at similar conditions (Figure 1-3). Operability in the continuous bottoms recycle mode was excellent, primarily due to the favorable bottoms compositions and low viscosities. Experiments conducted during the fourth quarter of 1982 showed no significant change in conversion due to low solvent quality with Burning Star No. 2 coal in the range of solvent quality index of 2.5 to 3.5. The liquid product slate was slightly heavier for a lower solvent quality index.

Figure 1-4 illustrates the effect of pressure and bottoms-to-coal ratio on the conversion and hydrocarbon yield of selected Burning Star coal experiments.

1.2.3 Pittsburgh No. 8 Bituminous Coal (Ireland Mine)

Once-through and bottoms recycle experiments were conducted with Pittsburgh No. 8 Ireland mine coal in RCLU. Coal conversion, yield slate, and product quality data were obtained for 94 yield periods at 30 separate experimental operating conditions. Table 1-1 details the highlights of the experiments conducted.

FIGURE 1-3

CONVERSION COMPARISON BETWEEN BURNING STAR COAL AND
THE SEMI-EMPIRICAL LIQUEFACTION MODEL FOR MONTEREY COAL

FIGURE 1-4
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED
RCLU BURNING STAR COAL EXPERIMENTS

In the second quarter of 1978, a limited screening study to determine the response of Pittsburgh Ireland coal to the EDS liquefaction process was carried out. The effect of varying nominal slurry residence time (25, 40, 60 minutes) at 840°F in the coal-only mode was determined to yield approximately the same conversion and liquid yields as Monterey mine coal. Operations were extremely smooth at all study conditions and were comparable to those experienced with Illinois No. 6 bituminous coal.

A more extensive study on the effects of liquefaction temperature and nominal residence time was conducted in the third quarter of 1979. At each nominal residence time investigated (25, 40, 60 and 100 minutes), three experiments were conducted at liquefaction temperatures of 800, 840, and 880°F (except for the 880°F, 100 minute and 800°F, 25 minute combinations). Conversion data for Ireland coal were similar to those obtained with Monterey coal at the same liquefaction conditions. However, liquid yields from Ireland coal showed a different trend from that observed with Monterey coal. Throughout the range of conditions studied, total liquid yield increased monotonically with increasing residence time, whereas Monterey liquid yields went through a maximum and began to drop beyond residence times of 40 minutes. Trends of other yields, such as C₁-C₃ gas make and hydrogen consumption, were similar to trends previously observed for Monterey coal.

Studies in the final quarter of 1979 thoroughly examined the effects of liquefaction pressure (750, 1000, 1500 and 2500 psig), hydrogen treat rate (2, 4 and 6 wt% on coal), and solvent quality index (1.9, 2.4, 3.3, and 4.3 SQI). Variations in hydrogen pressure were found to have significant effects on liquefaction yields, as well as unit operability. The data showed that coal conversion increased monotonically as pressure increased, although the rate of increase in conversion decreased as pressure increased. Total C₄-1000°F liquid yield also increased with increasing pressure. Liquefaction pressure had a significant effect upon unit operability. Runs at low pressures of 500 and 750 psig ended prematurely, presumably due to excessive liquid vaporization.

Results from the hydrogen treat rate study indicated essentially no differences in total C₁-C₃ gas, C₄-1000°F total liquid, or bottoms yields as a function of hydrogen treat rate. Increasing hydrogen treat rate does, however, appear to shift the distribution of liquid products toward more naphtha (C₄-400°F) and less distillate (400°F+). Variation in solvent quality over the SQI range from 2 to 4 resulted in significant increases in coal conversion and liquid yields that were qualitatively similar to the effects previously demonstrated for Monterey and Wyodak coals. This effect is shown in Figure 1-5. Low solvent quality did not appear to have any deleterious effects on unit operability.

Shakedown of continuous bottoms recycle operations was conducted during the first quarter of 1980 with Ireland mine coal to assess the feasibility of continuous, steady state bottoms recycle operations on RCLU. Section 1.3 of this report outlines the procedures used and results of these

FIGURE 1-5

EFFECT OF SOLVENT QUALITY ON IRELAND COAL CONVERSION

initial continuous bottoms recycle studies. Two different combinations of pressure and solvent-to-coal-to-bottoms ratio were investigated at liquefaction conditions of 840°F, 100 minutes nominal residence time and 4 wt% H₂ on coal. Little effect of bottoms recycle on yield distribution was observed at 1500 psig compared to coal-only operations at similar conditions. At 2500 psig bottoms recycle operations, significant increases were observed for gas (C₁-C₃), naphtha (C₄-400°F), total liquid (C₄-1000°F) yields and conversion, when compared to once-through operations at similar conditions. Also, product selectivity was shifted significantly toward lighter products. Bottoms viscosity decreased and asphaltene content increased with increasing hydrogen pressure, resulting in better overall unit operations at 2500 psig.

Experiments in the fourth quarter of 1982 were to provide process variable responses for bottoms recycle operations. This information was used to extend the data base for the semi-empirical liquefaction model and aid in determining the economically preferred liquefaction conditions for Ireland coal. The initial experiment during this study was conducted at low pressure (1500 psig). The results of the fourth quarter 1982 study suggest that low pressure bottoms recycle does increase conversion over the comparable once-through case and that, in the previously conducted experiments, severe liquefaction conditions (840°F, 100 minutes) resulted in regressive reactions (Figure 1-6); and thus low conversion.

Three experiments that were part of the RCLU reactor characterization program were also conducted during these Ireland studies to determine the effect of superficial gas velocity on gas hold-up and actual slurry residence time. Discussion of these hydrodynamic studies can be found in Section 1.6.

Figure 1-7 shows hydrocarbon yield distributions for selected Ireland coal experiments which illustrate the flexibility of the EDS process to produce the desired liquid product slate.

1.2.4 Pittsburgh No. 8 Bituminous Coal (Arkwright Mine)

Two once-through liquefaction experiments with Pittsburgh Arkwright mine coal were conducted on RCLU immediately following the second quarter 1978 Pittsburgh Ireland studies. A total of seven yield periods, as detailed in Table 1-1, were obtained. Arkwright mine coal was not a sponsor-selected coal, but was studied briefly because of delays in obtaining the Ireland mine coal.

In comparison to Ireland mine coal, Arkwright mine coal was considerably more difficult to convert. For the two operating conditions studied, the conversion and C₁-1000°F hydrocarbon yield for Arkwright were 5-8 wt% DAF less than either Ireland or Monterey No. 1 at equivalent liquefaction conditions. Figure 1-7 compares the relative hydrocarbon distribution of Arkwright and Ireland coal in the once-through mode.

FIGURE 1-6

RESPONSE OF PYRIDINE INSOLUBLE PRODUCT
TO RECYCLE OF IRELAND COAL BOTTOMS

FIGURE 1-7

HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED
RCLU IRELAND AND ARKWRIGHT EXPERIMENTS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, °F

H₂ PRESSURE, PSIG

NRT, MINUTES

S/C/B, BY WT.

H₂ TREAT, WT% ON COAL

RCLU NO.

YIELD PERIODS

50

55

66

72

840

840

840

840

1500

1500

2000

2000

60

60

60

60

1.6/1

1.6/1

1.2/1/0.5

1.2/1/1

4

4

8

8

1

1

1

1

529-531

651-652;686-687

1066-1069

1070-1073

Arkwright mine coal bottoms showed slightly higher viscosities than either Ireland or Monterey coal. These viscosities were still lower than those observed with lower rank coals and did not suggest operability problems.

1.2.5 Wyoming Subbituminous Coal (Wyodak Mine)

Once-through and bottoms recycle operations were conducted with Wyoming Wyodak coal on the RCLUs. Yield and product quality information were obtained for 221 yield periods, representing 42 different experimental operation conditions. Descriptions of the experiments conducted and highlights of experimental results are included in Table 1-1.

Experiments with Wyodak coal during the third and fourth quarters of 1977 focused on the effects of liquefaction severity for once-through liquefaction. Liquefaction conversion and product yield structure were investigated at higher severity conditions by increasing nominal slurry residence time from 25 to 100 minutes and by increasing liquefaction temperature from 840 to 880°F. Over this broad range of conditions, Wyodak coal conversions were greater than Illinois No. 6 Monterey coal due to higher water and carbon oxides yields. In contrast, C₄-1000°F liquid yield for Wyodak coal was lower than for Illinois coal at equivalent conditions. However, C₄-1000°F liquid yield at 840°F increases asymptotically with increasing residence time. This is in contrast to liquid yield from Illinois No. 6 bituminous coal, which exhibited a maximum within the same range of residence times. Increasing liquefaction temperature from 840 to 880°F allowed at least a two-fold reduction in the liquefaction residence time required to obtain the same liquid yield as at 840°F. Residual bottoms viscosity and pyridine extraction data also indicated that Wyoming coal required more severe liquefaction conditions to facilitate residual bottoms handling equivalent to that of Monterey coal.

Extensive studies with Wyodak coal from once-through liquefaction were conducted during the first quarter of 1978 to investigate the effects of solvent quality, hydrogen treat rate, and sulfur dioxide pretreatment of coal. The effect of the solvent quality index on once-through liquefaction conversion and product yield structure was investigated by varying the solvent quality index between 2 and 8. The remaining process variables were held constant at 840°F liquefaction temperature, 1500 psig pressure, and 4 wt% H₂ treat rate for 25 and 60 minutes nominal residence times. Coal conversion and liquid yield were shown to be independent of solvent quality above 4.0 SQI. As SQI decreases below 4.0, both conversion and liquid yield decrease significantly. This response is similar to that seen with Illinois No. 6 coal (Figure 1-5). In a hydrogen treat rate experiment the molecular hydrogen treat rate to the liquefaction reactor was reduced from 4 wt% to 2 wt% on dry coal, respectively. Unit operability with 2 wt% hydrogen treat was comparable to that at 4 wt% hydrogen treat rate. The data indicated no significant effect on yields or conversion as a result of decreasing the hydrogen treat rate at the study conditions.

Operability with Wyoming Wyodak coal for once-through liquefaction in RCLU generally was relatively poor due to high reactor solids accumulation rates. A coal pretreatment experiment was conducted which removed calcium to test the effect of reducing reactor solids accumulation. Pretreatment with sulfur dioxide (SO_2) showed partial success in preventing calcium carbonate scale formation in RCLU runs. Reactor scale formation was reduced substantially, but not eliminated, in only one out of four runs. Yields were similar to those from untreated Wyoming coal, except for slightly higher hydrogen sulfide and water makes due to the pretreatment step.

Experiments to reduce the reactor solids accumulation and improve unit operability with Wyodak coal were conducted again during the fourth quarter of 1978. The pretreatment of the coal with sulfur dioxide (SO_2) in this set of experiments included a mild oxidation step to stabilize the sulfite salt formed during pretreatment. The SO_2 /air pretreatment was successful in reducing calcium carbonate (CaCO_3) scale formation one hundred-fold compared to that from untreated Wyodak coal (less than 0.001 lbs per ton of coal fed). A similar decrease in CaCO_3 content of the free-flowing reactor solids was found. The pretreatment had no detrimental effect on conversion or liquid yield compared to untreated coal.

During the second and third quarters of 1978, two once-through liquefaction experiments were completed with Wyodak coal. The first determined that increasing hydrogen treat rate to 6 wt% on dry coal did not significantly affect the conversion or yields. The second experiment involved staged temperature liquefaction of Wyodak coal, as previously discussed in Section 1.2.1 for Monterey coal. The primary objective was to improve liquid yield by the use of a predissolver stage at low temperature and long residence time (700°F , 120 minutes). The data from staged temperature liquefaction of Wyodak coal showed no significant increase in either conversion or total liquid yield at the study conditions.

Simulated bottoms recycle studies with Wyodak coal were conducted during the second quarter of 1979. Process variables during this study were nominal liquefaction residence time (25 and 60 minutes) and solvent-to-coal ratio (1.6 and 2.4). Bottoms-to-coal ratio was held constant at 0.5. The experiments indicated what Wyodak bottoms recycle required more solvent than Monterey bottoms recycle for significant conversion of the bottoms to lighter products. A 2.4/1/0.5 solvent-to-coal-to-bottoms ratio was required with Wyodak to obtain the same level of bottoms conversion as Monterey coal with 1.6/1/0.5 solvent-to-coal-to-bottoms proportions at the study conditions.

Continuous bottoms recycle studies with Wyodak coal in the third quarter of 1980 demonstrated a significant increase in unit operability over once-through operations. The average run length increased from 65 hours for once-through to 230 hours with bottoms recycle. Inspection of liquefaction reactor residues revealed that reactor solids accumulation for bottoms recycle operations was about half that for once-through operations. Continuous bottoms recycle with Wyoming subbituminous coal during this period showed that significantly increased conversion and liquid yields can be obtained with lower rank subbituminous coals. Liquefaction

conditions during these experiments were varied from 775-840°F, 2000-2500 psig, and 40-140 minutes nominal residence time. The higher liquefaction temperatures significantly shifted the product slate toward the lighter products, and therefore, produced more C₁-C₃ hydrocarbon gas and C₄-400°F naphtha. These results indicated that bottoms recycle operations not only result in increased conversions but also can provide greater product flexibility.

Two coal-only experiments were also run in the third quarter of 1980 to evaluate the effects of higher hydrogen pressure (2500 psig) and higher solvent-to-coal ratio (3/1) on liquefaction yields in the absence of bottoms recycle. The increased solvent-to-coal ratio provided no additional liquids yield or conversion. Increasing pressure from 1500 to 2500 psig increased coal conversion 5 wt% DAF.

Previous coal-only operations indicated that liquefaction yields were independent of solvent quality at SQI above 4. Experiments conducted during the second quarter of 1981 were run to determine if similar solvent quality effects existed with Wyodak bottoms recycle operations. The SQI was varied from 3 to 8 for the study. The bottoms-to-coal ratio was 0.5 and other nominal liquefaction conditions were maintained at 840°F, 40 minutes nominal residence time, 2000 psig, and 6 wt% H₂ treat rate on dry coal. The conversion was insensitive to SQI throughout the range from 3 to 8. Total liquid yield response to SQI was similar to that of conversion.

Final operations with Wyoming Wyodak coal in support of the 250 ton-per-day Exxon Coal Liquefaction Plant (ECLP) were conducted during the fourth quarter of 1981. Details of these experiments can be found in Section 1.5.2.

Figure 1-8 shows hydrocarbon yield distributions for selected Wyodak coal experiments illustrating the effect of key process variables on product distributions.

1.2.6 Australian Black Subbituminous Coal (Wandoan Mine)

Liquefaction of Australian subbituminous coal from the Wandoan mine was conducted in both the once-through and bottoms recycle modes. A total of 45 yield periods at 12 different operating conditions were reported, as detailed in Table 1-1.

The initial screening study with Wandoan coal in the second quarter of 1979 focused on evaluating the response of Wandoan coal to the EDS process for once-through operations. Variables investigated included liquefaction temperature (800, 840 and 880°F), nominal slurry residence time (25, 40 and 100 minutes), and hydrogen pressure (1500 and 2500 psig). The coal used for this study was not cleaned, and contained about 20 wt% ash. This resulted in relatively high bottoms viscosities compared to Wyodak subbituminous coal

FIGURE 1-8
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED
RCLU WYODAK COAL EXPERIMENTS

700 - 1000°F	400 - 700°F	C4 - 400°F	C1 - C3
GAS OIL	DISTILLATE	NAPHTHA	GAS

DAF CONVERSION	57	63	62	73
LIQUEFACTION CONDITIONS				
TEMPERATURE, °F	840	840	820	840
H2 PRESSURE, PSIG	1500	2000	2000	2500
NRT, MINUTES	40	40	80	40
S/C/B, BY WT.	1.6/1/0	1.6/1/0.5	1.6/1/0.5	3/1/1
H2 TREAT, WT% ON COAL	4	6	6	6
RCLU NO.	2	2	2	1
YIELD PERIODS	84	261-263	278-282	773-777

bottoms. Nominal residence time experiments showed that at 840°F liquefaction temperature total liquid yield peaked at 35 wt% DAF coal for the relatively short residence time of 40 minutes for Wandoan coal. Raising liquefaction pressure at 840°F and 40 minutes increased overall conversion 2 wt% on a DAF coal basis, but the primary effect was to shift the liquid product slate to heavier liquids due to suppression of cracking reactions.

During liquefaction at 840°F and 1500 psig, solvent cracking was significant for nominal residence time exceeding 40 minutes, and solvent balanced operations with Wandoan coal became difficult for 100 minutes nominal slurry residence time. Similar solvent balance concerns were apparent at 880°F and 25 minutes. Maximum liquid yields in the once-through mode were found to occur at low temperature, high residence time conditions (800°F/100 minutes). Unit operations and liquefaction reactor solids accumulations were similar to those observed with Wyodak coal.

Studies with Wandoan coal during the first quarter of 1981 focused on the effects of continuous bottoms recycle and coal cleaning. Liquefaction variables investigated were temperature, nominal slurry residence time, hydrogen pressure, and solvent-to-coal ratio. Reducing the coal ash content by cleaning operations did not have any effect on coal conversion or product slate. The lower ash content of the feed coal resulted in lower bottoms ash content and thus lower viscosities. Conversion increases of up to 9 wt% (DAF coal) were identified for bottoms recycle operations compared to coal-only operations. In addition, high pressure bottoms recycle operations resulted in good unit operability because of low viscosity, high asphaltene content bottoms.

Figure 1-9 compares hydrocarbon yield distributions for related Wandoan coal experiments.

1.2.7 Texas Lignite (Big Brown Mine)

RCLU experiments with Texas lignite from the Big Brown mine were conducted in both the once-through and bottoms recycle modes. Complete product quality and yield information were obtained for 85 yield periods at 19 different operating conditions, as highlighted in Table 1-1.

Operations with Big Brown lignite in the once-through liquefaction mode were conducted in the third quarter of 1978 to investigate the liquefaction process variable response of a lignitic coal. Experiments were conducted at liquefaction temperatures of 800 and 840°F with nominal slurry residence times ranging from 25 to 100 minutes. Conversion for Big Brown was lower than for Wyodak coal at comparable liquefaction conditions, but paralleled the Wyodak coal conversion response to liquefaction residence time. The C₄-1000°F liquid yield for Big Brown decreased by 4 wt% on DAF coal as nominal residence time increased from 40 to 100 minutes at 840°F. A significant increase in C₁-C₃ gas yield for Big Brown lignite at 100 minutes residence time indicated that solvent cracking was responsible for liquid yield loss.

FIGURE 1-9
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED
RCLU WANDOAN COAL EXPERIMENTS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, °F	840	840	800
H ₂ PRESSURE, PSIG	1500	2000	2500
NRT, MINUTES	40	40	100
S/C/B, BY WT.	1.6/1/0	1.2/1/0.5	1.6/1/1
H ₂ TREAT, WT% ON COAL	4	6	6
RCLU NO.	1	2	2
YIELD PERIODS	625-628	202-205	189-193

Unit operability with Big Brown lignite in the coal-only mode at low pressure was very similar to that experienced with the other low rank coals run in RCLU. Liquefaction reactor and downstream separator line plugs were experienced. Calcium carbonate formation as wall scale and oolites were found in the liquefaction reactors following the Big Brown lignite runs and were very similar in composition to those from Wyodak coal runs.

Studies during the second quarter of 1981 were conducted in both the bottoms recycle and coal-only modes. Liquefaction temperature, nominal residence time, solvent-to-coal-to-bottoms proportions, and SQI effects on process yields were investigated. Increases in $C_4-1000^{\circ}\text{F}$ total liquid yields of up to 10 wt% (DAF coal basis) were obtained with bottoms recycle operations compared to once-through operations. Trends observed with Big Brown coal in response to liquefaction process variable changes paralleled the trends seen with other low rank coals, such as Wyodak. An SQI study for bottoms recycle operations determined that conversion was not significantly influenced by solvent quality. Considerable variability in feed coal ash content (9 to 18 wt%) was observed during these studies. This ash variability made steady state operations difficult to attain and resulted in larger than normal standard deviations for the series averaged yields. This caused difficulties in data interpretation.

Unit operations were generally smooth during bottoms recycle operations. Inspections of liquefaction reactor residues from bottoms recycle operations on Big Brown lignite showed that the CaCO_3 accumulation rate for bottoms recycle operations was about 40% of that for coal-only operations. The accumulation of free flowing solids was substantially reduced, while that of wall scale increased slightly.

Figure 1-10 illustrates the effect of bottoms-to-coal ratio on coal conversion and hydrocarbon yield distribution for Big Brown coal.

1.2.8 Texas Lignite (Martin Lake Mine)

Screening studies with Texas lignite from the Martin Lake mine were conducted on the RCLUs in the once-through and bottoms recycle modes. Yield data and product quality information were obtained for 56 yield periods at 14 different operating conditions, as shown in Table 1-1. The Martin Lake mine was selected as the source of low rank coal for ECLP operations late in 1981 due to the unavailability to the EDS program of Texas lignite from the Big Brown mine.

The initial screening studies in the first quarter of 1982 were conducted in the continuous bottoms recycle mode to investigate the effects of bottoms-to-coal ratio, slurry residence time, and liquefaction reactor temperature. The objective was to identify potential ECLP operating conditions for lignitic coal. Coal ash during these first series of experiments was about 20 wt% and showed considerable variability. Thus, as with Big Brown lignite, larger than normal standard deviations for the series averaged yields were obtained.

FIGURE 1-10
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED
RCLU BIG BROWN COAL EXPERIMENTS

700 - 1000°F 400 - 700°F C4 - 400°F C1 - C3
 GAS OIL DISTILLATE NAPHTHA GAS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, °F

H2 PRESSURE, PSIG

NRT, MINUTES

S/C/B, BY WT.

H2 TREAT, WT% DN COAL

RCLU NO.

YIELD PERIODS

59
 840
 1500
 40
 1.6/1/0
 4
 1
 532-536

71
 840
 2000
 40
 1.35/1/0.5
 6
 1
 816-820

75
 840
 2000
 40
 1.6/1/1
 6
 1
 806-810

The initial experiments in the first quarter of 1982 with high ash coal showed total liquid yield and conversion responses similar to Big Brown coal. However, the dramatic increase in solvent cracking at nominal slurry residence times greater than 40 minutes and 840°F that was seen with Big Brown lignite was not observed with Martin Lake coal. Thus, solvent balanced operations were easily achieved at all temperature/residence time combinations examined with Martin Lake coal. High bottoms ash content resulted in high viscosities. However, no viscosity-related unit problems were evident.

Operations during the third quarter of 1982 examined the effects of process variable changes around a base case experiment conducted during the first quarter 1982 studies. These studies utilized low ash content coal (10 wt% dry coal). The base case chosen represented a central point in the operating region from which the effects of different process variables could be measured. The data indicate that the Martin Lake conversion is relatively insensitive to pressure over the range 1500 to 2500 psig for bottoms recycle operations. A unique response to increasing the bottoms-to-coal ratio from 0.5 to 1.0 was observed at liquefaction conditions of 820°F and 40 minutes. This increase in bottoms-to-coal ratio yielded an additional 10 wt% (DAF basis) conversion. In contrast, only about 4 wt% DAF conversion change was observed for increasing bottoms-to-coal ratio from 0.5 to 1.0 at 800°F and 100 minutes nominal slurry residence time. Experiments also showed that changing the Solvent Quality Index between 2.8 and 4.8 had essentially no effect on conversion with Martin Lake lignite.

Unit operability with Martin Lake coal was very good. The average run length for Martin Lake was approximately 40% longer than observed with other low rank coals such as Big Brown lignite or Wyoming Wyodak.

Figure 1-11 highlights the flexibility of hydrocarbon yield distributions with Martin Lake lignite in the EDS process.

1.3 Bottoms Recycle

As outlined in Section 1.2.1, experiments to simulate bottoms recycle on RCLU were initially conducted during the fourth quarter of 1978 with Monterey No. 1 coal. Liquefaction bottoms from CLPP once-through operations were fed for one pass rather than operating in an actual recycle mode. This was done because this operation could be accomplished rapidly without unit modifications and once-through bottoms were expected to show the maximum yield incentive for bottoms recycle. Encouraging results in terms of increased liquefaction yields, improved bottoms properties, and improved operability promoted development of continuous bottoms recycle on RCLU.

Shakedown of continuous bottoms recycle operations was conducted during the first quarter of 1980 with Pittsburgh No. 8 coal from the Ireland mine. Continuous bottoms recycle was achieved in RCLU in a semi-continuous

FIGURE 1-11
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED
RCLU MARTIN LAKE COAL EXPERIMENTS

700 - 1000°F 400 - 700°F C4 - 400°F C1 - C3
 GAS OIL DISTILLATE NAPHTHA GAS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, °F

H₂ PRESSURE, PSIG

NRT, MINUTES

S/C/B, BY WT.

H₂ TREAT, WT% ON COAL

RCLU NO.

YIELD PERIODS

55
 820
 1500
 40
 1.6/1/0
 4
 1
 1038-1040

64
 820
 2000
 40
 1.6/1/0.5
 6
 1
 991-994

72
 820
 2000
 40
 1.6/1/1
 6
 1
 1028-1032

manner by collecting the residual bottoms in six-hour batches, cooling, pulverizing, and mixing with coal and recycle solvent. This recycle mode is equivalent to that used for continuous recycle of the donor solvent on RCLU. Bottoms samples from each six-hour batch were analyzed to monitor the approach to steady state conditions.

During the initial Ireland coal studies with continuous bottoms recycle, two experiments at different pressures and solvent-to-coal-to-bottoms proportions were conducted at liquefaction conditions of 840°F, 100 minutes nominal residence time and 4 wt% H₂ treat on dry coal. Data for Ireland coal indicated that at low pressure (1500 psig) bottoms recycle had no significant effect on coal conversion, water yield, or chemical gas production. The total C₁-1000°F hydrocarbon yields for bottoms recycle and coal-only operations at 1500 psig were essentially equivalent. However, bottoms recycle resulted in a lighter product slate with more C₁-C₃ gas and naphtha (C₄-400°F) produced at the expense of 400-1000°F distillate. Hydrogen consumption was slightly greater for the bottoms recycle case.

By contrast, continuous bottoms recycle at 2500 psig and 6 wt% hydrogen treat on dry coal had a significant effect on yields when compared to coal-only at the same conditions. Coal conversion increased significantly due to bottoms recycle and marked increases were observed in C₁-1000°F total hydrocarbon, C₄-1000°F liquid, C₁-C₃ gas and C₄-400°F naphtha yields. The 400-1000°F distillate yield decreased significantly resulting in a shift in liquid selectivity toward naphtha product for the bottoms recycle operations. This shift toward lighter products is accompanied by increased hydrogen consumption.

Bottoms composition for the initial 1500 psig operations with Ireland mine coal showed increased preasphaltene and pyridine insoluble contents for bottoms recycle compared to coal-only operations. This indicated the presence of regressive reactions. A low pressure (1500 psig) bottoms recycle experiment carried out in the third quarter of 1982 at lower liquefaction severity conditions of 840°F and 40 minutes nominal residence time (compared to 840°F, 100 minutes nominal residence time) indicated that low pressure bottoms recycle does result in increased conversion and liquid yields. No indication of the degradative back reactions to produce heavier, more complex pyridine insoluble and preasphaltene materials was evident (Figure 1-6). Thus, in the original bottoms recycle experiment the combination of high temperature, long residence time, and possible hydrogen starvation due to low hydrogen treat rate in the liquefaction reactor resulted in the regressive back reactions. For these 2500 psig operations and subsequent bottoms recycle operations, significant decreases in preasphaltenes and pyridine insoluble contents were found when compared to coal-only operations. Bottoms recycle data from different coals suggest sequential reactions of preasphaltene --> asphaltene --> oils occur in the liquefaction reactor.

The introduction of continuous bottoms recycle has added considerable process yield flexibility to the EDS process. Experiments at low liquefaction severity result in high distillate selectivity. At high

liquefaction severity, while maintaining solvent balanced operations, naphtha selectivity has been increased without large increases in C₁-C₃ make. Solvent quality studies with bottoms recycle of Ireland and Martin Lake coal have illustrated that there is a reduced sensitivity to low solvent quality, allowing for more variation in solvent quality without significantly affecting coal conversion.

Unit operability was greatly improved with the introduction of bottoms recycle. Improved bottoms properties, such as lower viscosity and lower pyridine insoluble contents, resulted in smoother operations in the bottoms stripping section. Also, reduced amounts of reactor solids and wall scale were found with bottoms recycle, thus reducing the occurrence of liquefaction reactor plugs in RCLU.

1.4 ECLP Support Studies

Experiments in support of Illinois No. 6 Monterey No. 1 mine bituminous coal and Wyoming Wyodak mine in the 250 ton-per-day EDS Coal Liquefaction Plant (ECLP) were conducted. These experiments were conducted to aid in assessing differences between ECLP yields and conversions and solvent quality from the historical small pilot plant data base.

1.4.1 Monterey No. 1 Mine Coal

Once-through operations with Monterey No. 1 coal were conducted during the third quarter of 1981 on RCLU. Forty-five yield periods comprising 13 series of conditions near the ECLP nominal slurry design conditions for liquefaction (840°F, 1500 psig, 40 minutes nominal slurry residence time, 1.6/1 solvent-to-coal ratio, and 4 wt% H₂ treat) were completed. These experiments demonstrated that the saturates content of the solvent can be controlled by the liquefaction and solvent hydrogenation conditions. For these experiments, saturates content was decreased by decreasing hydro-treater temperature or increasing liquefaction temperature. Further results indicate that for a solvent quality index (SQI) less than 3.5, conversions were somewhat lower than the historical RCLU data base, when compared at similar nominal liquefaction conditions.

Additional experiments conducted with Monterey coal simulated heavy vacuum gas oil (HVGO) recycle in support of ECLP operations. Low conversions obtained on ECLP with HVGO recycle were thought to be partially due to some detrimental effect of the presence of the heavy liquid (850-1000°F). RCLU results indicated no detrimental effects on liquefaction conversion or yields due to the HVGO.

1.4.2 Wyodak Mine Coal Operations

Operations during the fourth quarter of 1981 supported the initial bottoms recycle operations on ECLP. Variables investigated in the bottoms

recycle mode were liquefaction temperature (820, 825, 830°F), solvent-to-coal ratio (1.6, 1.9, 2.1), and bottoms-to-coal ratio (0.3, 0.5). All experiments showed little sensitivity of yields and conversion to the small changes in liquefaction temperature, solvent-to-coal, or bottoms-to-coal ratio in the experiments. An additional experiment which utilized gas swept mill dried coal from ECLP showed conversions 4 wt% (DAF coal basis) lower than those obtained with BARD dried coal, indicating possible oxidation problems in the gas swept mill process.

Hydrodynamic experiments were performed on RCLU during Wyodak operations using radioactive tracers. Details of results for the radioactive tracer work on RCLU are outlined in Section 1.5.

1.5 Liquefaction Reactor Hydrodynamics Tests

Liquefaction reactor characterization experiments were conducted on RCLU using radioactive tracers. Similar experiments were conducted on CLPP and ECLP to compare the reactor hydrodynamic characteristics of each size pilot plant reactor. In addition to providing a comparison between the pilot plants, the radioactive tracer experiments provided information for commercial reactor scale-up.

The radioactive tracer tests on RCLU injected a pulse of tracer material into the liquefaction reactors and measured the tracer signal strength at the liquefaction reactor outlet. Material balance information was used for vapor-liquid equilibrium calculations to determine inlet and outlet superficial velocities of the gas and liquid phases. The tracer information and gas and liquid velocities were used to determine hydrodynamic parameters such as phase holdups, dispersion and actual residence times.

Three series of tracer tests were performed on RCLU. The first series was a reliability test designed to assess the experimental technique and calculation procedures. This reliability test was conducted during ECLP support operations for Wyodak coal and established the suitability of argon as a gas phase tracer. Radioactive bromoadamantane was used as a liquid slurry tracer with inadequate results on RCLU. The bromoadamantane was held up in the liquefaction reactor with the result that calculated liquid residence times were unrealistically long.

The second series of tracer tests evaluated RCLU reactor characteristics while operating at nominal liquefaction conditions similar to conditions used for tracer tests on ECLP and CLPP with Wyoming coal. The phase holdups and actual liquid residence time established during the RCLU tests and the results for CLPP and ECLP tests are summarized in Table 1-2. The actual liquid residence time of CLPP and RCLU were approximately the same, with CLPP having about 4% less residence time relative to RCLU at the same nominal slurry residence time. Actual slurry residence time is defined as the volumetric flow rate or slurry divided by the actual slurry volume in

TABLE 1-2

ACTUAL SLURRY RESIDENCE TIME IN ECLP
SIGNIFICANTLY LOWER THAN IN SMALL PILOT UNITS

Coal	<u>Wyodak</u>		
<u>Nominal Liquefaction Conditions</u>			
Temperature, °F		820	
Hydrogen Pressure, psig		2200	
S/C/B, by wt		2.3/1/0.5	
H ₂ on Dry Coal, by wt%		6	
Gas Velocity, ft/sec	0.028	0.063	0.18
<u>Unit Conditions</u>			
Phase Holdup, vol%	<u>RCLU</u>	<u>CLPP</u>	<u>ECLP</u>
Gas	16	14	37
Solids	12	15	16
Slurry	72	71	47
Actual Slurry Residence Time,* Min.	55	56	35
Nominal Slurry Residence Time,** Min.	76	81	83
Unit Residence Time Relative to RCLU	1.0	0.96	0.55

* Defined as slurry volumetric flow rate divided by actual slurry volume.

** Defined as slurry volumetric flow rate divided by reactor volume.

the reactor. Nominal residence time is simply the slurry volumetric flow rate divided by the volume of the reactor. For the particular operations studied, ECLP had 55% of the liquid residence time, relative to RCLU, at the same nominal slurry residence time. This difference in actual liquid residence time accounted for a large portion of the difference in conversion between the small pilot plants (RCLU and CLPP) and ECLP.

A third series of tracer tests was performed on RCLU to establish the effect of gas velocity on gas holdup and liquid residence time. This information on the effect of gas velocity was necessary to allow commercial scaleup from RCLU yield data without additional RCLU tracer tests in the future. Tracer tests were performed on RCLU with Ireland coal at 800°F, 100 minutes nominal slurry residence time, 2000 psig hydrogen pressure and 2/1/0.5 solvent-to-coal-to-bottoms ratio. The gas velocity for the three experiments was varied by changing the hydrogen treat rate to 6, 12 and 18 wt% on dry coal. Thus, all the data were obtained for a constant slurry rate to liquefaction. Argon was used as the gas phase tracer. A gold colloid was used as the liquid phase tracer. This tracer responded similarly to bromoadamantine and results from the gold liquid tracer were not used for data analysis.

The phase holdups and average slurry residence time for the three Ireland coal experiments and the previously discussed Wyodak experiments are shown in Table 1-3. These experiments established the effect of superficial gas velocity on gas phase holdup. A more detailed discussion of these experiments is given in the October 1 - December 31, 1982 Quarterly Technical Progress Report (FE-2893-103).

1.6 Liquefaction Reactor Solids Summary

Inspection of the liquefaction reactor contents following liquefaction of lower rank coals in RCLU has proved important in identifying potential problems with solid deposits, e.g., the formation of calcium carbonate. Analyses of reactor residual solids following liquefaction of the higher rank coals run in RCLU were also initiated as part of the RCLU coal evaluation program. The primary purpose of these studies was to elucidate differences or similarities in reactor deposits for the different rank coals.

A common procedure was used for analysis of reactor solids. The reactor solids were drained from the reactor tubes and washed with toluene to remove the residual oil. The reactor tube walls were then washed with methyl ethyl ketone and mechanically scraped to remove any residual scale. The reactor solids were screened to separate the +20 mesh and the -50 +100 mesh size fractions for further examination. The +20 mesh size fraction was checked for pieces of reactor scale. The -50 +100 mesh size fraction was examined for evidence of particle growth. The oolites (calcium carbonate aggregates) and iron sulfide particles which grow larger than the RCLU feed coal top size (100 mesh) are found in this size fraction for the lower rank coals.

TABLE 1-3

SUMMARY OF RCLU TRACER TEST RESULTS

Coal Mine	<u>Ireland</u>	<u>Ireland</u>	<u>Ireland</u>	<u>Wyodak</u>
<u>Liquefaction Conditions</u>				
Temperature, °F	800	800	800	820
Nominal Slurry Residence Time, Min.	100	100	100	80
Hydrogen Pressure, psig	2000	2000	2000	2000
S/C/B, by wt	2/1/0.5	2/1/0.5	2/1/0.5	2.1/1/0.5
H ₂ TGR, wt% on Dry Coal	6	12	18	6
<u>Average Velocities (Ft/Sec)</u>				
Gas	0.019	0.046	0.075	0.028
Slurry	0.0073	0.0062	0.0050	0.0069
<u>Holdups (Volume %)</u>				
E _g	8	21	27	16
E _l	80	69	65	72
E _s	12	10	8	12
Average Slurry Residence Time, Min.	73	75	86	58
Conversion (DAF, wt%)	58	64	63	

Table 1-4 summarizes data from liquefaction reactor inspections for the different rank coals run in RCLU in once-through operations. RCLU operations with low rank coals in the past were frequently interrupted by plugging problems in the liquefaction reactor and downstream separations in RCLU. Inspection of the reactor contents revealed that the accumulation rate of reactor solids is greater with lower rank coals. Also, minerals, mainly calcium carbonates and iron sulfides, accumulate as wall scale deposits and as free-flowing solids (oolites). These deposits and free-flowing solids are thought to eventually contribute to the reactor plugging in RCLU.

The major crystalline species found in the reactor solids were essentially the same for all the coals: calcium carbonate (calcite and vaterite), iron sulfide, quartz and kaolinite. These reactor solids compositions are consistent with the mineral elements contained in these coals. Indian Head lignite formed a unique deposit of $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ during liquefaction, presumably because this coal contains much more sodium than the other coals. For all coals but Monterey No. 1 coal, growth of iron sulfide and calcium carbonate occurs during liquefaction. Monterey coal exhibits iron sulfide growth, but no evidence of calcium carbonate growth was found. Wall scale accumulation and composition data for these coals are shown in Table 1-5.

Following the initiation of continuous bottoms recycle operations on RCLU, a similar study on reactor residues was conducted. Objectives of this study were to investigate the effects of bottoms recycle operations on mineral accumulation in the reactor and to better understand the deposition mechanism.

Results from inspections on total residues from bottoms recycle operations are compared with those obtained earlier from once-through operations in Table 1-6. The total solids accumulation rate, as well as calcium carbonate accumulation rate for all coals in the bottoms recycle experiments, were substantially lower than those from the corresponding coal-only operations. This reduction in solids accumulation may be a contributing factor to the operability improvement on RCLU. The major crystalline species in bottoms recycle reactor solids were similar to those obtained from once-through operations.

1.7 Conclusions

The RCLU pilot plants have achieved all objectives as described in the EDS Cooperative Agreement for Phases III-B to V. EDS operations have been successfully demonstrated in both the once-through and bottoms recycle modes for coals of rank ranging from bituminous to lignitic. The bituminous coals studied include Illinois No. 6 for the Monterey No. 1 and Burning Star No. 2 mines, and Pittsburgh No. 8 seam coal from the Ireland and Arkwright mines. Subbituminous coals investigated include Wyoming coal from the Wyodak mine and Australian Black coal from the Wandoan mine. Lignitic coals

Table 1-4

COMPARISON OF LIQUEFACTION RESIDUAL REACTOR SOLIDS FROM DIFFERENT RANK COALS RUN IN RCLU

Coal	Illinois No. 6 Bituminous		Pittsburgh Seam Bituminous		Australian Black	Wyoming Subbituminous	Texas Lignite	North Dakota Lignite
Mine	Monterey No. 1	Burning Star No. 2	Ireland	Arkwright	Wandoan	Wyodak	Big Brown	Indian Head
<u>Reactor Solids¹</u>								
Accumulation, Lbs/100 Lbs Coal Fed	0.01-0.10	0.03-0.20	0.10-0.21	0.20-0.29	0.04-1.1	0.35-0.57	0.49-2.0	0.22-1.1
<u>Composition, Ranges, Wt %</u>								
Ash	52-69	24-71	89-90	54-73	60-76	56-70	78-82	57-67
CaCO ₃	4-9	7-50	5-10	3-9	43-57	24-83	67-74	17-49
Carbon	17-73	9-67	3-4	13-37	6-15	5-26	3-4	9-22
CaCO ₃ Accumulation (Avg), Lbs/Ton of Coal Fed	0.18	0.85	0.26	0.32	3.3	5.6	12.0	6.8
<u>Major Crystalline Species</u>								
	Calcite FeS SiO ₂	Calcite FeS Kaolinite SiO ₂ CaSO ₄	Calcite FeS Kaolinite SiO ₂	Calcite FeS Kaolinite SiO ₂	Calcite Vaterite FeS Kaolinite SiO ₂	Calcite Vaterite FeS SiO ₂	Calcite Vaterite FeS SiO ₂	Calcite Na ₂ Mg(CO ₃) ₂ FeS SiO ₂

¹Toluene washed

Table 1-5

COMPARISON OF REACTOR WALL SCALE FORMED DURING LIQUEFACTION OF DIFFERENT RANK COALS IN RCLU

Coal	Illinois No. 6 Bituminous		Pittsburgh Seam Bituminous		Australian Black	Wyoming Subbituminous	Texas Lignite	North Dakota Lignite
	Monterey No. 1	Burning Star No. 2	Ireland	Arkwright	Wandoan	Wyodak	Big Brown	Indian Head
Mine								
Scale Accumulation, Lbs/100 Lbs Coal Fed	Trace-0.001	0.00005-0.001	Trace-0.001	Trace-0.008	0.005-0.006	0.002-0.007	0.002-0.010	0.005-0.035
Composition, Wt %								
Ash (by TGA)	51-96	69-93	78-86	47-61	56-74	59-63	52-86	57-80
CaCO ₃ (by TGA)	5-14	8-15	9-41	57-73	36-48	71-85	53-86	64-84
Major Crystalline Species (by X-ray Diffraction)								
	FeS SiO ₂	Calcite FeS	Calcite FeS	Calcite FeS SiO ₂	Calcite Vaterite FeS SiO ₂ Kaolinite	Calcite Vaterite FeS SiO ₂	Calcite Vaterite FeS SiO ₂	Calcite FeS SiO ₂
Major Elements, Wt % (by X-ray Scan of Cross Section)								
Al	2-4	0.0-4	1-2	0.1-1	0.4-4	Not Analysed	0.1-5	Not
Ca	2-7	0.1-13	17-34	3-43	0.5-30		0.8-38	Analysed
Ti	0.2-7	0.0-12	2-4	0.0-0.6	0.1-2		0.0-0.7	
Fe	5-30	0.9-28	1-2	0.0-24	2-44		1-48	
S	3-25	0.7-18	0.5-1	0.1-20	0.1-26		0.2-34	
Si	2-27	0.1-4	0.4-1	0.1-0.8	0.6-6		0.4-5	

Table 1-6

COMPARISON OF LIQUEFACTION REACTOR RESIDUES FROM DIFFERENT RANK COALS (FROM ONCE-THROUGH AND BOTTOMS RECYCLE) RUNS IN RCLU

Coal	Illinois No. 6 Bituminous				Pittsburgh Seam Bituminous		Wyoming Subbituminous		Texas Lignite	
Mine	Monterey No. 1		Burning Star No. 2		Ireland		Wyodak		Big Brown	
Total Reactor Residue	Coal Only	Bottoms Recycle	Coal Only	Bottoms Recycle	Coal Only	Bottoms Recycle	Coal Only	Bottoms Recycle	Coal Only	Bottoms Recycle
<u>Total Solids Accumulation</u>										
Lbs/100 Lbs Coal Fed	0.01-0.10	0.02	0.03-0.2	0.07	0.10-0.21	0.23	0.35-0.57	0.25	0.49-2.0	0.32
<u>Composition Ranges, Wt%</u>										
Ash	52-69	30	24-71	60	89-90	70-88	56-70	60	78-82	54
CaCO ₃	4-9	7	7-50	NA	5-10	NA	24-83	66	67-74	74
Carbon	7-37	63	9-67	NA	3-4	4-23	5-26	16	3-4	NA
CaCO ₃ Accumulation (Avg) Lbs/Ton of Coal fed	0.18	0.03	0.85	NA	0.26	NA	5.6	3.2	12.0	4.8
<u>Major Crystalline Species</u>										
	Calcite FeS SiO ₂	Calcite FeS SiO ₂	Calcite FeS SiO ₂ Kaolinite	Calcite FeS SiO ₂ Kaolinite	Calcite FeS SiO ₂ Kaolinite	Calcite FeS SiO ₂ Kaolinite	Calcite FeS SiO ₂ Kaolinite	Calcite FeS SiO ₂ Kaolinite	Calcite FeS SiO ₂ Kaolinite	Calcite FeS SiO ₂ Kaolinite

NA = Not analyzed

examined were from the East Texas lignitic deposits, Big Brown and Martin Lake mines. An extensive data base detailing the effects of process variable changes on yields, conversions and product qualities for each coal has been established. Additional accomplishments include:

- Continuous bottoms recycle operations performed on RCLU demonstrated increased overall conversion and improved product slate flexibility over once-through operations. Bottoms viscosity characteristics also showed improvement over once-through liquefaction.
- RCLU liquefaction reactor hydrodynamics were characterized through the use of gas and slurry phase radioactive tracer tests. RCLU and CLPP were found to have much longer liquid residence times than ECLP.
- Support work during ECLP operations contributed to resolving differences between ECLP conversions and product yields and those of the small pilot plants.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

LIQUEFACTION PROCESS RESEARCH

2. Operation of the One Ton-Per-Day Coal Liquefaction Pilot Plant (CLPP)

The one ton-per-day Coal Liquefaction Pilot Plant (CLPP) is an integrated pilot plant with the capability of continuously recycling treat gas, solvent, vacuum gas oil (VGO), and vacuum bottoms to the liquefaction reactor. The CLPP was operated to confirm product yields obtained in the smaller pilot plants (RCLU's), to demonstrate integrated EDS operations, to furnish products for quality testing, to verify yields and conversions at economically preferred conditions and to provide support during the operation of the 250 ton-per-day EDS Coal Liquefaction Plant (ECLP).

The final CLPP configuration in use at the conclusion of operations is shown in Figure 2-1. The unit configuration in use at the beginning of the program has been documented (July, 1977 - June, 1978 EDS Annual Technical Progress Report, [FE-2893-17]) as have subsequent modifications for bottoms recycle (July, 1979 - June, 1980 EDS Annual Technical Progress Report [FE-2893-53] and VGO recycle (July, 1980 - June, 1981 EDS Annual Technical Progress Report [FE-2893-74]) operations.

Except for a scheduled downtime of six months in the fourth quarter of 1977 and the first quarter of 1978, the CLPP was operated from July, 1977 to July, 1982 in phases IIIB to V of the EDS coal liquefaction process development program. Table 2-1 lists the major studies that were completed during that time. Three bituminous coals, two subbituminous coals, and two lignites have been successfully processed on the CLPP. Once-through and bottoms recycle studies were conducted with Monterey, Ireland, and Wyodak coals and Big Brown lignite. Burning Star and Wandoan coals and Martin Lake lignite were processed in the bottoms recycle mode only. A total of 172 yield periods and 12 material balance periods were obtained. VGO recycle conversion was studied with all coals. VGO was taken as product, recycled directly to liquefaction, or hydrotreated with recycle solvent and returned to liquefaction in these studies. ECLP operations with Monterey and Wyodak coals and Martin Lake lignite were supported by CLPP operations with these coals. Liquefaction reactor hydrodynamics were examined through the use of two- and three-phase radioactive tracer tests during Monterey, Burning Star, and Wyodak operations. The maintenance of good quality process-derived solvent was demonstrated by extended runs with Monterey and Ireland coals. Engineering studies were conducted in early operations with Monterey and Wyodak coals to obtain ECLP design data. Finally, studies of liquefaction heat release and liquefaction reactor solids have been conducted throughout the program.

Table 2-1

SUMMARY OF CLPP STUDIES

<u>Coal Rank Mine</u>	<u>Illinois No. 6 Bituminous Monterey No. 1</u>	<u>Illinois No. 6 Bituminous Burning Star No. 2</u>	<u>Pittsburgh No. 8 Bituminous Ireland</u>	<u>Wyoming Subbituminous Wyodak</u>	<u>Wandown Black Subbituminous Queensland, Australia</u>	<u>Texas Lignite Big Brown</u>	<u>Texas Lignite Martin Lake</u>
<u>Liquefaction Modes</u>	Once-Through, Low-Pressure Bottoms Recycle, High-Pressure Bottoms Recycle	High-Pressure Bottoms Recycle	Once-Through, High Pressure Bottoms Recycle	Once-Through, High Pressure Bottoms Recycle	High Pressure Bottoms Recycle	Once-Through, High Pressure Bottoms Recycle	High-Pressure Bottoms Recycle
<u>VGO Disposition</u>	Product, Hydrotreating	Product, Liquefaction, Hydrotreating	Product, Liquefaction, Hydrotreating	Product, Liquefaction, Hydrotreating	Product, Liquefaction	Product, Hydrotreating	Hydrotreating
<u>Yield Periods</u>	250-265 285-296 303-311 320-325 345-350 404-410	389-397	297-302 369-384	245-249 266-284 312-319 326-330 351-357 385-388	358-360 362-368	331-344	398-403 411-416
<u>Results Reported</u>							
Yields and Product Quality	FE-2893-7, 41, 49, 57, 74, 97	FE-2893-93	FE-2893-49, 93	FE-2893-3, 25, 29, 53, 57, 74, 93	FE-2893-83	FE-2893-70	FE-2893-97
Liquefaction Heat Release	FE-2893-49, 57, 70		FE-2893-93	FE-2893-49, 57, 70	FE-2893-70, 74	FE-2893-70	FE-2893-97
Liquefaction Reactor Solids	FE-2893-45, 70, 93		FE-2893-45, 53, 93	FE-2893-25, 53	FE-2893-74	FE-2893-64, 74	FE-2893-97
Liquefaction Hydrodynamics	FE-2893-93	FE-2893-93		FE-2893-64, 93			
Solvent Quality Maintenance	FE-2893-74		FE-2893-93				
ELLP Reactor Solids	FE-2893-64, 78						
High Severity Vacuum Tower Operations	FE-2893-7, 41						
Slurry Preheater Studies	FE-2893-53				FE-2893-74		
VGO Conversion	FE-2893-74			FE-2893-74		FE-2893-74	

2.1 Sponsor Coal Evaluations

2.1.1 Monterey Coal Evaluation

Operations with Illinois No. 6 coal from the Monterey No. 1 mine were conducted on the CLPP in both once-through and bottoms recycle modes during this period. Yield and product quality information were obtained for a total of 56 yield periods at 9 different operating conditions, shown in Table 2-2. The first operations with Monterey coal began in August, 1977 and continued through October, 1977. The primary objective of these runs was to confirm process yields used in the initial EDS Study Design. Nominal liquefaction conditions were 840°F, 40 minutes slurry residence time, and 1500 psig hydrogen partial pressure. Solvent-to-coal proportions were 1.2/1 by weight. High severity vacuum flash operations were examined during this period. The vacuum flash tower was operated with flash zone temperatures up to 775°F, producing bottoms with 1000°F contents as low as 0.5 wt% by micro-lube distillation. Results indicated that above 720°F flash zone temperature there is significant degradation of Monterey bottoms, as evidenced by increasing pyridine insolubles content and decreasing H/C atomic ratio.

CLPP operations from April to June, 1979, focused on the development of an integrated system to recycle vacuum bottoms. The first bottoms recycle configuration (Bottoms Recycle I) was tested in this period. In this configuration, molten bottoms were contacted with the coal-solvent mixture at reaction pressure. Details of Bottoms Recycle I operation can be found in Section 2.2 of this report. Operating conditions selected for these operations were 830 to 840°F liquefaction temperature, 40 minutes nominal slurry residence time, and 1500 psig hydrogen partial pressure. Solvent-to-coal ratios ranged from 1.2/1 to 1.6/1 by weight, while bottoms-to-coal proportions ranged from 0.5/1 to 1/1.

The second bottoms recycle configuration (Bottoms Recycle II) was commissioned in October, 1979, and showed improved operability over Bottoms Recycle I. The second system was designed to contact molten recycle bottoms with the solvent and coal slurry in a well-stirred tank at atmospheric pressure. This configuration provided a well-mixed feed to the liquefaction feed pumps, resulting in smoother operations. Liquefaction conditions selected were 840°F, 60 minutes nominal slurry residence time, and 2000 psig hydrogen partial pressure. Solvent-to-coal-to-bottoms proportions were 1.8/1/0.5 and 1.8/1/1 by weight. These operations demonstrated integrated bottoms recycle operations and verified the associated yield and conversion improvements.

The February-March, 1980, CLPP operations with Monterey coal tested both the once-through and bottoms recycle modes of operation. High pressure once-through operations were run to compare yields and conversions with earlier low pressure runs. Conditions selected were 840°F liquefaction temperature, 60 minutes nominal slurry residence time, 2000 psi hydrogen partial pressure and 1.2/1 solvent to coal ratio. The results indicated no significant conversion benefit associated with higher liquefaction pressure

Table 2-2

CLPP OPERATIONS WITH MONTEREY MINE COAL

Operating Period	August, 1977- October, 1977	April, 1979- June, 1979	October, 1979- December, 1979	February, 1980- March, 1980	September- October, 1980	May, 1982
Liquefaction Mode	Once-Through	Bottoms Recycle (first configuration)	High Pressure Bottoms Recycle	Once-Through Bottoms Recycle	Bottoms Recycle	Bottoms Recycle
VGO Disposition	Product	Product	Product	Product Hydrotreating	Hydrotreating	Product
Yield Periods Obtained	250-265	285-296	303-311	320-325	345-350	404-410
Nominal Liquefaction Conditions						
Temperature, °F	840	830-840	840	840, 800	840	840
Slurry Residence Time, Minutes	40	40	60	60, 100	60	60
H ₂ Partial Pressure, psig	1500	1500	2000	2000	2000	2000
Solvent/Coal/Bottoms Proportions by Weight	1.2/1/0	1.2/1/0.5 1.6/1/0.5 1.6/1/1	1.8/1/0.5 1.8/1/1	1.2/1/0 1.8/1/1	1.3/1/0.3 1.6/1/0.5	1.6/1/0.5
Major Objectives						
1. Confirmation of yields at study design conditions.	X					
2. Solids Withdrawal Demonstration	X					
3. Product Generation	X	X	X	X	X	X
4. Vacuum Flash Severity Study	X					
5. Bottoms Recycle System Development		X	X			
6. Generation of Yield Product Quality Information	X	X	X	X	X	X
7. VGO conversion testing				X		
8. Confirmation of yields at preferred bottoms recycle conditions					X	
9. Liquefaction Hydro- dynamic Studies						X
10. Liquefaction Temp- erature profile studies						X

alone. Bottoms recycle studies during this period expanded the data base to include lower temperature, longer residence time runs. Nominal liquefaction conditions were 800°F, 100 minutes slurry residence time, and 2000 psi hydrogen partial pressure. Solvent/coal/bottoms proportions were 1.8/1/1 by weight.

Recycle of vacuum gas oil (VGO) was also investigated in the February-March, 1980 studies. VGO was continuously recycled as part of the solvent stream through the hydrotreaters back to the liquefaction reactors. Additional details of VGO conversion studies are discussed in Section 2-3 of this report.

Conditions were chosen for operations in September and October, 1980 based on economic studies by Exxon Liquefaction Engineering Department (ELED). Economic evaluation of yields and plant costs led to the selection of preferred liquefaction conditions. These conditions were 840°F liquefaction temperature, 60 minutes nominal slurry residence time, 2000 psi hydrogen partial pressure, and 1.6/1/0.5 solvent/coal/bottoms proportions. VGO was recycled through hydrotreating in these runs.

The final CLPP operations with Monterey coal occurred in May, 1982, and were directed toward improving the EDS liquefaction model. The impacts of liquefaction temperature profile and reactor hydrodynamics on yields and conversion were investigated. Liquefaction conditions were 840°F, 60 minutes nominal slurry residence time, 2000 psi hydrogen partial pressure, and 1.6/1/0.5 solvent/coal/bottoms proportions. VGO was taken as product.

Figure 2-2 shows hydrocarbon yield distributions for selected Monterey coal operations. As shown in the figure, C₁-1000°F hydrocarbon yield varied from about 45 wt% on DAF coal for low-pressure once-through operations to 55 to 65 wt% for high-pressure bottoms recycle operations. Mid distillate (400-700°F) production was maximized during bottoms recycle operations at 1.6/1/0.5 solvent/coal/bottoms proportions (YPs 346-350). These conditions were determined to be economically preferred over other conditions examined on CLPP. Maximum conversion was reached at 1.8/1/1 solvent/coal/bottoms proportions with an 8 wt% hydrogen treat rate (YPs 308-311). However, these severe conditions produced an undesirably high C₁-C₃ gas yield of 16 wt% on DAF coal.

High pressure coal-only operations did not show significant conversion increases over low pressure coal-only operations. The conversion enhancement of about 2 wt% for YPs 320 and 321 can be accounted for by the increased nominal residence time (60 vs 40 minutes). However, a substantial shift toward lighter products occurs in high pressure coal-only operations. C₁-C₃ gas yield was 13 wt% on DAF coal at 2000 psig hydrogen partial pressure, compared to 7.4 wt% at 1500 psig.

2.1.2 Burning Star Coal Evaluation

Liquefaction of Illinois No. 6 coal from the Burning Star No. 2 mine was studied on the CLPP from December, 1981, to February, 1982.

FIGURE 2-2

82B-11-150

HYDROCARBON YIELD DISTRIBUTIONS FOR
CLPP MONTEREY COAL OPERATIONS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, F

H₂ PRESSURE, PSIG

NRT, MINUTES

S/C/B, BY WT.

H₂ TREAT, WT% ON COAL

VGO DISPOSITION

YIELD PERIODS

57

59

69

77

840

1500

40

1.2/1/0

4

PROD.

256-258,
260-264

840

2000

60

1.2/1/0

4

PROD.

320, 321

840

2000

60

1.6/1/0.5

6

HYT.

346-350

840

2000

60

1.8/1/1

8

PROD.

308-311

Yield and product quality information was obtained for 9 yield periods in the bottoms recycle mode of operation. Conditions selected were 840°F liquefaction temperature, 60 and 80 minutes nominal slurry residence times, 2000 psi hydrogen partial pressure, and 1.6/1/0.5 solvent/coal/bottoms proportions. Vacuum gas oil (VGO) recycle conversion was studied in these operations. VGO was taken as product, recycled directly to liquefaction, or recycled through the hydrotreaters as part of the solvent stream. Results and conclusions of the VGO conversion studies are discussed in Section 2.3 of this report.

Figure 2-3 shows hydrocarbon yield distributions for the Burning Star coal studies compared to results from Monterey coal operations at similar conditions. The results shown Burning Star coal to be less reactive than Monterey coal in the EDS process. Burning Star coal produces 7 wt% less naphtha and 3 wt% less distillate than does Monterey coal at 60 minutes slurry residence time. Burning Star conversion can be increased by increasing residence time to 80 minutes. However, liquid yields are slightly reduced and gas make increases significantly as a result.

2.1.3 Ireland Coal Evaluation

Once-through and bottoms recycle operations were conducted on the CLPP using Pittsburgh No. 8 coal from the Ireland mine. Once-through operations were conducted in September, 1979, and were aimed at assessing yields and operability at base case conditions. Conditions selected were 840°F liquefaction temperature, 40 and 60 minutes nominal slurry residence times, 1500 psi hydrogen partial pressure, and 1.6/1 solvent-to-coal proportions. Bottoms recycle operations began in June, 1981, and lasted through August, 1981. Conditions were chosen to study the effects of bottoms-to-coal ratio, VGO disposition, and liquefaction temperature/residence time trade-offs.

CLPP operations with Ireland coal were very smooth and free of process-related problems. Record length runs of 17 and 20 days were achieved in the bottoms recycle mode of operations. Part of the credit for the smooth operations can be attributed to the low viscosity of the vacuum bottoms. Recycle bottoms viscosities ranged from 2 to 10 poise (at 550°F and 21 sec⁻¹ shear rate) with corresponding 1000°F contents of 2 to 8 wt% by microlube distillation. As shown in Figure 2-4, Ireland bottoms viscosities are lower than Monterey bottoms viscosities from comparable liquefaction conditions.

Figure 2-5 shows hydrocarbon yield distributions for CLPP Ireland coal operations. At liquefaction conditions of 840°F, 60 minutes nominal slurry residence time, and 0.5/1 bottoms-to-coal ratio, conversion and liquid yields were both increased by 7 wt% over once-through operations. Furthermore, there was a significant increase in mid-distillate production for the bottoms recycle cases. Mid-distillate (400-700°F) yield averaged 4 wt% for the once-through cases versus 15 to 20 wt% for bottoms recycle.

FIGURE 2-3

**HYDROCARBON YIELD DISTRIBUTIONS FOR
CLPP ILLINOIS NO. 6 COAL OPERATIONS**

MINE

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, °F

H₂ PRESSURE, PSIG

NRT, MINUTES

S/C/B, BY WT.

H₂ TREAT, WT% ON COAL

VGO DISPOSITION

YIELD PERIODS

BURNING STAR

MONTEREY

52

56

69

840

840

840

2000

2000

2000

60

80

60

1.6/1/0.5

1.6/1/0.5

1.6/1/0.5

6

6

6

HYT.

HYT.

HYT.

393-395

390-392

346-350

FIGURE 2-4

**VACUUM BOTTOMS VISCOSITIES FROM
CLPP BOTTOMS RECYCLE BITUMINOUS COAL OPERATIONS**

FIGURE 2-5

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HYDROCARBON YIELD DISTRIBUTIONS FOR
CLPP IRELAND COAL OPERATIONS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, F	840	840	800	840	840
H2 PRESSURE, PSIG	1500	1500	2000	2000	2000
NRT, MINUTES	40	60	100	60	60
S/C/B, BY. WT.	1.6/1/0	1.6/1/0	1.6/1/0.5	1.6/1/0.5	1.6/1/1
H2 TREAT, WT% ON COAL	4	4	6	6	6
VGO DISPOSITION	PROD.	PROD.	LIQ.	LIQ.	LIQ.
YIELD PERIODS	297-300	301, 302	381-384	370-374	375-377

2.1.4 Wyodak Coal Evaluation

Once through and bottoms recycle operations with Wyoming subbituminous coal from the Wyodak mine were conducted in the CLPP. Yield and product quality information was obtained for a total of 49 yield periods and five 12-hour material balance periods. Table 2-3 summarizes the operating periods and major objectives achieved. The first operation with Wyodak coal was in continuation of studies to determine conditions for optimum liquid yield in once-through operations. Liquefaction temperature ranged from 800-840°F in these experiments and nominal slurry residence times of 60 and 100 minutes were used. Hydrogen partial pressure was 1500 psi and the solvent-to-coal ratio was 1.6/1 by weight. In addition to obtaining yield and product quality data, operation of the liquefaction solids withdrawal system was demonstrated and a twin-screw pump was tested in vacuum bottoms service. This pump was similar to the one later used in the 250 ton-per-day Exxon Coal Liquefaction Pilot Plant (ECLP).

Once-through operations in May to November, 1978, focused on more severe liquefaction conditions as a means of reducing vacuum bottoms viscosity and improving operability. Liquefaction conditions selected included 810, 820, 830 and 840°F temperatures, 60, 80 and 100 minutes nominal slurry residence times and 1500 psi hydrogen partial pressure. Solvent-to-coal ratio ranged from 1.4 to 2.2/1 by weight. Liquefaction solids withdrawal was again demonstrated in these runs.

Initial bottoms recycle operations with Wyodak coal were conducted in January, 1980. Liquefaction conditions were 800°F, 100 minutes nominal slurry residence time, and 2000 psi hydrogen partial pressure. Solvent/coal/bottoms proportions of 2.5/1/1 and 2/1/1 were used. Results from bottoms recycle operations showed significant improvement in liquid yield and conversion compared to coal-only operations. Operability was also improved, as demonstrated by a record length 17-day operation during this period.

Bottoms recycle operations resumed in April, 1980. Limited high pressure once-through operations were also conducted at that time. Conditions chosen were 800°F, 100 minutes nominal slurry residence time, 2000 psig hydrogen partial pressure. Feed slurry proportions were 1.6/1 solvent-to-coal in the once-through operations and 2/1/0.5 solvent/coals/bottoms for bottoms recycle. Results from high pressure once-through operations indicated no significant conversion benefit associated with higher liquefaction pressure alone. Vacuum gas oil (VGO) was recycled through hydrotreating to liquefaction in these operations as part of a study to determine the convertibility of this stream. Details of the VGO conversion studies are given in Section 2.3 of this report.

Operations in December, 1980, through February, 1981, were at liquefaction conditions chosen as economically preferred. These conditions were 840°F liquefaction temperature, 60 minutes nominal slurry residence time, 2000 psi hydrogen partial pressure, and 1.6/1/0.5 solvent/coals/bottoms proportions. VGO was recycled directly to liquefaction and taken as product in these runs.

Table 2-3

CLPP OPERATIONS WITH WYODAK MINE COAL

<u>Operating Period</u>	<u>July, 1977</u>	<u>May, 1978- Nov., 1978</u>	<u>January, 1980</u>	<u>April, 1980</u>	<u>December, 1980- February, 1981</u>	<u>September, 1981- November, 1981</u>
<u>Liquefaction Mode</u>	Once-Through	Once-Through	Bottoms Recycle	Once-Through, Bottoms Recycle	Bottoms Recycle	Bottoms Recycle
<u>VGO Disposition</u>	Product	Product	Product	Hydrotreating	Liquefaction, Product	Liquefaction, Hydrotreating
<u>Yield Periods Obtained</u>	245-249	266-284	312-319	320-325	351-357	MS 8-12 385-388
<u>Nominal Liquefaction Conditions</u>						
Temperature, °F	800-840	810-840	800	840, 800	840	790-825
Slurry Residence Time, Minutes	60-100	60-100	100	60, 100	60	60-80
H ₂ Partial Pressure, psig	1500	1500	2000	2000	2000	2000
Solvent/Coal/Bottoms Proportions by Weight	1.6/1/0	2.2/1/0 1.4/1/0 1.6/1/0	2.5/1/1 2/1/1	1.2/1/0 1.8/1/1	1.6/1/0.5	2.1/1/0.3
<u>Major Objectives</u>						
1. Generation of Yield and Product Quality Information	X	X	X	X	X	X
2. Product Generation	X	X	X	X	X	X
3. Solids Withdrawal Demonstration	X	X				
4. Engineering Studies	X					
5. VGO Conversion Studies				X	X	X
6. Confirmation of yields at preferred bottoms recycle conditions					X	
7. ECLP Support						X
8. Liquefaction Hydro- dynamic Studies						X

The final CLPP Wyodak operations were conducted from September to November, 1981 and were in support of operations at ECLP. The CLPP operating conditions were chosen to parallel those at ECLP. Liquefaction temperatures ranged from 790 to 825°F; nominal slurry residence times were 60 and 80 minutes, and hydrogen partial pressure was 2000 or 2250 psig. Solvent/coal/bottoms proportions were approximately 2.1/1/0.3 by weight. VGO was recycled directly to liquefaction and through hydrotreating to liquefaction. These operations focused on liquefaction yields and recycle solvent quality maintenance. Liquefaction reactor hydrodynamic studies were conducted using radioactive tracers. The purpose of these studies was to determine CLPP reactor gas and liquid phase holdups for comparison with the smaller and larger scale pilot plants, RCLU and ECLP, respectively. The results from these tests are summarized in Section 2.4 of this report.

Figure 2-6 shows hydrocarbon yield distributions for selected once-through and bottoms recycle Wyodak operations. As shown in the figure, C₁-1000°F hydrocarbon yield ranged from about 40 wt% in low pressure, once-through operations to about 50 wt% in high pressure bottoms recycle operations. Conversion was maximized in bottoms recycle at 1/1 bottoms-to-coal ratio and 8 wt% hydrogen treat rate. However, this condition also produced the highest C₁-C₃ gas yield, which is economically undesirable. The maximum distillate yield was produced for conditions deemed economically preferred. Liquefaction conditions of 840°F, 2000 psig hydrogen partial pressure, 60 minutes nominal slurry residence time and 1.6/1/0.5 solvent/coal/bottoms proportions produced a 400-700°F distillate yield of 15.8 wt%. Total C₁-1000°F hydrocarbon yield was 48 wt%, and conversion was 67 wt%, on a DAF basis, for these conditions.

High pressure once-through operations did not produce significantly higher conversion over lower pressure operations. Conversion was 59 wt% (DAF basis) for 2000 psi once-through operations versus 58 wt% for 1500 psi operations at similar conditions.

Vacuum gas oil (VGO) yield was lower for the VGO recycle cases than the VGO product cases. VGO yield ranged from 2-5 wt% for recycle of VGO to liquefaction and hydrotreating, versus 5-12 wt% for VGO taken as product. Additional information on VGO recycle conversion is presented in Section 2.3.

2.1.5 Wandoan Coal Evaluation

Bottoms recycle operations were conducted on the CLPP with Wandoan Black coal from Queensland, Australia from March to May, 1981. Study conditions were chosen to maximize C₄-1000°F liquid yield while limiting solvent and bottoms recycle rates to economically preferred ranges. Nominal liquefaction conditions were 800°F, 100 minutes slurry residence time (NRT) and 840°F, 60 minutes NRT, with 2000 psig hydrogen partial pressure and 1.6/1/0.5 solvent/coal/bottoms proportions. VGO was recycled to liquefaction and taken as product in these operations.

As shown in Figure 2-7, C₁-1000°F yield for Wandoan coal liquefaction was 49 wt% in 840°F, 60 minute NRT operations versus 43 wt% for

FIGURE 2-6

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HYDROCARBON YIELD DISTRIBUTIONS FOR
CLPP WYODAK COAL OPERATIONS

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, F	840	800	800	840	800	800	800
H2 PRESSURE, PSIG	1500	1500	2000	2000	2000	2000	2000
NRT, MINUTES	60	100	100	60	100	100	100
S/C/B, BY WT.	1.6/1/0	1.6/1/0	1.6/1/0	1.6/1/0.5	2/1/0.5	2/1/1	2.5/1/1
H2 TREAT, WT% ON COAL	4	4	4	6	6	6	8
VGO DISPOSITION	PROD.	PROD.	HYT.	LIQ.	HYT.	PROD.	PROD.
YIELD PERIODS	267-270	245, 246	326	351, 353	328-330	318, 319	312-315

FIGURE 2-7

**HYDROCARBON YIELD DISTRIBUTIONS FOR
CLPP SUBBITUMINOUS COAL OPERATIONS**

MINE**DAF CONVERSION****LIQUEFACTION CONDITIONS****TEMPERATURE****H₂ PRESSURE, PSIG****NRT, MINUTES****S/C/B, BY WT.****H₂ TREAT, WT% ON COAL****VGO DISPOSITION****YIELD PERIODS**

WANDOAN		WYODAK	
54	63	63	67
800	840	840	840
2000	2000	2000	2000
100	60	60	60
1.6/1/0.5	1.6/1/0.5	1.6/1/0.5	1.6/1/0.5
6	6	6	6
LIQ.	LIQ.	PROD.	LIQ.
358 - 360	362 - 365	366 - 368	351 - 353

the 800°F, 100 minute condition. Conversion was 9 wt% less in the lower temperature case. The C₁-1000°F hydrocarbon yield for Wandoan coal is approximately equal to that for Wyodak coal at similar conditions. However, Wandoan coal produces a lighter product slate, as evidenced by 4 wt% higher gas and naphtha yields, and 5-7 wt% lower distillate yield.

2.1.6 Big Brown Lignite Evaluation

Liquefaction of Texas lignite from the Big Brown mine was studied on the CLPP from May to August, 1980. Liquefaction conditions of 800°F and 100 minutes nominal slurry residence time were chosen to maximize C₄-1000°F liquid yields. To minimize potential operability problems, the initial solvent/coal/bottoms proportions selected were 2.5/1/1 and the hydrogen treat rate was 8 wt% on coal. Since operability was very good in the initial Big Brown operations, subsequent feed proportions and hydrogen treat rates were reduced to more economically favored conditions. A single yield point was obtained in the once-through liquefaction mode for comparison with bottoms recycle results. VGO conversion studies were also conducted, and VGO was recycled through hydrotreating or taken as product in these operations. Results from VGO conversion studies are discussed in Section 2.3 of this report.

As shown in Figure 2-8, total C₁-1000°F hydrocarbon yield was approximately constant for Big Brown bottoms recycle operations. There were no significant effects of solvent-to-coal or bottoms-to-coal ratios on C₁-1000°F liquid yield or conversion at the conditions examined. However, liquid yield distribution was affected by slurry feed proportions. Naphtha (C₄-400°F) yield was about 32 wt% at 2.5/1/1 solvent/coal/bottoms proportions, decreasing to 26 wt% for 2/1/0.5 and 1.6/1/0.5 proportions. (Mid-distillate (400-700°F) yield increased concomitantly from 10 wt% to about 13 wt%. Once-through operations produced significantly lower conversion and yields compared to bottoms recycle operations. Conversion was 59 wt% and C₁-1000°F yield was 45 wt% compared to ranges of 69-73 wt% and 50-55 wt%, respectively, for bottoms recycle. VGO recycle reduced 700-1000°F yield and increased 700°F liquid yield with no significant effect on conversion.

2.1.7 Martin Lake Lignite Evaluation

Two sets of operations were conducted on the CLPP with Texas lignite from the Martin Lake mine. The first operations were conducted in March and April, 1982, and conditions were chosen to assess the operability of Martin Lake lignite in advance of planned ECLP operations. Liquefaction temperature was varied to investigate solvent production rates and solvent quality maintenance. Nominal conditions included 850, 830 and 820°F liquefaction temperatures, 2000 psig hydrogen partial pressure, 40 minutes nominal slurry residence time, and 1.6/1/0.5 solvent/coal/bottoms proportions. VGO was taken as product.

FIGURE 2.8

83B-11-155

HYDROCARBON YIELD DISTRIBUTIONS FOR
CLP? BIG BROWN LIGNITE OPERATIONS

DAF CONVERSION
LIQUEFACTION CONDITIONS

TEMPERATURE, F	340	800	800	800	800
H2 PRESSURE, PSIG	2000	2000	2000	2000	2000
NRT, MINUTES	60	100	100	100	100
S/C/B, BY WT.	1.6/1/0	1.6/1/0.5	1.6/1/0.5	2/1/0.5	2.5/1/1
H2 TREAT, WT% ON COAL	4	6	6	6	8
VGO DISPOSITION	HYT	PROD.	HYT	HYT	HYT
YIELD PERIODS	344	341 - 343	338 - 340	335 - 337	331 - 333

The second set of operations used a high ash fraction of Martin Lake lignite as feed and again focused on operability in support of ECLP. The minus 1/16-inch fraction of crushed lignite was obtained from screening operations at the mine site for these studies. Conditions examined included 840, 830 and 820°F liquefaction temperature, 2000 psi hydrogen partial pressure, 60 minutes nominal slurry residence time and 1/7/1/0.5 solvent/coal/bottoms proportions. VGO was recycled through hydrotreating in these operations.

Operability was very good in both sets of operations. Concerns over possible bottoms pumping problems at ECLP were diminished when CLPP studies showed Martin Lake bottoms viscosities to be in the range of viscosities experienced with other coals.

As shown in Figure 2-9, conversion and total C_1 -1000°F hydrocarbon yield were lower for the high ash fraction of lignite than for the whole coal. Conversion and C_1 -1000°F hydrocarbon yield were 4 wt% and 7 wt% less, respectively, for the screened coal, even though the residence time was 50% greater (at slightly lower liquefaction temperature, however). Furthermore, the screened coal showed little conversion response to bottoms-to-coal ratio as conversion was approximately equal for 0.5/1 and 1/1 bottoms-to-coal ratios. The cause of the observed differences in liquefaction response is most likely related to the screening process itself. Either lower reactivity materials were concentrated during screening or the screening and storage processes resulted in oxidation of the coal, reducing its reactivity.

2.2 Evaluation of Bottoms Recycle

A major effort was undertaken on CLPP to study the effects of vacuum bottoms recycle on coal liquefaction. In the initial bottoms recycle system (Bottoms Recycle I), molten bottoms were contacted with a preheated mixture of coal and solvent at liquefaction pressure (about 1500 psig). The operability of this system was poor, and there were concerns over the mixing of the molten bottoms and slurry in the relatively short transfer line between the preheaters and the liquefaction reactors. To improve the contacting between bottoms and slurry, a second configuration was developed for CLPP, as illustrated in Figure 2-10. In this system (Bottoms Recycle II), molten bottoms are first mixed with a portion of recycle solvent in a static mixer, then contacted with the coal slurry in a mix tank (M-2) at atmospheric pressure. The Bottoms Recycle II configuration has proved to be very reliable and has been used for all bottoms recycle studies since October, 1979.

A major advantage of bottoms recycle over one-through liquefaction is that coal conversion can be increased without a commensurate increase in gas yield, thus maintaining solvent balance. Figure 2-11 shows the effect of bottoms recycle on yields for Monterey, Ireland, and Wyodak coals. Conversion increases by 7 to 10% with bottoms recycle, while C_1 - C_3 gas yield stays approximately constant. Mid-distillate (400-700°F) yield increases

FIGURE 2-9

83B-1-10

HYDROCARBON YIELD DISTRIBUTION FOR
CLPP MARTIN LAKE LIGNITE OPERATIONS

FEED

DAF CONVERSION

LIQUEFACTION CONDITIONS

TEMPERATURE, F

H₂ PRESSURE, PSIG

NRT, MINUTES

S/C/B, BY WT.

H₂ TREAT, WT% ON COAL

VGO DISPOSITION

YIELD PERIODS

WHOLE COAL		HIGH ASH FRACTION	
67	65	61	62
850	830	820	820
2000	2000	2000	2000
40	40	60	60
1.6/1/0.5	1.6/1/0.5	1.7/1/0.5	1.7/1/1
6	6	6	6
HYT	HYT	HYT	HYT
398, 399	401, 402	412, 413	414-416

FIGURE 2-10

82B-11-156

CLPP BOTTOMS RECYCLE II SYSTEM

FIGURE 2-11

82B-11-157

HYDROCARBON YIELD DISTRIBUTIONS FOR CLPP
ONCE-THROUGH AND BOTTOMS RECYCLE OPERATIONS

COAL	MONTEREY		IRELAND		WYODAK	
LIQUEFACTION MODE	ONCE-THROUGH	B/R	O/T	B/R	ONCE-THROUGH	B/R
DAF CONVERSION	57	59	55	62	58	67
LIQUEFACTION CONDITIONS						
TEMPERATURE, F	840	840	840	840	340	800
H2 PRESSURE, PSIG	1500	2000	1500	2000	1500	2000
NRT, MINUTES	40	60	60	60	60	100
S/C/B, BY WT.	1.2/1/0	1.2/1/0	1.6/1/0.5	1.6/1/0	1.6/1/0	1.6/1/0.5
H2 TREAT, WT% ON COAL	4	4	4	6	4	6
VGO DISPOSITION	PROD.	PROD.	HYT.	PROD.	PROD.	LIQ.

markedly, from 2-4 wt% for once-through operations to 12-16 wt% in bottoms recycle. Naphtha (C_4 -400°F) yield effects are mixed; Monterey bottoms recycle produces about 3 wt% more naphtha, while Ireland and Wyodak bottoms recycle produce 8 wt% and 4 wt% less naphtha, respectively. There is no evidence of significant effects of bottoms recycle on VGO yield; VGO yield data are somewhat scattered and are influenced by VGO disposition.

Another important advantage of bottoms recycle is that process operability is improved through improved bottoms properties. Figure 2-12 compares vacuum bottoms compositions from Monterey and Wyodak once-through and bottoms recycle operations. Asphaltene content of Wyodak bottoms increases from 5 wt% (on 1000°F⁺, ash free basis) for once-through operations to 30-50 wt% for bottoms recycle cases. Monterey bottoms show similar increases in asphaltene content with bottoms recycle. Also, for both coals asphaltene content increases with bottoms recycle rate. In conjunction with increases in asphaltene content, there is a decrease in preasphaltenes in the bottoms. Pyridene insolubles are roughly comparable for all cases. These alterations in bottoms characterization result in lower viscosity bottoms for bottoms recycle operations.

2.3 VGO Recycle Conversion Evaluation

The CLPP was also used to study the effects of recycling vacuum gas oil (VGO), a nominally 800-1000°F boiling hydrocarbon liquid. Two methods of VGO recycle were devised. In the first, VGO was mixed with unhydro-treated solvent, hydrotreated, and recycled to liquefaction. In the second method, VGO was recycled directly to liquefaction. In both methods, all the VGO condensed in the vacuum splitter tower (F-2) was recycled, except for VGO samples taken during the yield period.

One of the difficulties encountered in assessing the impact of VGO recycle is that some VGO is recycled with recycle bottoms and recycle solvent in all CLPP operations. This is due to the fact that the separations are not perfect - i.e., there is 800-1000°F material in the 1000°F⁺ bottoms and in the nominally 400-800°F solvent. For this reason, it is not possible to have complete extinction of VGO as some 800-1000°F material is withdrawn with the bottoms and product solvent. Another difficulty in assessing VGO conversion data is that the accuracy of boiling point determinations for high molecular weight materials, such as VGO, is limited. This limited accuracy produces significant scatter in the data.

With these limitations noted, the data in Figure 2-13 are presented. The figure shows 800-1000°F VGO yield as a function of total 800-1000°F VGO recycled. No distinction is made between VGO recycled through hydrotreating or directly to liquefaction, as no significant difference in VGO conversion was observed between the two methods. As expected, the data show reduced VGO yield (increased VGO conversion) with increasing VGO recycle rate. While difficult to quantify due to the data scatter, it appears that 50% conversion of VGO can be obtained with a VGO recycle rate in the range of 20-30 wt% of the coal feed rate (on a DAF basis). Higher VGO conversions should be possible with greater VGO recycle rates.

FIGURE 2-12
CLPP VACUUM BOTTOMS COMPARISONS FROM
ONCE-THROUGH AND BOTTOMS RECYCLE OPERATIONS

82B-11-158

COAL	MONTEREY			WYODAK		
	ONCE-THROUGH	BOTTOMS RECYCLE		ONCE-THROUGH	BOTTOMS RECYCLE	
LIQUEFACTION MODE						
LIQUEFACTION CONDITIONS						
TEMPERATURE, F	840	840	840	800	840	800
H ₂ PRESSURE, PSIG	1500	2000	2000	1500	2000	2000
NRT, MINUTES	40	60	60	100	60	100
S/C/B, BY WT.	1.2/1/0	1.6/1/0.5	1.8/1/1	1.6/1/0	1.6/1/0.5	2.5/1/1
H ₂ TREAT, WT% ON COAL	4	6	8	4	6	8
VGO DISPOSITION	PROD.	HYT.	PROD.	PROD.	LIQ.	PROD.
YIELD PERIODS	256-258 260-264	346-350	308-311	245-246	351, 353	312-315

FIGURE 2-13

CLPP VGO CONVERSION STUDIES

In conclusion, CLPP experiments have shown that it is possible to convert VGO into lighter products by recycling a stream containing VGO back to the liquefaction reactors. No differences in VGO conversion rate were observed between recycling VGO with solvent through the hydrotreaters or directly to liquefaction.

2.4 Liquefaction Reactor Hydrodynamic Tests

In order to determine the liquefaction reactor hydrodynamic characteristics, radioactive tracer studies were performed on the CLPP during November, 1981 and April/May 1982. Radioactive argon was used as the gas-phase tracer, and colloidal gold chloride, tetraphenyl geranium and bromoadamantane were tested as slurry phase tracers. Of the liquid tracers, colloidal gold worked the best. A pulse of tracer was injected, and the residence time distributions were measured at various locations in the liquefaction reactors. This information was then used along with vapor-liquid equilibrium calculations and other data to determine hydrodynamic parameters such as phase holdups, dispersion and actual residence time.

The values of actual slurry residence time (ART) determined by the tracer injections are shown in Table 2-4, along with the nominal residence time (NRT) for the three sets of CLPP tests. Actual slurry residence time is the volumetric flow rate of slurry divided by the actual volume of slurry in the reactor as calculated from the results of the tracer tests. Nominal slurry residence time, on the other hand, is the volumetric flow rate of slurry divided by the reactor volume. The November 1981 tests were conducted during Wyodak ECLP support operations. For a nominal slurry residence time of 81 minutes, the tracer data indicated an ART of 56 minutes, or 69% of the NRT. For the April and May tests, ARTs of 37 and 45 minutes were determined for NRTs of 62 and 61 minutes, respectively. These actual residence times were useful when comparing yields and conversions from different pilot units operating at the same nominal conditions.

TABLE 2-4
CLPP REACTOR HYDRODYNAMIC TEST RESULTS

<u>Date</u>	<u>Coal</u>	<u>Nominal Residence Time, Minutes</u>	<u>Actual Residence Time, Minutes</u>	<u>Actual Time Nominal Time</u>
Nov. 1981	Wyodak	81	56	0.69
Apr. 1982	Monterey	62	37	0.60
May 1982	Monterey	61	45	0.70

2.5 Liquefaction Heat Release Studies

Measurements of EDS liquefaction temperature increases in the CLPP reactors have been discussed in previous EDS Technical Progress Reports (FE-2893-49, 57, 70, 74, 93). This section summarizes previous results and presents new data for Burning Star coal and Martin Lake lignite. The information is presented in Table 2-5.

Table 2-5

CLPP LIQUEFACTION REACTOR
ESTIMATED ADIABATIC TEMPERATURE RISES

<u>Coal</u>	<u>Monterey</u>		<u>Burning Star⁽³⁾</u>	<u>Ireland</u>	<u>Wyodak</u>		<u>Wandoan</u>	<u>Big Brown</u>	<u>Martin Lake⁽³⁾</u>
<u>Liquefaction Mode</u>	<u>Once-Through</u>	<u>Bottoms Recycle</u>	<u>Bottoms Recycle</u>	<u>Bottoms Recycle</u>	<u>Once-Through</u>	<u>Bottoms Recycle</u>	<u>Bottoms Recycle</u>	<u>Bottoms Recycle</u>	<u>Bottoms Recycle</u>
<u>VCO Disposition</u>	<u>Product</u>	<u>Hyt.</u>	<u>Hyt.</u>	<u>Liq, Product⁽⁴⁾</u>	<u>Product</u>	<u>Liq, Product⁽⁵⁾</u>	<u>Liq</u>	<u>Hyt., Product⁽⁶⁾</u>	<u>Hyt.</u>
<u>Nominal Liquefaction Conditions⁽¹⁾</u>									
<u>Temperature, °F</u>	840	840	840	840	840	840	840	800	850
<u>Slurry Residence Time, minutes</u>	60	60	60	60	60	60	60	100	40
<u>Solvent/Coal/Bottoms proportions by weight</u>	1.2/1/0	1.6/1/0.5	1.6/1/0.5	1.6/1/0.5	1.6/1/0	1.6/1/0.5	1.6/1/0.5	1.6/1/0.5	1.6/1/0.5
<u>Yield Periods</u>	257, 260, 264	346-350	393-395	370-374, 378-380	267, 269	351-357	362-365	338-343	398-400
<u>Approximate Liquefaction Temperature Rise, °F⁽²⁾</u>	50	80	60	110-120	80	110	70	110	80

(1) Hydrogen partial pressure was 1500 psig for once-through cases, 2000 psig for bottoms-recycle.

(2) Rounded to nearest 10°F.

(3) New Data

(4) YPs 370-374 to Liq, YPs 378-380 Product

(5) YPs 351-353 to Liq, YPs 354-357 Product

(6) YPs 333-340 to Hyt, YPs 341-343 Product

Once-through coal liquefaction study design conditions produced adiabatic temperature rises of 50°F for Monterey coal and 80°F for Wyodak coal. The recycle of bottoms at a 0.5/1 bottoms-to-coal ratio by weight produced an additional 30°F temperature rise, to 80°F for Monterey and 110°F for Wyodak. Liquefaction temperature rise measurements for the balance of the EDS program coals have been made for bottoms recycle operations only. They ranged from 60°F for Burning Star coal to 110°F for Ireland coal and Big Brown lignite. Wandoan coal and Martin Lake lignite produced intermediate temperature rises of 70°F and 80°F, respectively. As can be seen, overall liquefaction temperature rises are rank-independent. Attempts to correlate observed temperature rises with coal properties were unsuccessful, due to the limited amount and accuracy of the data. However, it is expected that for given liquefaction conditions temperature rise would increase with increasing coal heteroatom content and decrease with increasing coal ash levels.

2.6 Liquefaction Reactor Solids Summary

The CLPP liquefaction reactors are upflow vessels with no internals. The upward flow of reactants is insufficient to suspend all particles of unconverted coal. Therefore, some particles accumulate in the reactors. Early studies of the Recycle Coal Liquefaction Units (RCLUs) showed that reactor solids growth and reactor wall scale accumulation were potentially serious problems in the EDS process, particularly in once-through liquefaction of lower-ranked coals. Later experiments on CLPP confirmed solids growth in Wyodak once-through liquefaction, but demonstrated that the reactor solids could be controlled using a solids withdrawal system. The institution of bottoms recycle operations on the CLPP reduced concern over reactor solids, as little or no particle growth or wall scale accumulation have been experienced in bottoms recycle operations. Table 2-6 shows that +30 mesh reactor solids were a very small fraction (less than 5 wt%) of the total solids for Wyodak, Big Brown, and Martin Lake bottoms recycle operations. In comparison, Wyodak once-through operations produced about one-third +30 mesh particles.

Even though solids growth was not a problem in CLPP bottoms recycle operations, calcium carbonate did accumulate to significant amounts, particularly during lignite operations. It is, therefore, possible that large solids could accumulate under different circumstances. For example, while large particles did not accumulate during Wyodak bottoms recycle operations on the CLPP, they did accumulate during RCLU bottoms recycle operations at relatively low superficial liquid velocities.

In conclusion, reactors solids have not been a major problem during CLPP operations, particularly during bottoms recycle operations. However, significant amounts of calcium carbonate accumulate in the reactor solids during lignite operations and may be a potential concern in a commercial plant.

TABLE 2-6
LIQUEFACTION REACTOR SOLIDS FROM
CLPP OPERATIONS

<u>Coal</u>	<u>Monterey</u>		<u>Ireland</u>		<u>Wyodak</u>		<u>Big Brown</u>	<u>Martin Lake</u>
<u>Liquefaction Mode</u>	<u>Once-Through</u>	<u>Bottoms Recycle</u>	<u>Once-Through</u>	<u>Bottoms Recycle</u>	<u>Once-Through</u>	<u>Bottoms Recycle</u>	<u>Bottoms Recycle</u>	<u>Bottoms Recycle</u>
<u>Reactor Solids</u> ⁽¹⁾								
Accumulation, lbs/100 lbs Coal Fed	0.6	0.2-0.5	0.2	0.2	0.3	0.1	0.6-0.7	0.5-0.7
Composition Ranges, Wt%								
Ash	70-85	69-79	75-90	70-88	27-37	68-78	73-86	70-80
Calcium as CaO	N/A	17-19	3-4	1-3	N/A	22-28	17-24	12-24
CaCO ₃ Accumulation (Avg) lbs/Ton Coal Fed	N/A	0.6	<0.1	<0.1	N/A	0.4	5	3
+30 Mesh Particles, Wt%	0.1-0.4	0-0.2	<1.0	0-0.9	29-35	0.2-1.6	0.1-2.0	0.1-4.1

(1) Toluene washed and dried

2.7 Conclusions

The CLPP has achieved all objectives set out in Phases IIIB-V in the EDS development program. Integrated EDS operations have been successfully demonstrated for bituminous, subbituminous, and lignitic coals. CLPP product yields confirmed yields from the smaller pilot plants (KCLU's) and verified yields at economically preferred conditions. Vacuum bottoms, vacuum gas oil, solvent, and naphtha products were generated for quality testing. ECLP operations with Monterey, Wyodak, and Martin Lake coals were supported with CLPP operations with these coals. In addition to these accomplishments some other achievements were realized:

- A continuous bottoms recycle system was developed for CLPP and demonstrated associated conversion and operability improvements.
- Recycle conversion of vacuum gas oil into lighter products was demonstrated.
- Liquefaction reactor hydrodynamics were assessed through the use of gas and slurry-phase radioactive tracers.
- The overall EDS liquefaction reaction was determined to be exothermic, causing an estimated adiabatic temperature rise in the reacting fluid between 60 and 110°F for the conditions studied.
- Examination of reactor solids revealed that significant growth of reactor solids did not occur during bottoms recycle operations. However, calcium carbonate accumulation was observed and was greatest during lignite operations.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

LIQUEFACTION PROCESS RESEARCH

3. Solvent Hydrogenation Studies

Solvent hydrogenation studies during phases IIIB-V of the EDS program have focused on long-term activity maintenance of Ni/Mo-10 catalyst, process variable studies for solvents from various coals (bituminous, subbituminous, and lignitic) using various process alternatives (e.g., split-stream hydrotreating), catalyst screening evaluations and support of ECLP solvent hydrogenation operations. A list of key studies is given in Table 3-1.

3.1 Experimental Facilities and Procedures

Laboratory studies of solvent hydrogenation are conducted in small once-through fixed bed reactor systems. A simplified flow diagram of the bench scale hydrotreaters used in this program is shown in Figure 3-1. These units, designated M20, M21 and M22, are equipped with sufficient automatic monitoring and shutdown devices to allow safe and reliable overnight unattended operations. In general, these units are capable of running continuously for several months on a single catalyst charge.

One of the three bench units, M22, is operated as a dual reactor catalyst testing unit. This unit is similar to M20 and M21 but uses a single sandbath for isothermal temperature control of two separate reactor systems and incorporates dual feed pump and product accumulator capabilities. Smaller reactors (10 ml catalyst volume compared to 70 ml catalyst volume used in M20 and M21) are used in this dual-train unit.

Solvent feed and product are characterized by mass spectrometry. Mass spectrometry provides a measure of the component distribution (both aromatics and saturates) and how this distribution is affected by the hydrogenation process. Of particular importance are the donor hydrogen and saturates characteristics of the feeds and products.

3.2 Catalyst Activity Maintenance Studies

Four studies were conducted to determine if Ni/Mo-10 catalyst could maintain acceptable hydrogenation activity over an extended period of time. Long-term (> 1 yr.) maintenance of hydrogenation catalyst activity has important economic as well as process implications on the EDS process.

The first study (Run 14M21) demonstrated that acceptable hydrogenation activity can be maintained for at least one year on solvent from an Illinois No. 6 (Monterey No. 1 mine) bituminous coal. A temperature

Table 3-1

SUMMARY OF KEY SOLVENT HYDROGENATION STUDIES PERFORMED DURING EDS PROGRAM

<u>Type of Study</u>	<u>Run Numbers</u>	<u>Period</u>	<u>References</u>
o Activity Maintenance (Ni/Mo-10 catalyst)	14M21	3Q/77	FE-2893-3
	17M21	4Q/79	FE-2893-45
	18M21	2Q/80	FE-2893-53
	20M22	3Q/80	FE-2893-57
	21M22	3Q/81	FE-2893-93
o ECLP Support			
+ Catalyst Screening (Co/Mo-10 vs Ni/Mo-10)	10M22	3Q/77	FE-2893-3
	11M22	4Q/77	FE-2893-7
	14M22	3Q/78	FE-2893-21
	15M22	4Q/78	FE-2893-25
+ Low Pressure Studies	24M21	2Q/81	FE-2893-74
	26M21	3Q/81	FE-2893-78
+ Heavy Solvent Studies	20M20	4Q/77	FE-2893-7
	21M20	1Q/78	FE-2893-12
	28M21	2Q/82	FE-2893-93
	24M22	1Q/82	FE-2893-89
	26M22	3Q/82	FE-2893-99
+ Texas Lignite Solvent Study (Martin Lake mine)	28M21	3Q/82	FE-2893-99

Table 3-1 (Cont'd)

SUMMARY OF KEY SOLVENT HYDROGENATION STUDIES PERFORMED DURING EDS PROGRAM

<u>Type of Study</u>	<u>Run Numbers</u>	<u>Period</u>	<u>Reference</u>
+ ECLP Catalyst Activity Studies	22M22	4Q/81	FE-2893-83
	27M22	4Q/82	FE-2893-103
o Process Improvement Studies			
+ Split Stream Studies	23M21 (base)	1Q/81	FE-2893-70
	25M21	2Q/81	FE-2893-74
	23M22 (base)	1Q/82	FE-2893-89
	27M21	1Q/82	FE-2893-89
	25M22	3Q/82	FE-2893-99
+ ECLP Test Canister Catalyst Evaluations	30M21	4Q/82	FE-2893-103
	27M22	4Q/82	FE-2893-103
	28M22	4Q/82	FE-2893-103
o Carbon Oxide Impurity Study			
	12M22	2Q/78	FE-2893-17
	13M22	2Q/78	FE-2893-17

FIGURE 3-1

SIMPLIFIED FLOW DIAGRAM OF BENCH SCALE HYDROTREATERS

increase of $\sim 10^\circ\text{F}/\text{wk}$ was required to maintain constant donor hydrogen concentration at 1500 psig hydrogen pressure. This finding was later confirmed during Runs 17-18M21 for solvent derived from Wyoming (Wyodak mine) subbituminous coal.

A second study (Run 20M22) investigated the effects of higher hydrogen partial pressure (2000 psig) and a high boiling back-end solvent on catalyst deactivation. Recycle of HVGO to liquefaction through solvent hydrogenation is a method of reducing the amount of heavy liquids in the product slate. One train of the dual train unit was used to hydrogenate a nominal 400-700°F Illinois No. 6 (Monterey No. 1) solvent while the other train hydrogenated the same Illinois solvent with a 5 wt% HVGO spike. After 135 days on solvent (end-of-run), the 400-700°F solvent showed essentially no catalyst deactivation effects. The heavy solvent showed only slight deactivation of the catalyst.

A third study (Run 21M22) investigated the effects of low hydrogen partial pressure (900 psig) and a heavy back-end solvent (8 wt% HVGO) on the rate of catalyst deactivation. Low pressure (≤ 1200 psig) hydrogenation was proposed as a possible method of improving solvent quality at ECLP (see Section 3.3 of this report, Run 26M21). Heavy solvent from Illinois No. 6 (Monterey Mine No. 1) coal was fed to one train of the unit while a nominal 400-700°F Illinois Monterey solvent was fed to the other train. Over the 10 week length of this study the temperature was increased $1.5^\circ\text{F}/\text{wk}$ to maintain constant product donor hydrogen, indicating more rapid catalyst deactivation at lower hydrogen partial pressures than reflected by the $1.0^\circ\text{F}/\text{wk}$ increase required at 1500 psig. No difference in the relative activity of the heavy solvent vs. the nominal 400-700°F solvent was observed.

These studies have demonstrated that Ni/Mo-10 catalyst can maintain acceptable hydrogenation activity for at least one year at hydrogen partial pressures of 1500 psig or greater (see Section 3.3.5 of this report). At lower pressures the deactivation rate increases, thus reducing the useful life of the catalyst. Catalyst deactivation rates for EDS solvent are independent of coal rank. It has also been demonstrated that the addition of up to 8 wt% HVGO to the solvent does not significantly increase the rate of catalyst deactivation.

3.3 ECLP Support Studies

A number of process variable studies were conducted to determine the response of EDS solvents to changes in solvent hydrogenation process conditions. The process variables studied include temperature, pressure, space velocity, hydrogen treat rate, catalyst type and HVGO addition. These studies have provided guidance for ECLP operations and have allowed continued refinement of the empirical solvent hydrogenation model (see Section 4 of the Laboratory Process Research and Development Report for a description of the empirical solvent hydrogenation model).

3.3.1 Catalyst Screening (Ni/Mo-10 vs Co/Mo-20)

During 1977 and 1978 evaluation of Ni/Mo-10 and Co/Mo-20 catalysts continued. Earlier work had shown Ni/Mo-10 to be the more active catalyst for Illinois No. 6 (Monterey No. 1) solvent (see January-December 1976 EDS Annual Technical Progress Report [FE-2353-9]). Runs 10M22, 11M22, 14M22 and 15M22 were conducted to determine if Ni/Mo-10 was the more active catalyst regardless of solvent type. Run 10M22 used an Illinois No. 6 (Monterey No. 1) heavy solvent as feed, while the other tests used Wyoming (Wyodak) solvents.

Ni/Mo-10 catalyst was found to be the more active catalyst in each case. Also, it was discovered that the Illinois heavy solvent was harder to hydrogenate than the nominal 400-700°F boiling range Illinois solvent. A temperature increase of 50°F in the heavy solvent was required for the heavy solvent donor hydrogen concentration to match donor hydrogen concentration obtained with 400-700°F solvent. This finding has impact on pilot/commercial plant hydrotreater operations with heavy solvents and led to a set of process variable studies (Runs 24M22 and 28M21) which investigated the effects of HVGO addition on solvent product quality (see below).

3.3.2 Heavy Solvent Process Variable Studies

Two studies (28M21, 24M22) were conducted during 1982 to form a data base for heavy solvent hydrogenation operations. Earlier catalyst activity maintenance and process variable studies (Runs 10M22, 20M22, and 21M22) indicated that the addition of 5-10 wt% HVGO to the solvent before hydrogenation significantly reduces the donor hydrogen concentration of the product solvent. This reduction could not be predicted by the empirical hydrogenation model. The data base formed from these studies has been used to expand the empirical hydrogenation model to include simulations of solvents containing 5 and 10 wt% HVGO.

Figures 3-2 through 3-5 show parity plots of model predictions and experimental data for Monterey and Wyoming solvents containing 5 and 10 wt% HVGO. The model fits the experimental data well except for high temperatures and low space velocities with 10 wt% HVGO. The model predicts overhydrogenation of the solvent at these conditions, which was not observed experimentally.

3.3.3 Low Pressure Studies

Two studies (Runs 24M21 and 26M21) investigated the effect of reduced hydrogen partial pressure on the donor hydrogen and saturates concentrations of the solvent. Previously, solvent hydrogenation operations were conducted at 1500 psig H₂, or higher. Lower hydrogen partial pressures were suggested as a means of reducing product saturates while maintaining solvent donor hydrogen (i.e., improved selectivity). The pressures studied ranged from 500 psig to 1250 psig.

FIGURE 3-2

PARITY PLOT OF MODEL AND EXPERIMENTAL
DONOR HYDROGEN CONCENTRATIONS FOR 5 WT% HVGO ADDITION

FIGURE 3-3

PARITY PLOT OF MODEL AND EXPERIMENTAL
SATURATES CONCENTRATIONS FOR 5 WT% HVGO ADDITION

FIGURE 3-4

PARITY PLOT OF MODEL AND EXPERIMENTAL
DONOR HYDROGEN CONCENTRATIONS FOR 10 WT% HVGO ADDITION

FIGURE 3-5

PARITY PLOT OF MODEL AND EXPERIMENTAL
SATURATES CONCENTRATIONS FOR 10 WT % HVGO ADDITION

The results of these studies indicate that constant donor hydrogen concentrations can be maintained during hydrogenation by balancing decreases in hydrogen partial pressure with increases in temperature (see Run 24M21 results, Table 3-2). The increase in selectivity is slight, however.

It was also determined that the Ni/Mo-10 catalyst deactivates more rapidly at lower pressures. During Run 26M21 the unit was returned to start-of-run conditions (900 psig) after 55 days on solvent. The change in donor hydrogen concentration during hydrogenation was 87% of the start-of-run value, indicating that rapid deactivation had occurred. A low pressure catalyst activity maintenance study (Run 21M22-See section 3.2 of this report) found a 50% higher temperature increase was required to maintain product donor hydrogen concentration at 900 psig than at 1500 psig. This rapid rate of catalyst deactivation would make low pressure hydrogenation undesirable in a commercial plant.

The empirical solvent hydrogenation model was tested at all conditions studied in Run 26M21 to determine the validity of the model at low pressures. The model was found to be valid down to at least 900 psig.

A series of yield periods was conducted at 1250 psig to determine the effect of high hydrogen treat rates on the product solvent. Treat rates as high as 3.1 x RV SCF/Bbl were used, compared to the 0.94 x RV SCF/Bbl treat rate typically used. No difference in the donor hydrogen or saturates characteristics of the product solvent was noticed between yield periods conducted at high and normal treat rates.

3.3.4 Martin Lake Process Variable Study

A study (Run 29M21) was conducted in 3Q/1982 to determine if the empirical hydrogenation model is valid for a solvent derived from a lignitic coal (Martin Lake mine) in addition to bituminous and subbituminous solvents. The study showed that the model predicted donor hydrogen concentrations extremely well. Saturates predictions also agreed acceptably with experimental data.

3.3.5 ECLP Catalyst Activity Studies

Runs 22M22 and 27M22 were conducted in 4Q/1981 and 4Q/1982 respectively to determine the activity of spent ECLP Ni/Mo-10 catalyst relative to fresh Ni/Mo-10. The results of these studies have provided insight regarding the rate of hydrogenation catalyst deactivation in large, integrated liquefaction units. Previously, the only information on catalyst deactivation rates was from small bench units.

Run 22M22 evaluated ECLP Ni/Mo-10 catalyst which was on solvent for approximately 13 months. This catalyst, as well as fresh Ni/Mo-10 catalyst, were used to hydrogenate a Wyoming solvent in the dual train hydrogenation unit (M-22). By comparing the donor hydrogen concentrations produced by

Table 3-2

LOW PRESSURE HYDROGENATION RESULTS

(Run 24M21)

- o Illinois spent solvent, Donor Hydrogen = 1.34 x RV wt%
- o Ni/Mo-10 Catalyst
- o Increasing Temperature balances decreasing pressure

<u>H₂ Pressure</u> <u>(Psig)</u>	<u>Temperature</u> <u>(-RV, °F)</u>	<u>Space Velocity</u> <u>(xRV, wt%)</u>	<u>Donor Hydrogen</u> <u>(xRV, wt%)</u>
1500	65	0.89	1.73 ± 0.06*
1200	65	0.89	1.59 ± 0.00
790	90	0.88	1.73 ± 0.01

* One standard deviation

each catalyst, a spent catalyst relative activity of 0.60 was determined. This finding is within the activity range which would be expected from bench experience.

A second evaluation was performed (Run 27M22) on ECLP Ni/Mo-10 catalyst after approximately 18 months on solvent. For this study Illinois (Burning Star) solvent was used to determine the activity of the spent catalyst relative to fresh Ni/Mo-10. The spent catalyst activity was found to be 0.46 in this study. Again, this value is consistent with previous bench experience.

These studies have shown that the unsteady state conditions often encountered during the operation of ECLP's SHU did not seriously affect the rate of hydrogenation catalyst deactivation. This, along with the high quality solvent produced at ECLP during Texas (Martin Lake mine) lignite operations, indicates that the useful life of Ni/Mo-10 catalyst should be at least 18 months in a commercial plant.

3.4 Process Improvement Studies

Several studies were conducted to explore possible improvements to the traditional EDS solvent hydrogenation process. One concept tested was split-stream hydrotreating. This involves fractionating the solvent at a desired temperature and hydrogenating the fractions separately under different conditions. Prior to liquefaction, the two hydrotreated solvent streams would be recombined to form the recycle solvent stream. A second improvement tested was the use of catalysts other than Ni/Mo-10 or Co/Mo-20 for solvent hydrogenation.

3.4.1 Split-Stream Studies

Three studies (Runs 25M21, 27M21, 25M22) were conducted to determine the feasibility of hydrogenating the light (600°F^-) and heavy (600°F^+) fractions of an EDS solvent separately. This process has a possible advantage over the practice of hydrogenating the entire solvent stream. By hydrogenating the two solvent fractions separately and then blending the products prior to hydrogenation, it might be possible to produce a higher quality solvent than hydrogenating the full-stream solvent.

Run 25M21 was conducted during 2Q/1981 to determine the response of the 550°F^- fraction of an Illinois solvent to typical hydrogenation conditions. The results of this study showed that the 550°F^- fraction of this solvent was severely hydrogenated (up to 80 wt% saturates) at RV + 115°F to RV + 165°F and 0.66 x RV W/H/W to 1.32 x RV W/H/W.

In order to determine conditions that would not result in over-hydrogenation of a light solvent fraction, Run 27M21 was conducted during 1Q/1982 using the 600°F^- fraction of a Wyoming solvent. The temperature

range was reduced to between RV - 35°F and RV + 65°F. The space velocity was held constant at RV x 1.32 W/H/W. The 600°F⁻ fraction was only mildly hydrogenated at these temperatures, indicating that light solvent fractions alone are unlikely to produce high quality solvents using Ni/Mo-10 catalyst.

The heavy 600°F⁺ fraction of the same Wyoming solvent used in Run 27M21 was studied during run 25M22. The solvent was hydrogenated at temperatures ranging from RV + 65°F to RV + 215°F and space velocities from 0.66 x RV to 2.63 x RV W/H/W. The 600°F⁺ solvent was more difficult to hydrogenate than the full-stream Wyoming solvent (Run 23M22) and had a lower maximum donor hydrogen as well.

No blend of 600°F⁻/600°F⁺ products would produce a solvent of higher quality than could be attained by hydrogenation of the full-stream solvent. For this reason, there is no incentive to hydrogenate the heavy and light fractions of an EDS solvent separately.

3.4.2 ECLP Test Canister Studies

A series of studies was conducted to determine the fresh and spent relative catalyst activities of six commercially available solvent hydrogenation catalysts. A sample of each catalyst was loaded into a specially designed canister. The canister was then suspended in the second solvent hydrogenation reactor at ECLP (R-302). After 13 months on solvent, the canister was removed and sent to BARD. Fresh catalyst samples were also obtained to allow side-by-side testing of fresh and spent catalyst. The six catalysts studied were Ni/Mo-10, Ni/W, Ni/Mo denitrogenation, Co/Mo desulfurization, Co/Mo-A, and Ni/Mo-A.

Relative activities for each catalyst were determined using the empirical solvent hydrogenation model. The model catalyst relative activity was varied at each condition until the model matched the donor hydrogen concentration of the product solvent. The same procedure was repeated for the saturates concentrations.

The relative activities for each catalyst are shown in Table 3-3. Ni/W catalyst is clearly superior to Ni/Mo-10 in terms of more hydroaromatics and less saturates production. Fresh Ni/Mo-A catalyst was found to be highly selective to saturates. However, spent Ni/Mo-A was found to be superior to both fresh Ni/Mo-A and fresh Ni/Mo-10. Although the remaining catalysts showed a slightly greater selectivity to hydroaromatics than Ni/Mo-10, they are much less active than Ni/Mo-10.

3.5 Carbon Oxide Impurity Studies

A study (Runs 12M22 and 13M22) was conducted to determine if CO_x impurities in the hydrogen treat gas would adversely affect the hydrogenation of solvents using Ni/Mo-10 catalyst. The results of this study indicate that the extent of hydrogenation was not affected by up to 4 mole % CO_x impurities. However, the denitrogenation and desulfurization activities were reduced by approximately 20 percent.

Table 3-3

AVERAGE RELATIVE ACTIVITIES FOR ECLP TEST CANISTER CATALYST SAMPLES

<u>Catalyst</u>	<u>Average Catalyst Activity Relative To Fresh Ni/Mo-10</u>	
	<u>Donor Hydrogen Basis</u>	<u>Saturates Basis</u>
o Ni/Mo-10 (fresh)	1.00*	1.00
(spent)	0.60	0.55
o Ni/W (fresh)	1.34	0.46
(spent)	0.62	0.19
o Ni/Mo (fresh)	0.78	0.34
Denitrogenation (spent)	0.49	0.16
o Co/Mo (fresh)	0.68	0.29
Desulfurization (spent)	0.32	0.21
o Co/Mo-A (fresh)	0.39	0.22
(spent)	0.30	0.20
o Ni/Mo-A (fresh)	1.00	1.40
(spent)	1.06	0.89

* One Standard Deviation 0.05 for all of these determinations

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

LIQUEFACTION PROCESS RESEARCH

4. Bench Units, Modeling and Correlation Studies

Batch tubing bomb autoclaves and continuous flow reactors were employed to provide yield and operability data for a variety of coals. The yield data from the bench scale hydrotreaters and the liquefaction pilot units were correlated to provide models for recycle solvent hydrogenation and liquefaction which were used for process simulation.

Bench unit studies from the beginning of Phase IIIB (3077) to the completion of the EDS program (4082) are outlined in Table 4-1. Bench studies performed on OTCLU have been listed separately from those conducted in tubing bomb autoclaves.

4.1 Tubing Bomb Autoclave Studies

Tubing bombs (Figure 4-1) have principally been used for bench scale research in the various areas of coal liquefaction classified below:

- o Direct comparison of reactivity of coals in terms of overall conversion to both liquids and gas. Tubing bombs are useful tools for coal screening studies prior to pilot plant testing.
- o Evaluation of potential process improvements, e.g., staged temperature, staged liquefaction, bottoms recycle, and coal pretreatment effectiveness.
- o Process variable studies to determine the effects of temperature, holding time, hydrogen partial pressure, solvent quality and solvent/coal ratio on liquefaction conversion.

The advantages of using the tubing bomb autoclave as a research tool are: small sample requirement, rapid results, low cost per data point, and well-defined operating conditions. However, because the tubing bomb autoclave is a batch system, continuous flow units are needed to address steady state process concerns.

The important tubing bomb studies performed during Phases IIIB-V of the EDS program are summarized below and reported in Table 4-1.

4.1.1 Correlations of Coal Conversion with Coal Properties

Stepwise multiple regression analysis of tubing bomb autoclave conversion data was performed to develop a correlation expressing liquefaction

Table 4-1

Bench Unit Experimental Programs Conducted During the EDS Program

Unit	Study	References	Unit	Study	References
• Tubing Bomb Autoclaves	+ Correlation of Coal Conversion with Coal Properties	3Q78 [FE-2893-21] 4Q78 [FE-2893-25] AN78-79 [FE-2893-35] 3Q79 [FE-2893-41] 1Q80 [FE-2893-49] AN79-80 [FE-2893-53]	o OTCLU	- Texas (Martin Lake Mine) Lignite	4Q81 [FE-2893-83] 1Q82 [FE-2893-89] AN81-82 [FE-2893-93]
	+ Liquefaction Conversion of Wyoming Coal Bottoms from CLPP	4Q78 [FE-2893-25] AN78-79 [FE-2893-29]		+ Tubing Bomb Evaluation of Solvent Quality Effects on Bottoms Recycle Coal Conversion	3Q80 [FE-2893-57] 4Q80 [FE-2893-64] AN80-81 [FE-2893-74]
	+ Tubing Bomb Investigation of Bottoms Recycle of Sponsor Coals	1Q79 [FE-2893-29] AN78-79 [FE-2893-35] 3Q79 [FE-2893-41]		+ Reactor Hydrodynamic Support Study	3Q81 [FE-2893-78] 4Q80 [FE-2893-83] AN81-82 [FE-2893-93]
	+ Heavy Liquid Recycle-Tubing Bomb Simulation	4Q79 [FE-2893-45] 1Q80 [FE-2893-49] AN79-80 [FE-2893-53]		+ Gas-Swept Mill Coal Drying Study	3Q80 [FE-2893-57] 1Q81 [FE-2893-70] AN80-81 [FE-2893-74] 1Q82 [FE-2893-89] AN81-82 [FE-2893-93] 3Q82 [FE-2893-99] 4Q82 [FE-2893-103]
	+ Solvent Cracking Studies	CA 3Q79 [FE-2893-41] CA AN79-80 [FE-2893-53]		+ Slurry Drying Study	4Q82 [FE-2893-103]
	+ Coal Screening and Process Variable Studies;			+ Validation of OTCLU Yields	AN78-79 [FE-2893-35] 3Q79 [FE-2893-41] 4Q79 [FE-2893-45] AN79-80 [FE-2893-53]
	- Illinois No. 6 (Burning Star No. 2 mine) Bituminous Coal	3Q78 [FE-2893-21] 4Q78 [FE-2893-25] 1Q79 [FE-2893-29] AN78-79 [FE-2893-35] 3Q81 [FE-2893-78]		+ Operability Study Wyoming Coal	3Q77 [FE-2893-3] 4Q77 [FE-2893-7] 1Q78 [FE-2893-12] AN77-78 [FE-2893-17] 3Q78 [FE-2893-21] 4Q78 [FE-2893-25] 1Q79 [FE-2893-29] AN78-79 [FE-2893-35]
	- Pittsburgh (Ireland Mine) Bituminous Coal	1Q79 [FE-2893-29] AN78-79 [FE-2893-35] 3Q79 [FE-2893-41] AN79-80 [FE-2893-53]		+ High Pressure, Coal-only Study on OTCLU	4Q79 [FE-2893-45] 1Q80 [FE-2893-49] AN79-80 [FE-2893-53] 3Q80 [FE-2893-57] 4Q80 [FE-2893-64] AN80-81 [FE-2893-74]
	- Australian (Wandoan) Black Coal	4Q78 [FE-2893-25] AN78-79 [FE-2893-35] 3Q80 [FE-2893-57] AN80-81 [FE-2893-74]		+ Solvent Cracking Study	CA AN79-80 [FE-2893-53]
	- Illinois No. 6 (Monterey No. 1 Mine) Bituminous Coal	4Q79 [FE-2893-45] AN79-80 [FE-2893-53]		+ Liquefaction of Neat Bottoms	1Q80 [FE-2893-49] AN79-80 [FE-2893-53] 3Q80 [FE-2893-57] AN80-81 [FE-2893-74]
	- Wyoming (Wyodak Mine) Subbituminous Coal	4Q79 [FE-2893-45] AN79-80 [FE-2893-53]		+ Vacuum Gas Oil (VGO) Conversion Study	3Q80 [FE-2893-57]
	- Texas (Big Brown Mine) Lignite	1Q80 [FE-2893-49] AN79-80 [FE-2893-53]			

FIGURE 4-1

SCHEMATIC DIAGRAM OF TUBING BOMB AUTOCLAVE

conversion and yields as functions of measurable coal properties. Independent variables included ultimate, proximate, and petrographic analyses. The dependent variable was tubing bomb conversion (dry, ash-free) at 840°F/40 minutes/1500 psig hydrogen partial pressure and 1.6/1 tetralin-to-coal ratio. A total of 16 coals ranging from bituminous to lignitic were included in the data base (4Q78 [FE-2893-25]).

The following observations were made based on the correlations:

- + percent volatile matter was the most significant variable
- Volatile matter was highly correlated with percent carbon, atomic H/C ratio, and percent exinite.
- + total sulfur content, in addition to volatile matter, was significant in correlating conversion.
- + C₁-C₃ gas make correlated highly with H/C ratio and volatile matter content.
- + total gas make correlated well with percent carbon, percent oxygen, and atomic O/C ratio.

Tubing bomb conversions for coals not in the data base were predicted well by the derived statistical correlation (1Q80 [FE-2893-49], AN79-80 [FE-2893-53]). Tubing bomb conversion trends were in reasonable agreement with continuous pilot plant results.

4.1.2 Liquefaction Conversion of Wyoming Coal Bottoms from CLPP

This study was conducted to test the reactivity of Wyoming (Wyodak mine) coal bottoms during bottoms recycle. Tubing bomb liquefaction experiments were conducted with two CLPP bottoms samples liquefied separately in the absence of coal. The results indicated that significant additional liquid yield could be achieved by recycling Wyoming bottoms (4Q78 [FE-2893-25]). Subsequent to this study, all program and sponsor coals were investigated for bottoms recycle potential.

4.1.3 Tubing Bomb Investigation of Bottoms Recycle of Sponsor Coals

A tubing bomb study to screen sponsor coals for possible yield incentives for operating the EDS process in a bottoms recycle mode was conducted. The primary objective of the study was to estimate the extent to which the liquefaction residues for the sponsor coals could be converted. The seven program and sponsor coals employed in this study were Texas (Big Brown mine) lignite, Wyoming (Wyodak mine) subbituminous coal, Australian (Wandoan) black coal, two Illinois No. 6 (Monterey No. 1 mine and Burning Star No. 2 mine) and two Pittsburgh seam (Ireland and Arkwright mines)

bituminous coals. Liquefaction residues employed in the study had been generated on RCLU at operating conditions of 840°F and 40 minutes nominal residence time during preliminary screening studies on each of the coals.

During the initial part of this study, neat bottoms were liquefied at a temperature of 840°F for 40 minutes reaction time, with a 4 wt% hydrogen treat rate and 1.6 solvent (hydrogenated MPSS)-to-bottoms ratio. Cyclohexane conversions for all the bituminous coals and Wandoan coal were roughly equivalent to 22 wt%. Wyodak bottoms yielded only 16 wt% conversion, and Big Brown bottoms gave only 11 wt% conversion.

For the remainder of the study, mixtures of coal plus bottoms in a 2/1 ratio were liquefied at 840°F and 40 minutes reaction time for solvent-to-solids ratios of 1.6 and 1.07. The results indicated that the conversion and gas yield for Wandoan and the bituminous coals were independent of the solvent-to-solids ratio in the range studied. On the other hand, Wyodak and Big Brown samples showed a strong conversion synergism of about 10 wt% (on bottoms) between coal and bottoms. In addition, the synergism for Wyodak coal plus bottoms was strongly affected by the solvent-to-solids ratio (AN78-79 [FE-2893-35]).

4.1.4 Tubing Bomb Simulation of Heavy Liquid Recycle

The recycle of heavy liquid products to liquefaction provides potential for process and product slate flexibility. Two such alternatives, vacuum gas oil (VGO) recycle and coker liquid recycle, were screened in tubing bombs.

+ Vacuum Gas Oil (VGO) Recycle

Tubing bomb liquefaction experiments were carried out with VGO (CLPP A-2) derived from CLPP operations with Wyodak coal. Various temperature/residence time combinations were tested in tubing bombs in the presence of 2000 psig hydrogen partial pressure. No donor solvent was added. Gas chromatographic distillation on feed and products revealed that heavy liquid fractions (700°F+) were converted into lighter fractions (400°F- and 400-700°F) as liquefaction severity increased. Gas make, comprised of C₁-C₃ hydrocarbons, CO₂ and H₂S, also increased (1Q80 [FE-2893-49]).

The results indicated that 700-1000°F VGO could be recycled to extinction in liquefaction, yielding additional 700°F- liquid and gas products. This study was extended in the Once-Through Coal Liquefaction Unit (OTCLU) and is summarized separately in Section 4.2.

+ Coker Liquid Recycle

Coker liquids derived from coking operations at two different coking temperatures (RV-60°F and RV+70°F) were tested. This study complemented

an earlier brief tubing bomb study and a more extensive RCLU study. The results of the earlier studies are reported in the January, 1976-June, 1977, EDS Final Technical Progress Report (FE-2353-20).

The purpose of this study was to see if the temperature at which the coker liquids were produced had an effect on their conversion under liquefaction conditions. Reaction temperature was kept constant while the initial hydrogen pressure, solvent-to-coker liquids ratio and residence time were varied.

Coker liquids derived at low coking temperature were more reactive in liquefaction than the high temperature derived coker liquids. However, since low temperature coking produces less coker liquids, the overall impact on net 1000°F conversion products was unchanged. Assuming no interactions existed between coal and coker liquids conversion in liquefaction, recycle of coker liquids to liquefaction resulted in approximately 3-4 wt% extra conversion to 1000°F liquids based on dry feed coal. This increased conversion estimate was independent of the coking temperature.

Coker liquids conversion increased with increased liquefaction severity. The solvent-to-coker liquids ratio was the most sensitive variable. However, on a dry coal feed basis, this sensitivity resulted in only small additional conversion incentive (~1 wt% on coal) (1Q82 [FE-2893-49], AN79-80 [FE-2893-53]).

4.1.5 Solvent Cracking Study in Tubing Bombs

A series of tubing bomb experiments was conducted to determine the extent to which solvent cracking occurs under liquefaction conditions. The solvent samples used were hydrogenated multipass spent solvent (MPSS) from CLPP, a saturates-rich raffinate, and an aromatics-rich extract from sulfolane extraction of the MPSS. Each of these samples was run at four different sets of liquefaction conditions in order to assess the effect of residence time and temperature on cracking.

Results show that gas make increases with liquefaction severity and is greatest for the raffinate (which has the highest saturates content). The results indicated that the cracking of hydroaromatics, as well as saturates, is significant. Furthermore, hydroaromatics decreased with increasing severity, indicating that the loss of solvent quality is due both to dehydrogenation and cracking (3Q79 [FE-2893-41]). Solvent cracking characteristics were identical with and without the presence of mineral matter (AN79-80 [FE-2893-53]).

4.1.6 Coal Screening and Process Variable Studies

Coal screening and process variable studies in tubing bombs were normally performed prior to testing a coal in the Recycle Coal Liquefaction Unit (RCLU). The scope and depth of the studies varied from coal to coal, but the primary purpose was to provide guidance for subsequent pilot plant operations.

Two level factorial designs were used to screen the effects of reaction temperature, reaction time, hydrogen partial pressure, solvent-to-coal ratio and bottoms-to-coal ratio. Process variable studies in the coal-only operating mode were conducted for Illinois No. 6 (Burning Star No. 2 mine) coal (4Q78 [FE-2893-25]), AN78-79 [FE-2893-35], and Pittsburgh (Ireland mine) coal (4Q79 [FE-2893-45]). Process variable studies incorporating bottoms-to-coal ratio included Australian (Wandoan mine) coal (4Q78 [FE-2893-25], 3Q80 [FE-2893-57]), Illinois No. 6 (Monterey No. 1 mine) coal (3Q79 [FE-2893-41]), Wyoming (Wyodak mine) coal (4Q79 [FE-2893-45]), Texas (Big Brown mine) lignite (1Q80 [FE-2893-49]), AN79-80 [FE-2893-53]) and Texas (Martin Lake mine) lignite (1Q82 [FE-2893-89], AN81-82 [FE-2893-93]). Results indicated that significantly improved liquid yields were achievable with bottoms recycle compared to coal-only operations.

4.1.7 Tubing Bomb Evaluation of Solvent Quality Effects on Bottoms Recycle Coal Conversion

A tubing bomb study was conducted to investigate the effects of solvent quality index (SQI) on coal conversion with simulated bottoms recycle. The three coals employed in this study were Illinois No. 6 (Monterey No. 1 mine), Wyoming (Wyodak mine), and Texas (Big Brown mine) lignite. All experiments were done at constant temperature, time, and solvent-to-coal-to bottoms. Two levels of pressure were examined.

Conversion response plateaued at higher SQI with bottoms recycle liquefaction than with once-through liquefaction (4Q80 [FE-2893-64], AN80-81 [FE-2893-74]). The results were used in planning future RCLU solvent quality investigations.

4.1.8 Reactor Hydrodynamic Support Study

A tubing bomb support study for selection of a suitable liquid phase radioactive tracer to be used in characterizing liquefaction reactor hydrodynamics was conducted. The criteria used in the tubing bomb study for selecting a liquid phase tracer were:

- o compatability with a coal, solvent, and hydrogen atmosphere at liquefaction conditions.
- o ability to disperse in coal liquids.
- o distribution in the gas, liquid, and solid phases at liquefaction conditions.

Using these criteria, several organic and inorganic compounds were tested. Early tests identified 1-bromoadamantane and 9-bromophenanthrene as

possible candidates for testing in RCLU (3Q81 [FE-2893-78], 4Q81 [FE-2893-83]). Further testing identified tetraphenylgermanium as the best candidate for the soluble radioactive liquid phase tracer (AN81-82 [FE-2893-93]).

4.1.9 Gas Swept Mill Coal Drying Study

A tubing bomb investigation of coal drying effects in the gas-swept mill (GSM) was conducted due to unexpected low coal conversions observed in ECLP. Early tubing bomb results showed no conversion debit due to GSM processing for Illinois No. 6 (Monterey No. 1 mine) coal (3Q80 [FE-2893-57]). However, tests in tubing bombs and RCLU identified a 5 wt% debit for a sample of GSM processed Wyoming (Wyodak mine) coal (1Q82 [FE-2893-89]), prompting this investigation.

Coal was prepared for liquefaction in the GSM, a process which first crushes coal and then dries the crushed coal particles in a hot flue gas. This drying procedure was shown to be detrimental to coal liquefaction yields due to the high temperature (often > 600°F) and large oxygen concentration (8-12 mole %) of the flue gas. The bench program utilized a small fluidizing unit (SFU), shown in Figure 4-2, to determine the controlling variables. Bench tests revealed that extremely severe drying conditions could produce liquefaction conversion liquid yield debits as large as 20 wt% for both Wyodak subbituminous coal and Martin Lake lignite. However, ECLP drying conditions typically produced debits in the 2 to 5 weight percent range. The debits resulted from pyrolysis and oxidation of the coal, which occurred while drying coal in the mill. With the ECLP operating scheme, debits for Wyodak coal were initiated at 575°F inlet gas temperature and debits for Martin Lake lignite were initiated at 620°F inlet gas temperature (3Q82 [FE-2893-99]).

Conventional analytical tests failed to detect any chemical changes in the dried coal although the mild pyrolysis/oxidation induced liquefaction debits as large as 10-12%. Coal-only liquefaction in tubing bombs proved to be the most sensitive test for detecting the effects of mild oxidation/pyrolysis. This result had significant impact on the evaluation procedures used to determine the effects of coal preparation processes on subsequent liquefaction.

A safe operating range for the gas-swept mill was determined that would avoid the liquefaction debits. Control strategy centered on reducing the coal feed rate, but several design options are available for a commercial unit that would not restrict the coal feed rate. Furthermore, bottoms-recycle liquefaction significantly reduced the debits due to GSM processing for Martin Lake lignite, but had little effect on Wyodak coal debits (4Q82 [FE-2893-103]). The coal conversion debits associated with ECLP gas-swept mill drying are not a concern for a commercial process.

FIGURE 4-2
SCHEMATIC OF SFU APPARATUS

4.1.10 Slurry Drying Study

Due to conversion debits observed with gas-swept mill coal drying, a short experimental program was conducted to determine whether similar debits could occur during slurry drying. Bench tests were performed on Wyoming (Wyodak mine) coal and Texas (Martin Lake mine) lignite. Both coals showed no subsequent conversion debits after being slurry dried at nominal ECLP conditions at 3.4 SQI. Furthermore, no deleterious effect was observed when Wyodak coal was slurry dried at 2.0 SQI (4Q82 [FE-2893-103]). Based on the laboratory results from tubing bomb experiments, slurry drying at nominal ECLP conditions poses no commercial concerns.

4.2 Design and Operation of 15 pound-per-day Once-Through Coal Liquefaction Unit (OTCLU)

A 15 pound/day Once-Through Coal Liquefaction Unit (OTCLU) was designed and built to fill a gap between small batch reactors and the fully integrated pilot unit facilities. The unit is low-cost, easy to operate, and large enough to produce products for distillation, but small enough to conduct a complete screening study on less than one barrel of coal.

A schematic flow plan of the OTCLU is given in Figure 4-3. Feed slurry and hydrogen are metered through separate preheaters to the up-flow liquefaction reactors which are contained in a fluidized sandbath. The reactors are designed to operate at temperatures up to 1000°F and pressures up to 3000 psig. The total gas, liquid and solid products exit the liquefaction reactors into two high pressure accumulators where the solids and liquids are collected for each yield period. The gas continuously leaves the accumulator through a pressure let-down valve and is measured in a dry test meter.

Several validation experiments were carried out with the OTCLU using various coals and at different operating conditions (AN78-79 FE-2893-35, 3Q79 FE-2893-41, 4Q79 FE-2893-45, AN79-80 FE-2893-53). Objectives of these experiments were to check the reproducibility of the unit and to test the operability limitations of the unit. Coals used for these experiments were Illinois No. 6 (Monterey Mine No. 1), Pittsburgh seam (Ireland mine) bituminous coal, Wyoming (Wyodak mine) subbituminous coal and Texas (Big Brown) lignite.

The results indicated that the unit generates reproducible data, and that the yields obtained were in reasonable agreement with the 50 pound/day Recycle Coal Liquefaction Unit (RCLU-1) at comparable conditions. Operational problems were experienced only in once-through coal operations with Big Brown lignite, due to the high viscosity of the product slurry.

FIGURE 4-3

OTCLU FLOW DIAGRAM

4.2.1 Operability Study with Wyoming Coal

During the liquefaction of low rank coals, such as Wyoming (Wyodak mine) coal, the calcium contained in the form of salts of humid acids decomposes to form calcium carbonate (CaCO_3). This calcium carbonate accumulates in the liquefaction reactor as wall scale and free-flowing aggregates (oolites). The OTCLU was used to test proposed solutions to the calcium carbonate deposition problems. These solutions can be classified as mechanical or chemical solutions. Mechanical solutions are those in which the process conditions, process configuration or mechanical equipment are modified to alleviate the problems due to the CaCO_3 deposition. Chemical solutions are those in which the chemical form of the calcium is changed by pretreatment, or a chemical is added to the coal slurry before it is liquefied.

During EDS Phase IIIA, pretreatment of low-rank coals with dilute sulfuric acid was shown to be effective in preventing CaCO_3 formation. The kinetics of H_2SO_4 pretreatment were studied with wet Wyoming coal (3Q77 [FE-2893-3]). Pretreatment of moist Wyodak coal with SO_2 gas was also found to be an effective means of converting calcium in coal to calcium salts which are stable during liquefaction (4Q77 [FE-2893-7]). Calcium carbonate formation in liquefaction was prevented by another means, e.g., ion-exchange with various metal salts. Ferrous sulfate, ferric sulfate, and sodium carbonate were all effective in eliminating CaCO_3 wall scale and agglomerates (AN77-78 [FE-2893-17]). No mechanical solutions were found.

4.2.2 High Pressure, Coal-only Study

The purpose of this study was to generate coal-only liquefaction yields at high pressure to be used for developing yield correlations for bottoms recycle operations. Experiments were conducted with Illinois No. 6 (Monterey No. 1 mine), Pittsburgh seam (Ireland mine), Wyoming (Wyodak mine), and Texas (Big Brown mine) coals. Considerable data scatter and operational problems were encountered during this study, especially with the lower rank coals, Wyodak and Big Brown (1Q80 [FE-2893-49], AN79-80 [FE-2893-53], 3Q80 [FE-2893-57]). Results showed practically no effect of pressure in the range 2000-2500 psig for Monterey No. 1 and Wyodak coals (1Q80 [FE-2893-49], AN79-80 [FE-2893-53]), and only a slight effect on Big Brown lignite (AN80-81 [FE-2893-74]). OTCLU experienced lower conversions than RCLU for Ireland coal (AN79-80 [FE-2893-53]). The OTCLU results at high pressure were implemented into the EDS coal liquefaction model.

4.2.3 Solvent Cracking Study on the Once-Through Coal Liquefaction Unit (OTCLU)

A process variable study analyzing solvent cracking characteristics was carried out on OTCLU with unhydrotreated NPSS from CLPP and hydrogenated raw creosote oil (HCO). The results supported the earlier conclusions based on a similar tubing bomb solvent cracking study.

The main conclusions from this study were (CA AN79-80):

- As the temperature was increased from 750 to 950°F, naphtha and gas make increased, whereas saturates content and solvent quality decreased. Both CLPP MPSS and HCO have essentially the same temperature response regarding gas and naphtha makes and reduction of solvent quality.
- The increase in gas and naphtha makes and decrease in saturates and donor hydrogen contents were more dramatic at temperatures above 850°F and were practically insignificantly at 750°F.
- For the same reaction temperature, an increase in pressure from 1500 to 2500 psig did not result in any significant effect on either gas and naphtha make, or saturate depletion.
- The percentage change in concentration of specific hydroaromatics and aromatics components also demonstrated strong dependence on temperature at 850°F and above, and practically no dependence on pressure from 1500 to 2500 psig.

4.2.4 Liquefaction of Neat Bottoms

In support of continuous bottoms recycle operations, and to aid in developing yield correlations for bottoms recycle, an OTCLU process variable study was conducted on the liquefaction of neat bottoms from CLPP operations on Illinois No. 6 (Monterey No. 1 mine) coal. Results indicated that liquid make (C₄-1000°F) increased as the pressure increased for recycled bottoms, but not for single-pass bottoms (AN79-80 [FE-2893-53]). A similar study for Texas lignite (Big Brown mine) bottoms was aborted due to operational difficulties (3Q80 [FE-2893-57], AN80-81 [FE-2893-74]).

4.2.5 Vacuum Gas Oil (VGO) Conversion Study

A process variable study was carried out on OTCLU to assess vacuum gas oil (VGO) conversion trends at various process conditions (3Q80 [FE-2893-57]). The VGO sample was obtained from CLPP during Illinois No. 6 (Monterey No. 1 mine) coal operations.

Several conclusions have been drawn based on the results:

- There is a net conversion of 700°F+ fractions in VGO to a lighter distillate fraction (700°F-). This result is directionally comparable with an earlier VGO conversion study conducted in tubing bombs (see Section 4.1).
- The 1000°F conversion is independent of pressure for 1500 and 2500 psig but is dependent on temperature/residence time (°F/minutes) combinations. The 1000°F conversions are equal at 840/40 and 880/25, but is significantly lower at 800/100.

Hydrogen pressure has a positive effect on lighter liquid (IBP-700°F) yield. This indicates that VGO undergoes hydrocracking to form lighter products.

Gas yield was very small (~1 wt% on VGO) for all process variable combinations, except at 880°F/25 minutes/1500 psig and 880°F/25 minutes/2500 psig. The gas make at these two conditions was about 4 wt% on VGO.

4.3 EDS Coal Liquefaction Model Development

The conversion of coal into useful hydrocarbon products through hydrogenation reactions is a very complicated system. The hydrogen comes either directly from molecular hydrogen or indirectly through a "donor" solvent. In the EDS process, spent solvent is recycled through a solvent hydrotreating unit to upgrade the solvent quality and restore its donor capability. Both coal and the donor solvent are very complex and consist of many components. The process is even more complicated with the incorporation of bottoms recycle operations. Therefore, it became important to develop a means of correlating pilot plant yields for both coal-only and bottoms recycle operations. To accomplish this required that the contributions of individual reactants to the product slate be identified, and the effects of process variables on the contributions be determined.

Table 4-2 summarizes the EDS liquefaction modeling activities during EDS Phases IIIB-V. The earliest model developed was an empirical model which correlated liquefaction yields with coal conversion. In an effort to more fully understand the chemistry of coal conversion, a fundamental model was developed. Finally, a semi-empirical model was developed which can accurately predict the product slate at processing conditions within the data base for RCLU and CLPP.

An integrated liquefaction yield model was then developed by linking the semi-empirical model and the solvent hydrogenation model to predict steady state solvent quality and liquefaction yields. With the accumulated learnings from this research and development program, the semi-empirical model was successfully upgraded to a generic model which will be used in the EDS licensing package to provide predictions of EDS liquefaction yields for any coal with known properties.

4.3.1 Empirical Coal Liquefaction Model

The mechanisms of the donor solvent liquefaction reactions were formulated into an empirical kinetic model. The model involved the use of an empirical classification of reactive coal types and lumped kinetic parameters. Coal contains several types of chemical bonds and thus exhibits a wide distribution of reactivities. It is convenient to lump portions of the coal into reactive types. In this model, the feed coal is lumped into four classes according to reactivity.

Table 4-2

EDS COAL LIQUEFACTION MODELING ACTIVITY

<u>Model</u>	<u>Description</u>	<u>References</u>
1. Empirical Coal liquefaction Model	Coal conversion is function of Temperature, Reaction time, and hydrogen pressure. Component yields are expressed in terms of coal conversion. Developed for coal-only operations for Illinois and Wyoming coals.	FE-2353-2 FE-2893-17
2. Fundamental Coal liquefaction Model	Coal is separated into chemically similar groups. Each group is treated as a pure substance. Developed for coal-only operations.	FE-2353-9 FE-2353-17 FE-2353-35
3. Solvent hydrogenation Model	Solvent is separated into groups of chemical homologs and each homolog series has its unique rate constant.	FE-2353-6 FE-2353-9 FE-2893-17 FE-2893-35
4. Semi-Empirical Coal liquefaction Model	Coal conversion and component yields are all correlated as functions of processing conditions following a proposed reaction scheme. Applies to both coal-only and bottoms recycle operations.	FE-2893-53 FE-2893-74 FE-2093 93
5. Integrated EDS liquefaction Model	The solvent hydrogenation model and the semi-empirical model are combined through a saturates balance routine. This model produces liquefaction yields and solvent quality simultaneously.	FE-2893-93
6. EDS Generic Coal Liquefaction Model	Coal conversion and yields are functions of coal properties and processing conditions. Formulation similar to the semi-empirical model.	FE-2893-103

This model predicts 1000°F+ liquefaction yields for a given liquefaction reactor temperature, nominal residence time and total pressure in the reactor. The yields of the other components: C₁-C₃ gas, H₂, H₂O, chemical gases, (H₂S, NH₃, CO, CO₂) C₄-400°F liquids, 400-700°F liquids, 700-1000°F liquids are obtained by fitting quadratic equations based on conversion.

These kinetic parameters were calculated to insure a best fit of the RCLU pilot unit once-through liquefaction data for Illinois and Wyoming coals, and thus reflect RCLU measured yields of solids, liquids, and gases. This model provides a means for extrapolating the data to other conditions, as well as a means for optimizing liquefaction conditions. The data cover a wide range of liquefaction conditions: 700-900°F, 1500-2500 psig, and a ten-fold variation in residence time.

This model gave an acceptable correlation of the Recycle Coal Liquefaction Unit (RCLU) once-through data and was incorporated into the Exxon Donor Solvent (EDS) Process Model to provide yield information for coal-only operations. Also, it can be used to optimize liquefaction conditions. A disadvantage of the model was that it did not predict the effects of process variables on product slate distribution. Further details of this model have been presented in the January-June, 1976, EDS Quarterly Technical Progress Report (FE-2353-2) and the July 1977-June 1978, EDS Annual Technical Progress Report (FE-2893-17).

4.3.2 Fundamental Coal Liquefaction Model

To gain a better understanding of the chemistry of coal liquefaction and to predict more precisely the product distribution, a more fundamental coal liquefaction model was developed. Because coal and the liquefaction donor solvent are both very complex systems made up of many components, it is impossible to write down each chemical reaction explicitly. For this reason, classes of chemical species and reactions are lumped together and represented by one equation and one rate constant. The chemical species and reactions chosen are based on the known chemistry of coal, coal liquids, and donor solvent. In this model, eight reactions with hydrogenation, polymerization, and hydrocracking of nine chemical species were formulated.

From these reactions, rate equations are derived and integrated numerically to give concentrations of the chemical species as a function of temperature, reaction time and solvent-to-coal ratio. The model was developed based on RCLU once-through liquefaction data for Illinois coal, and gave acceptable fit to the data base. This model agrees qualitatively with RCLU and CLPP pilot plant data not included in the data base, especially in the shape of the net solvent fraction (400-700°F) and heavy liquid yield curves. This model was also used to successfully predict results of low pressure (1500 psig) bottoms recycle simulations on RCLU.

The major disadvantage of the model was the extent of analytical description required for the data base, making extension of the model to other coals very costly. Details of this model are presented in the January-December 1976, July 1977-June 1978, and July 1978-June 1979 EDS Annual Technical Progress Report (FE-2353-9, FE-2893-17, and FE-2893-35).

4.3.3 Semi-Empirical Coal Liquefaction Model

A semi-empirical coal liquefaction yield model was developed which can be used to predict coal conversion and liquefaction yields with coal-only and bottoms recycle operations. The objectives of this activity were to guide process development, facilitate data interpretation, and develop a tool for evaluation of EDS project coals. This correlation predicts conversion and yields as functions of 7 key process variables (pressure, temperature, nominal residence time, solvent to coal ratio, bottoms-to-coal ratio, solvent quality index, and hydrogen treat rate) and identifies contributions of the individual reactants to the overall product slate. Data for these correlations were produced on the 75 pounds-per-day Recycle Coal Liquefaction Units (RCLU-1 and RCLU-2) and the 1 ton-per-day Coal Liquefaction Pilot Plant (CLPP). The data base covers a wide range of processing conditions.

The formulation of this model is based on the following concepts:

- o All reactions are single step reactions and follow first order, irreversible kinetics.
- o Coal can be separated into five distinct fractions.
- o Solvent hydrocracks in the liquefaction reactor to form C₁-C₃ gas and C₄-400°F naphtha.

Predictions of coal conversion, hydrogen consumption, C₁-C₃ gas yield, C₄-400°F naphtha yield, C₁-1000°F total hydrocarbon yield, 700-1000°F VGO yield and water make are directly obtained from correlations, while 400-700°F distillate yield is calculated by difference in order to satisfy material balance criteria. The correlation coefficients (R^2) for the key component yields, i.e., coal conversion, C₁-C₃ gas yields, C₄-1000°F total hydrocarbon liquid yields, and hydrogen consumption, are all high (>.90). Less satisfactory correlations were observed for the chemical gas and VGO yields. This model has been used extensively to provide operating guidance on RCLU, CLPP, and ECLP operations.

Details of this model development are summarized in the July 1980-June 1981 and July 1981-June 1982 Annual Technical Progress Reports (FE-2893-74 and FE-2893-93).

4.3.4 Solvent Hydrogenation Model

A model capable of accounting for the possible variations in solvent composition has been developed for the EDS process based on a set of proposed reaction paths of individual molecular species. This model assumes that all reactions follow first order kinetics.

The effects of catalyst deactivation are also incorporated. This model was developed for both Co/Mo-10 and Ni/Mo-10 catalysts at 1500 psig hydrogen pressure. Heteroatoms removal reactions are also included for the Ni/Mo-10 model.

4.3.5 Integrated EDS Coal Liquefaction Yield Model

Although liquefaction and solvent hydrotreating are two independent unit operations, they are intimately connected via the recycling of process solvent. The performance of either unit depends not only on its own processing conditions, but also on the conditions of the other unit. For this reason, an integrated model was developed which links the liquefaction and solvent hydrogenation models together and predicts the steady state process yields and solvent quality for a given set of operating conditions.

The link between the liquefaction model and the solvent hydrogenation model is a saturates balance routine which equates the saturates depletion rate in the liquefaction reactor to the saturates production rate in the solvent hydrotreater. The saturates cracking rates were derived from tubing bomb autoclave tests 4Q82 (FE-2893-103). This cracking algorithm proved to be valid, showing excellent agreement with results from an extended 21 yield period RCLU operations (YP's 489-509).

This model has been successfully used to explain the observed high saturates and low quality solvent during the initial operations of ECLP. Effective solutions were suggested by employing this model in planning ECLP operations. In addition, this model has been used to establish an operating window for each of the project coals in terms of the maximum attainable solvent quality (FE-2893-93).

The integrated EDS coal liquefaction model was also used to simulate the hydrogen partial pressure profile in the ECLP liquefaction reactors to determine the operating temperature limits for Monterey coal bottoms recycle operations. Results indicated that the hydrogen pressure drops rapidly in the first reactor and then gradually decreases to its final value through the successive reactors. This information has been used by ECLP together with vapor-liquid equilibrium (VLE) data and the Nelson curve (API publications No. 941, Operating Limits for Steels in Hydrogen Services) to establish an upper bound of liquefaction temperature for ECLP operation (FE-2893-93).

Details of the integrated yield model were presented in the July 1981-June 1982 EDS Annual Technical Progress Report (FE-2893-93).

4.3.6 EDS Generic Coal Liquefaction Model

A generic coal yield model for EDS coal liquefaction process has been developed which can be used to predict the yield responses for any new coal with rank in the range from lignitic to high volatile bituminous. The data base used for this model development is mainly from 6 EDS program coals tested in RCLU: Illinois No. 6 bituminous coal (Monterey No. 1 mine); West Virginia bituminous coal (Ireland mine); Illinois No. 6 bituminous coal (Burning Star No. 2 mine); Wyoming sub-bituminous coal (Wyodak mine); Australian black coal (Wandoan mine); and Texas lignite (Big Brown mine). The data base contains 172 processing conditions with 711 yield periods and covers a wide range of processing conditions varying from low severities at coal-only operations to high severities with bottoms recycle operations.

The basic formulations used in this generic model development, except for coal conversion, are identical to the ones used in the semi-empirical yield model development. However, the coal fractions and rate constants are set as functions of coal properties, including the elemental, proximate, and petrographic analysis. A new formulation has been developed for the coal conversion correlation, which treats the bottoms as residues from coal and assumes that they still retain the characteristics of their precursors.

This model fits the experimental results well with high correlation coefficients and low standard deviations. The validity of this model has been checked using the RCLU results on Texas (Martin Lake mine) lignite. This model will be used in the licensing activities for the EDS coal liquefaction process. With this model, a complete product slate at preferred processing conditions can be predicted for a given coal with known properties. This information then can be used in preliminary economic screening studies to determine if this coal merits further evaluation.

Details of this model are summarized in the October-December 1982 EDS Quarterly Technical Progress Report (FE-2893-103).

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

LIQUEFACTION PROCESS RESEARCH

5. Product Quality Studies

5.1 Summary of Research Results

The specific objectives of the EDS Product Quality Program during Phases IIIB-V were to conduct product quality studies, define potential end-use applications for coal liquids, and evaluate the properties of these coal liquids relative to requirements of these potential applications. The ultimate product of these studies is an identification of the most attractive markets for coal liquids. The process can also produce LPG (C_3/C_4) and high Btu gas (C_1/C_2) as co-products. However, these C_4 -minus co-products are adequately characterized by their molecular compositions and therefore were not included as part of the Product Quality Program.

The EDS coal liquefaction process exhibits broad feed coal and product slate flexibility. It handles a wide range of coals (bituminous, sub-bituminous, and lignitic), and can produce a product slate varying from predominantly heavy fuel oil through a clean product slate (naphtha/distillate) to a high naphtha yield slate^{1, 2}.

Recent advances in EDS process understanding permit varying the product slate through control of key process variables. This flexibility, combined with the necessary economic information on costs of producing a given product slate, allow for judicious selection of process conditions/configuration. In light of this flexibility, it is helpful to highlight the product quality characteristics of EDS-derived products to these three broad categories (naphtha, distillate, fuel oil).

Highly cyclic EDS naphthas represent unique and outstanding catalytic reforming feedstocks. High volumes of high octane motor gasoline blendstock are produced while liberating a considerable quantity of high purity molecular hydrogen. These qualities have been demonstrated in DOE-sponsored programs conducted by Universal Oil Products, Inc. (Contract No. EF-77-C-01-2566) and more recently by Chevron Research Company (Contract No. DE-AC22-76ET10532). These exceptional properties suggest a definite role for naphtha product.

¹EDS Commercial Plant Study Design Update, Illinois Coal, Interim Report, FE-2893-61, February, 1981.

²EDS Wyoming Coal Bottoms Recycle Design, EDS Monthly Technical Progress Report, July 1, 1982-July 31, 1982, FE-2893-94.

Without external upgrading, EDS distillates satisfy most of the performance characteristics for application as a home heating oil and as a stationary gas turbine fuel. While not meeting the current petroleum-based gravity specifications for ASTM No. 2 fuel oil and emitting somewhat higher NO_x levels (although there is no current specification for domestic heating oil), EDS distillates have been successfully demonstrated in both of these potential applications.

The properties of EDS distillates can be enhanced through hydro-treating. Extensive work has been carried out within the project to define the extent of hydrotreating required to meet any desirable distillate qualities, including products which meet all current specifications for No. 2 petroleum fuel oil and auto diesel fuel.

In stationary gas turbine applications EDS distillates are considered satisfactory and could be used commercially. These conclusions are based on studies addressing this potential application conducted by Westinghouse under EPRI-sponsorship (Program No. RP989-1). Non EDS-funded studies of EDS distillates are currently underway for low and medium speed diesel engines.

EDS-derived fuel oils vary considerably in properties depending on actual blend components used. Product quality studies with EDS fuel oils have demonstrated acceptable combustion characteristics of Illinois and Wyoming coal-derived blends. At the same time, however, several technical concerns have been identified. These relate to relatively high nitrogen content (NO_x emissions), incompatibility with many petroleum products, and handling concerns (wall deposits, water separation, potential toxic nature). Relative to petroleum, EDS fuel oils have exhibited high levels of PNA emissions based on small-scale combustion tests. However, more recent commercial scale tests have indicated PNA emissions levels similar to those from petroleum fuels. Regarding handling, certain fuel oil blends may not meet ASTM No. 6 fuel oil specifications and would have to be marketed as specialty fuels. Depending on compatibility, handling of fuel oil blends in separate facilities may be required.

Improvement in fuel oil characteristics is possible through hydro-treatment. In addition, alternate and possibly more attractive product slates of naphtha and distillate fractions produced directly from the process have been investigated.

The above considerations, in addition to the major conclusions presented in Table 5-1, demonstrate the wide diversification of EDS products and their potential suitability for meeting a broad range of petroleum product needs.

5.2 End-Use Applications of EDS Products

A broad range of end-use applications for EDS product streams have been tested in the product quality program. Table 5-2 summarizes the most likely preferred disposition of individual product streams. In cases

Table 5-1

MAJOR CONCLUSIONS OF THE EDS PRODUCT QUALITY PROGRAM

- Consideration of future market needs, combined with generic properties of EDS-derived products, may suggest a clean product slate (naphtha/distillate) as the most desirable, long-range EDS product objective.
- Properties of lighter EDS product streams (naphtha, distillates) are essentially independent of liquefaction operating conditions for a given coal. This applies to both coal-only and bottoms recycle operations.
- With the exception of heterocyclic content, primarily sulfur, properties of lighter EDS product streams (naphtha, distillates) are very nearly coal-independent.

Table 5-2

EDS PRODUCT DISPOSITION/PRIMARY PROCESSING OPTIONS

<u>Stream</u>	<u>Disposition</u>	<u>Primary Processing</u>
C ₁ /C ₂	Pipeline Gas	--
C ₃ /C ₄	LPG	--
C ₂ /C ₄	Ethylene, Propylene	Steam Cracking
C ₄ /160°F Naphtha	Mogas	Hydrotreating
160/350°F Naphtha	Mogas Chemicals (BTX)	Hydrotreating/Reforming Extraction
350/430°F Naphtha	Mogas	Hydrotreating
<u>Middle Distillate</u>	Turbine Fuel	Direct Use
350/750°F and/or 430/750°F Solvent	Low, Medium Speed Diesel Fuel Home Heating Oil Blendstock No. 6 Fuel Oil Blendstock	Direct Use Likely Limited Direct Use Direct Use
	Home Heating Oil	Direct Use With Burner Adjustment
	Auto Diesel Blendstock	Moderate Hydrotreating
	Jet/Auto Diesel/No. 2 Fuel Oil	Severe Hydrotreating/ Hydroconversion
750/1000°F VGO	Fuel Oil Blendstock FCC or Hydroconversion Feed	Direct Use/Hydrotreating Hydrotreating
Coker Gas Oil and/or Scrubber Liquids	Fuel Oil Blendstock FCC or Hydroconversion Feed Fuel Oil Blendstock	Direct Use/Hydrotreating Hydrotreating Direct Use/Hydrotreating

where such disposition requires immediate processing the primary processing technology is identified. Any C₄-minus co-products produced can be processed to meet pipeline gas (HGB) and LPG specifications or serve as chemical feedstocks for ethylene/propylene production.

It is expected that following hydrotreating and reforming, EDS naphtha (160°F-350°F) will be used almost exclusively as a prime mogas blendstock. Alternatively, or in conjunction with mogas disposition, the EDS naphtha can serve as a source of valuable chemicals. For example, raw naphtha is an abundant source of phenol/cresols, while the reformat contains high concentrations of benzene, toluene and xylenes (BTX). Extractive processing can be used to liberate these and many other desirable chemicals.

The use of 350-430°F hydrotreated heavy naphtha as a direct mogas pool blendstock has also been demonstrated. This stream is the front end of the 350-750°F middle distillate (solvent) fraction shown in Table 5-2. The solvent can be viewed as a fuel for several applications. Without additional upgrading, potential applications include fuel for stationary gas turbines and low or medium diesel engines, as well as No. 2 or No. 6 fuel oil blendstocks. Moderate hydrotreating improves this product stream for these applications and provides the upgrading needed for use as an auto diesel blendstock. Severe hydrotreating is required to meet all current specifications for jet, No. 2 diesel and No. 2 fuel.

The last three product streams, if present in a given EDS configuration, can be blended into the fuel oil pool. Contingent upon specific blend situations, they normally require no separate upgrading. In other situations, upgrading of these streams, or more likely of the total fuel oil blend, may be required to meet the applicable nitrogen and/or sulfur specifications. Finally, it is noteworthy that conversion studies by UOP, Inc. and Chevron Research indicate that the EDS mid-distillate and vacuum gas oil may be used as potential conversion feedstocks through the use of catalytic cracking or hydrocracking processing.

Except for C₄-minus co-products, discussion of each of the applications identified in Table 5-2 comprises the major portion of this Product Quality Report.

5.3 Future Product Quality Needs

One of the key objectives of the product quality program was to identify areas pertaining to product quality requiring further development.

Table 5-3 summarizes potential end-use applications of EDS products and the associated constraints and limitations which have been identified as a result of product quality testing. In addition to those recognized limitations, there are technical uncertainties pertaining to several potential applications which could not be explored within the scope of the EDS program.

Table 5-3

EDS PRODUCT QUALITY ASSESSMENT

Stream/Product	Application	Identified Limitations/Constraints	Technical Uncertainty
A. C ₁ /C ₂	Pipeline Gas	None	Likely None ¹
B. C ₃ /C ₄	LPG	None	Likely None ¹
C. C ₂ /C ₄	Chemical Feedstock	None	Likely None ¹
D. C ₆ /160°F Naphtha	Gasoline Blendstock	Hydrotreating Required to Eliminate Gas Forming Tendencies	Engine Performance
E. 160/350°F Naphtha	1. Extraction (Phenol, Cresols) 2. Hydrotreating (Pre-Reforming)	Low Naphtha Exhibits Poor Storage Stability	1. Scale-up/Equipment 2. Activity Maintenance
F. 160/350°F Reformate	Gasoline Blendstock	None	Engine Performance
G. 350/430°F Naphtha	Gasoline Blendstock	1. Hydrotreating Required (EDS Solvent H/T) 2. Low Octane, Volatility	None
H. 350/750°F Distillate	1. Gas Turbine Fuel 2. Low, Medium Speed Diesel Fuels 3. Home Heating Oil Blendstock 4. No. 6 Fuel Oil Blendstock 5. Auto Diesel Blendstock 6. Jet/Auto Diesel/No. 2 Fuel Oil 7. Extraction of Aromatics	1. H-Content Lower than Petroleum • Higher Aromaticity • More Luminous Flame H-Content Higher than Petroleum 2. Not Yet Tested 3. API Gravity <30 • Burner Adjustment Required Higher NO _x Emissions 4. None 5. Hydrotreating Required • Filtration May be Required 6. Severe Hydrotreating Required 7. High Aromatic Content Reverse of Petroleum	1. Large Scale Demonstration 2. Demonstration 3. Long Term Performance 4. None 5. Activity Maintenance 6. Activity Maintenance Engine/Burner Performance 7. Scale-up/Equipment/Solvent
I. 750/1000°F Vacuum Gas Oil	1. Specialty Fuel Oil 2. Hydrotreating Feedstock 3. No. 6 Fuel Oil Blendstock	1. Segregated Storage/Handling Facilities • Limited Compatibility With Petroleum • Specific Gravity >1.0 High PMA - Handling High H-Level - NO _x Emissions 2. Guard Chamber Likely Required 3. Hydrotreating Required Large H ₂ Consumption Required For Low H, Compatible Fuel	1. Large Scale Demonstration 2. Activity Maintenance 3. None with Adequate Hydrotreating

¹Conventional processing of light hydrocarbons to meet interstate specifications likely adequate.

Technical uncertainties for the most part can be classified within the following three categories.

- Engine Performance

End-use applications such as hydrotreated EDS light naphtha (C₄/160°F) and reformat (160/350°F) as gasoline blendstocks, hydrotreated EDS distillate as an auto diesel blendstock, or severely hydrotreated/converted distillate as jet or auto diesel fuel must be considered as potential applications until certified through extensive engine test programs.

- Large Scale Demonstration

Utilization of EDS distillate as a gas turbine fuel, a low or medium speed diesel fuel or even a fuel oil blendstock appears promising based on laboratory or sub-scale tests of relatively short duration. However, extensive testing to assess long-term equipment performance and life is ultimately required.

- Catalyst Activity Maintenance

Upgrading studies (e.g., hydrotreatment) have focused primarily on the effects of process variables using relatively fresh catalysts. Acceptable long-term activity maintenance, a concern with coal-derived products generically high in heterocyclic content, has not been included in these programs.

LABORATORY PROCESS RESEARCH AND DEVELOPMENT

BOTTOMS PROCESS RESEARCH

6. Coking and Gasification Studies

The objective of bottoms coking and gasification studies performed during Phases IIIB-V of the EDS program was, initially, to investigate the feasibility of FLEXICOKING^R for EDS bottoms processing. After completion of IKG runs on CLPP Illinois (Monterey) and Wyoming (Wyodak) bottoms, further laboratory studies investigated the potential problems observed during IKG operation. Extensive data of coking yields, feed bottoms properties and gasification kinetics were obtained to support the study design of a FLEXICOKING unit and the planning of the prototype pilot plant demonstration.

Coke formation in a coal slurry preheater was observed during early ECLP operation. Laboratory bench studies were carried out to identify the causes and important process variables responsible for coke formation in the preheater. A continuous flow unit was also developed to simulate ECLP slurry preheater operation. Operation of this unit allowed identification of operating conditions which are conducive to coke formation in the slurry preheater for various feed coals.

6.1 EDS FLEXICOKING Studies

6.1.1 Experimental Facilities and Procedures

Severe bench units and pilot units were developed to simulate the individual reactors of the FLEXICOKING unit for bottoms processing. The schematic diagrams and operating procedures of these units are described in the EDS Technical Progress Reports referenced in Table 6-1. The functions of these units are briefly described as follows:

- o The Minicoker is a fixed-bed bench unit used to obtain preliminary coking yield data using one gram bottoms samples. The unit is also useful for process variable screening studies, especially for bottoms samples of limited availability.
- o The Continuous Stirred Coking Unit (CSCU) is a pilot unit with the capability of feeding molten bottoms continuously at a rate of approximately 20 grams per minute. This unit was used to obtain coker product distributions at various coking conditions for study design and planning the prototype pilot plant demonstration.
- o The Fluid Coker Bogging Unit (FCBU) is a 3" diameter fluid bed unit with continuous feeding of molten bottoms into a fluidized bed of bottoms coke. This unit was used to determine the bogging limit in simulations of a fluid coker using bottoms feed.

Table 6-1

BENCH AND PILOT UNITS FOR COKING/GASIFICATION STUDIES

<u>Unit</u>	<u>EDS Progress Report Reference</u>
Minicoker Bench Unit	1,2Q76 (FE-2353-2)
Continuous Stirred Coking Unit (CSCU)	1,2Q76 (FE-2353-2)
Fluid Bed Boggling Unit (FCBU)	1,2Q76 (FE-2353-2)
Large Stirred Coking Unit (LSCU)	1,2Q76 (FE-2353-2)
Fluid Bed Gasifier (FBG)	1Q77 (FE-2353-14)
Minigasifier Bench Unit	3Q77 (FE-2893-3)
Integrated Coking/Gasification Pilot Plant (IKG)	3Q77 (FE-2893-3)
Small Fluid Bed Unit (SFU)	3Q78 (FE-2393-21)

- The Large Stirred Coking Unit (LSCU) is a scale-up of the CSCU and is designed to produce about 2-1/2 barrels of coker liquid products per week. These products were used for product quality evaluation and burning studies.
- The Fluid Bed Gasifier (FBU) is a 3" diameter fluid bed gasifier. This unit is designed to allow batch gasification of coke samples (approximately 4 lbs charge) with air and steam. FBU was used to determine the effect of gasification on coke particle integrity and to investigate the effect of bed stagnation on sintering.
- The Minigasifier is a fixed bed bench unit using a charge of 1-2 gram. This unit was used to determine the relative gasification reactivity of various bottoms cokes. The data were used to formulate gasification kinetic models.
- The Small Fluidized Bed Unit (SFU) is a bench gasifier unit with a 1" diameter fluid bed reactor. This unit was used to study the process variable effects on sintering and coke particle attrition under simulated gasification conditions.
- The Integrated Coking/Gasification (IKG) pilot plant used for developing the petroleum FLEXICOKING^R process was modified to allow feeding of CLPP bottoms. The primary objective of IKG operation was to assess FLEXICOKING^R operability on EDS vacuum bottoms from Illinois and Wyodak coals.

6.1.2 Major Conclusions and Results

Results of these coking/gasification studies in various bench and pilot units have been reported in EDS Technical Progress Reports, as tabulated in Table 6-2. The major conclusions are discussed here briefly.

Coking yields were obtained in CSCU runs on bottoms from all EDS program coals. The coker liquid yields from bottoms for various coals were not appreciably different. Once-through coking operations without 1000°F⁺ recycle were found preferable because of the low thermal conversion of the bottoms feed. The coking temperature of 70+RV°F and 25% steam/feed ratio were recommended for the FLEXICOKING^R study design. Bottoms/coal blends were also found feasible with a product yield equivalent to the total contribution from coal and bottoms coked separately. Bottoms feed showed a lower tendency to bog than the reference petroleum residuum in FCBU runs on Illinois (Monterey) and Wyodak bottoms. Bed bogging should not present an operating problem because the Exxon proprietary bogging correlation based on petroleum feeds can be used to size the coking reactor. In coker product quality evaluations, sufficient liquid products from Illinois (Monterey) and Wyodak bottoms were produced from LSCU operations. Results of the product evaluation studies have been reported in the EDS Product Quality Final Report (FE-2893-97, p. 215, September 1982).

SUMMARY OF TOPICS COVERED IN EDS PROGRESS REPORTS - COKING/GASIFICATION STUDIES

Report	Topics and Results Covered
1,1976 (FE-2353-2)	<ul style="list-style-type: none"> • Description of design and procedure of a bench-scale coking unit (minicoker) • Results of coking yields at various temperatures by minicoker tests • Description of design and operating procedures for Continuous Stirred Coking Unit (CSCU) • Results of CSCU runs to show the process variable effect (temperature, steam/feed ratio and vapor residence time) on coker liquid yields • Description of design and start-up of Fluid Coker Bogging Unit (FCBU) for fluid coking bogging study • Description of design and planning of Large Stirred Coking Unit (LSCU) for producing coker products for quality evaluation
3Q76 (FE-2353-6)	<ul style="list-style-type: none"> • Discussion of CSCU runs for recycle simulation, process variable effects and liquefaction/coking interaction • Validation of FCBU by bogging tests with petroleum residuum • Preliminary evaluation of viscometric behavior of coker liquids • Progress of LSCU construction
76 Annual (FE-2353-9)	<ul style="list-style-type: none"> • Summary of CSCU results • Bench study of heavy hydrocarbon carryover during coke circulation of fluid coker by minicoker tests • Completion of bogging study by FCBU runs for Illinois bottoms • Description of a bench-scale minigasifier for studying the gasification kinetics of bottoms coke • Results of IKC fluid coking runs on CLPP bottoms
1Q77 (FE-2353-14)	<ul style="list-style-type: none"> • Bench coking study to investigate the effect of sulfuric acid treating of Wyodak coal on coking yield • CSCU runs on CLPP Illinois bottoms • Correlation of coke and liquid yield with CSCU runs in 1976 • Discussion of difference between Microlube and HIVAC-C distillation of coker liquids
1,2Q77 (Phase IIIA Final, FE-2353-20)	<ul style="list-style-type: none"> • Summary of bench-scale minicoker test results • Summary of coking results from CSCU runs • Summary of bogging results from FCBU runs • Correlation of feed bottoms properties with coking yield • Correlation of heating value with elemental analysis for coker liquids
3Q77 (FE-2893-3)	<ul style="list-style-type: none"> • Minicoker runs to study liquefaction severity on coking yield and the feasibility of feeding coal/bottoms mixture • CSCU runs on CLPP Wyodak bottoms • Correlation of bottoms properties with coking yield • Minigasifier runs to determine gasification rates of bottoms coke samples • Initiation of FBU runs to study coke particle integrity • Results of initial operation of IKC FLEXICOKING mode; observation of sinter formation in gasifier bed • Laboratory inspection of IKC sintered deposits

SUMMARY OF TOPICS COVERED IN EDS PROGRESS REPORTS - COKING/GASIFICATION STUDIES

Report	Topics and Results Covered
4Q77 (PE-2893-7)	<ul style="list-style-type: none"> • CSCU runs on CLPP Illinois bottoms under updated study design condition on RCLU under longer residence time • Summary of coking product quality from Illinois and Wyodak bottoms • Discussion of initial LSCU runs • Results of initial minigasifier runs on Illinois bottoms coke sample from IKG • Results of FBU runs for investigating the particle integrity under simulated gasification condition • Summary of results from IKG FLEXICOKING runs
1Q78 (PE-2893-12)	<ul style="list-style-type: none"> • Effect of temperature on coker liquid yield by CSCU runs • Results of gasification rate of Illinois and Wyodak bottoms cokes by minigasifier runs • Study of fines generation under the gasification condition by FBU runs • Start-up of IKG pilot plant for continuation of FLEXICOKING runs
1978 Annual (PE-2893-17)	<ul style="list-style-type: none"> • Study of bottoms viscosity reduction by fluxing oils for preparation of bottoms feed for FLEXICOKING pilot plants • Summary of coking yields from CLPP once-through Illinois and Wyodak bottoms by CSCU runs • Correlation of coking yields with coking condition and feed bottoms properties • Gasification kinetic study by minigasifier for Illinois and Wyodak bottoms cokes • FBU runs for study of fines generation and sinter formation in gasifier • Summary of results from IKG runs
3Q78 (PE-2893-21)	<ul style="list-style-type: none"> • CSCU runs on CLPP Wyodak and Big Brown bottoms, CLPP Illinois recycled bottoms and Illinois bottoms with fluxing oils or 15X coal • Sintering studies by Small Fluidized Unit (FBU) runs • Effect of percent gasification on fines make by FBU runs • Cold model studies to investigate the fluidization behavior in IKG • Product yields, coke properties and gasification rates of IKG runs
4Q78 (PE-2893-25)	<ul style="list-style-type: none"> • Study of handling bottoms as bulk solids - friability (drop shatter test) and moisture susceptibility • CSCU runs on Illinois bottoms with coal and Big Brown bottoms • Gasifier bed sintering studies by SFU and FBU runs
1Q79 (PE-2893-29)	<ul style="list-style-type: none"> • Coking yields from CLPP Wyodak bottoms by minicoker runs • CSCU runs on RCLU bottoms from Burning Star coal • Plan of LSCU runs to prepare coker liquid samples for various program studies • Gasifier bed sintering studies by SFU and FBU runs • Study of gasification rate of Wyodak bottoms coke by minigasifier runs

SUMMARY OF TOPICS COVERED IN EDS PROGRESS REPORTS - COKING/GASIFICATION STUDIES

Report	Topics and Results Covered
1979 Annual (FE-2893-35)	<ul style="list-style-type: none"> • CSCU runs on RCLU Arkwright bottoms and Wandoan bottoms • Progress of LSCU run to prepare coker liquids for various program studies • Modeling of coke gasification kinetics • Discussion of gasifier bed sintering from results of SFU runs • Review of carryover fines study by FBU • Review of IKC operation
3Q79 (FE-2893-41)	<ul style="list-style-type: none"> • Comparison of CSCU and minicoker product yields • CSCU runs on RCLU Burning Star bottoms • Bogging study for bottoms feed diluted with fluxing oil by FCBU • Study of bottoms coke kinetics by minigasifier runs • Study of sinter formation in gasifier or burner bed by SFU runs • Effect of additive in bottoms feed on sinter formation in gasifier by SFU runs
4Q79	<ul style="list-style-type: none"> • CSCU runs on RCLU Ireland and Wandoan bottoms • Bogging results of Monterey bottoms feed diluted with 20% cresote oil by FCBU runs • Relative sintering tendency of bottoms coke from program coals by SFU runs • Effect of CaO additive in bottoms feed on sinter formation
1Q80 (FE-2893-49)	<ul style="list-style-type: none"> • CSCU runs on feed bottoms with 20% HRCO • Study of fines retention at a temperature close to bogging (sticky bed operation) by FCBU
1980 Annual (FE-2893-53)	<ul style="list-style-type: none"> • CSCU runs on CLPP Illinois and Wyodak recycled bottoms • Summarized FDBU run result for studying fines retention by "sticky" bed • Coke particle attrition study under the simulated coking and gasifier condition by SFU runs • Effect of MgO additive in bottoms feed on sinter formation by SFU runs
3Q80 (FE-2893-57)	<ul style="list-style-type: none"> • Bogging tests on recycled bottoms feed by FCBU • SFU attrition under simulated gasification condition
4Q80 (FE-2893-70)	<ul style="list-style-type: none"> • SFU attrition tests under simulated combustion and gasification conditions • Updated correlation of coking yield with the feed bottoms properties

IKG pilot plant operation demonstrated FLEXICOKER operability by processing approximately 6000 pounds each of CLPP Monterey and Wyodak bottoms. Ash sintering and fines generation were identified as potential problem areas in applying bottoms FLEXICOKING on a commercial scale. FBU runs identified bed stagnation around the gas inlet as the major cause of sinter formation in the gasifier bed. In addition, a non-sintering region mapped with process variables was defined by SFU runs for bottoms cokes produced from various feed coals. Laboratory studies also showed that fines generation increased with the increase of carbon gasified. The fines loss could be controlled at a tolerable level by limiting the carbon gasification to less than 70%.

6.2 Refractory - Coal Ash Interactions Study

A study was undertaken to determine the effect of slag chemical corrosion on refractories under conditions expected in a partial oxidation (POX) gasifier. A commercial unit will have temperatures up to 3000°F with a reducing atmosphere of hydrogen, carbon monoxide, and steam under pressures up to 1000 psig. Under these severe conditions, refractory life will also be greatly affected by erosion and by spalling from thermal shock, in addition to chemical disintegration of the refractory caused by molten ash. The current goal for refractory life in a commercial slagging gasifier is a minimum of two years ("Design, Engineering, and Evaluation of Refractory Linkings for Slagging Gasifiers," FE-2785-T2, p. 1). Currently operating POX pilot plants have not reported achievement of this goal.

In addition to having superior resistance to chemical attack by coal ash constituents, a refractory suitable for POX slagging gasifiers must have low porosity to minimize slag penetration. Other necessary refractory properties include a high melting temperature (no liquid phases below 3000°F), low thermal conductivity, extreme hardness to resist erosion, resistance to spalling by thermal shock, and resistance to decomposition by hydrogen and carbon monoxide in the reducing atmosphere gas. In all probability, a single refractory will not have the optimum of each of these individual properties. Thus, a trade-off may be necessary in certain areas (e.g., porosity vs. spalling) in developing or choosing the best overall refractory for a slagging gasifier environment.

The seven commercially-available refractories that were examined in this study are listed in Table 6-3, along with a brief description of the individual compositions. The first three refractories are fused cast at very high temperatures and show relatively low porosity. The last four materials are sintered or partially sintered blocks that have not gone through a molten state. The relative porosity of these samples is much greater than that for the fused cast refractories (see Table 6-3).

The three ash materials used in this experimental program are derived directly from EDS bottoms from the Coal Liquefaction Pilot Plant (CLPP). The coal residues and CLPP yield periods are Illinois No. 6

Table 6-3

REFRATORIES EXAMINED IN ASH/REFRACTORY STUDY

Type	Description	Apparent Porosity, Percent
1. Fused Cast Alumina (99%)	Mostly α - Al_2O_3 with some " β - Al_2O_3 "	1.1
2. Fused Cast Chromia (80%)- (80%)-Magnesia (8%)- Alumina (4%)- Ferric (8%)	A Complex Chrome Spinel	5.4
3. Fused Cast Alumina (60%)-Chromia (30%)-Magnesia (6%)	An Alumina-Chromia Solution within a Magnesia- Chromia-Alumina Spinel	4.2
4. Alumina (90%) - Chromia (10%)	An α - Al_2O_3 Matrix Bond Bonded with Alumina- Chromia Solution	16.0
5. Magnesia (55%) - Chromia (20%) - Alumina (8%) - Ferric (11%)	Magnesium Oxide with Magnesium-Chrome Spinel	14.0
6. Alumina (90%) - Chromia (10%)	Similar to No. 4	15.8
7. Alumina (86%) - Chromia (9%) - Silica (2%)	Similar to No. 4, Silica added to Increase Spalling Resistance	18.6

* Data Supplied by Refractory Manufacturer.

(Monterey) from YP-311, Wyoming (Wyodak) from YP-269, and Big Brown lignite from YP-336. The ash element analyses for these three materials are given in Table 6-4.

The initial phase of this project involved the testing and subsequent examination of ash/refractory combinations exposed in an air-atmosphere furnace for three days. The samples were prepared by placing a pressed pellet of ash (5-10 gm) in a 3/4" diameter hole (ca. 1/2" deep) that had been drilled into a small block of refractory (ca. 2" x 1-1/2" x 1"). All twenty-one ash-refractory combinations were tested at 2500°F, 2650°F, and 2800°F.

The effect of temperature was most evident upon visual examination of the individual slag/refractory samples. As the temperature increased from 2500°F to 2800°F, both the Wyodak and Big Brown slags showed increased penetration into the refractory. The Monterey slag has a higher viscosity at these same temperatures in air atmosphere, and generally showed less penetration than the other two ashes. The effect of slag penetration was also dependent upon the porosity of the refractory. One of the most porous samples, refractory 5 (see Table 6.3), allowed all three types of slag to penetrate readily at all three temperatures tested. The three low-porosity, fused-cast refractories (1, 2, and 3) showed the least penetration. This reduced slag penetration in refractories, 1, 2, and 3 was also accompanied by an increase in thermal cracking, especially for Sample 2.

After the high-temperature exposure is concluded, the sample is sliced into sections and polished for subsequent microscopic examination. In addition, selected fractions of the slag and slag/refractory layers are ground to a fine powder for X-ray diffraction analysis in order to identify the individual crystalline phases present, including reaction products formed at the slag/refractory interface.

Examination of the slag-refractory interface by optical and electron microscopy reveals a layer formation on the refractory surface for some of the samples. This is particularly evident with refractory sample 3 with Monterey ash. The layer is of a spinel of mixed-stoichiometry $(\text{Fe, Mg})\text{O} \cdot (\text{Fe, Al, Cr})_2\text{O}_3$ and was evidently formed as a reaction product of slag and refractory constituents. It appears that the effect of the spinel layer is to act as a barrier to slow down further refractory degradation. Similar spinel-type layers have been identified in other samples, particularly those containing alumina and chromia. The spinel layer "barrier" is well-formed on the surface of the low-porosity refractories, especially samples 2 and 3. For the more porous samples such as 4, 6, and 7, this spinel layer shows more discontinuity. Typically, the spinel layer was approximately twice as thick for the samples exposed at 2800°F compared to those at 2500°F. Refractory reference standards showed virtually no change over this temperature range.

In addition to the three-day tests described above, a twelve-week, long-term test at 2500°F was undertaken in the air atmosphere furnace. Again, all twenty-one combinations of seven refractories and three

TABLE 6-4

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ASH MATERIALS BEING EXAMINED IN THIS STUDY

ASH ELEMENTS	ILLINOIS NO. 6	WYODAK	BIG BROWN LIGNITE
SiO ₂	51.34	39.04	50.91
Al ₂ O ₃	18.60	17.46	17.85
Fe ₂ O ₃	19.54	5.19	7.38
CaO	5.09	26.89	17.48
MgO	0.90	6.63	3.47
Na ₂ O	1.29	1.92	0.55
K ₂ O	2.04	0.36	0.65
TiO ₂	0.86	1.05	1.59
P ₂ O ₅	0.35	1.46	0.11
SOFTENING TEMPERATURE °F, ASTM, TYPICAL			
REDUCING	2030	2180	2130
OXIDIZING	2400	2230	2200
B/A RATIO	0.41	0.71	0.42

NOTE: ASHES WERE PREPARED BY MILD OXIDATION OF EXTRACTED EDS BOTTOMS ACQUIRED FROM ACTUAL CLPP YIELD PERIODS. ASH ANALYSIS IS GIVEN ON AN "SO₃-FREE" BASIS.

ashes were tested along with reference standards of each refractory. For most of the long duration samples, the spinel layer buildup was a little greater than twice that of the short-term tests, even though the exposure time was almost thirty times as long. This observation tends to support the role of the spinel layer as a chemically resistant barrier to further refractory decomposition.

The second phase of this experimental program consisted of studies of similar ash-refractory combinations in a high temperature, controlled atmosphere furnace that will allow simulation of reducing atmosphere compositions to be found in a partial oxidation gasifier. A representative diagram of the controlled atmosphere furnace is given in Figure 6-1. This two-inch diameter tube furnace is capable of sustained temperatures greater than 3000°F. The refractory/ash samples were prepared in the same way as for the air atmosphere samples.

The first series of tests in the controlled atmosphere furnace were at 2650°F for a period of three days under a reducing atmosphere of 52% CO, 40% H₂, and 8% CO₂ (similar to the product gas composition (water-free) from a POX gasifier). For samples containing Illinois No. 6 ash, some metallic iron was observed to have formed in addition to an iron-rich spinel layer similar to that reported earlier in air atmosphere runs. In addition, the Illinois slag was much more fluid under this reducing atmosphere than under air atmosphere, resulting in greater slag penetration problems (see the ASTM softening temperatures in Table 6-4). Wyodak and Big Brown ashes showed similar behavior, although less metallic iron was present. All twenty-one combinations of three ashes and seven refractories were run under the above conditions.

Another series of tests were carried out at 3000°F in the same highly reducing 52% CO/40% H₂/8% CO₂ atmosphere. Refractories 1, 2, and 3 (all fused-cast with low porosity) and one of the sintered 90% alumina - 10% chromia materials were tested under these conditions as an upper temperature limit of a POX gasifier environment. In combination with the three ash materials, a total of twelve samples were tested. During the 24 hour test period at 3000°F, greater decomposition at the refractory surface was more apparent than at 2650°F. Refractory 1 (99% alumina) showed worse degradation than the other refractories, particularly with Wyodak and Big Brown slags. Refractory 3 (60% alumina - 30% chromia - 6% magnesia) appeared to perform best at 3000°F and also displayed little slag penetration. A well-defined spinel layer was also present at the slag/refractory interface.

A final series of tests was performed in the controlled atmosphere furnace under a less reducing atmosphere of 50% CO/50% CO₂ at 2650°F for three days. Under these conditions no metallic iron was observed to have formed in the slag/refractory samples. Magnetite, Fe₃O₄, was the primary iron-containing phase in the slag. Most of the samples tested under the 50% CO/50% CO₂ atmosphere also showed a well defined iron-rich spinel layer at the slag/refractory interface.

FIGURE 6-1

CONTROLLED ATMOSPHERE HIGH TEMPERATURE FURNACE

- + CONCENTRIC ALUMINA TUBE DESIGN
- + MAXIMUM TEMPERATURE 3200 °F
- + CAPABILITY OF HIGH VACUUM, REDUCING, OR OXIDIZING ENVIRONMENT
- + PROGRAMMABLE HEATING AND COOLING RATE

The following conclusions can be made from this work:

- Formation of a spinel layer on certain chromium-containing refractories can act as a chemically resistant barrier to further decomposition,
- Refractories #3 (60% Al_2O_3 -30% Cr_2O_3 -6%MgO) and #4 (90% Al_2O_3 -10% Cr_2O_3) show good chemical resistance to slag degradation,
- Slag viscosity and refractory porosity are major factors in determining the rate of refractory decomposition.

6.3 Laboratory Studies of ECLP Preheater Coking

6.3.1 Bench Slurry Coking Studies

Tubing bomb tests were used to simulate EDS coal slurry preheater conditions. The procedure for these tests was described in the July 1, 1980-June 30, 1981 Annual Technical Progress Report (FE-2893-74). A coking bomb test was also used to simulate coke formation on the preheater wall while allowing for solvent evaporation. This test was described in the 1981 July-September EDS Technical Progress Report (FE-2893-78). Results from these laboratory tests were reported in EDS Technical Progress Reports as listed in Table 6-5.

Inspection of ECLP preheater coke samples by polarized light microscopic examinations showed that the coke adjacent to the preheater wall consisted of highly anisotropic carbon with large domains, as evidenced by the mosaic morphology. The observation of mesophase spherules in the coal residues from the tubing bomb tests confirmed the coke formed in the preheater via a liquid crystal mesophase. Coke is not formed as the coal slurry flows through the preheater furnace within the nominal residence time. Rather, coke formation is believed to be initiated with the deposition of mesophase spherules and/or coal slurry agglomerates on the preheater tube wall. These deposits subsequently coke.

Coking severity is dependent on tube wall temperature, time, and solvent quality. Coking does not occur at appreciable rates below about 800°F, and the time required for coking to occur decreases rapidly as the tube wall temperature is increased. Improving solvent quality decreases coking tendency at a given temperature for both Monterey and Wyodak coals. Further studies performed to evaluate the role of solvent parameters in slurry preheater coking show that hydrogen donating ability is more important than solvency in reducing coking severity. Polar or heterocyclic aromatic constituents in EDS solvents are not major contributing factors to coking in the ECLP slurry preheater.

6.3.2 Slurry Preheater Coking Studies in a Flow Unit

The small flow unit shown in Figure 6-2 was used to determine the relative coking tendencies of EDS program coals in the bottoms recycle mode at 0.5 bottoms/coal ratio. The flow unit simulates the time/temperature/chemical environment of the ECLP slurry preheater. The coals tested

Table 6-5

SUMMARY OF TOPICS COVERED IN EDS PROGRESS REPORTS - SLURRY PREHEATER COKING STUDIES

Report	Topics and Results Covered
81 Annual (FE-2893-74)	<ul style="list-style-type: none"> • Laboratory inspections of ECLP preheater coke plug • Solvent quality effect on coking tendency by thermal gravimetric analysis • Tubing bomb tests under simulated preheater condition
3Q81 (FE-2893-78)	<ul style="list-style-type: none"> • Evidence of the presence of mesophase spherules under the simulated ECLP preheater condition • Effect of temperature/time on coke formation by coking bomb tests • Microscopic studies of ECLP preheater coke deposits
4Q81 (FE-2893-83)	<ul style="list-style-type: none"> • Relative sticky tendency of coal, bottoms and HVGO • Study of chemical changes involved in coke formation • Effect of temperature and solvent quality on coking severity • Initiation of slurry preheater coking studies in a flow unit
1Q82	<ul style="list-style-type: none"> • Effect of phenol content in solvent on coking tendency • Effect of solvent solvency on coking tendency • Mapping of SQI/tube temperature for Wyodak coal and Martin Lake coal slurries by CCLU runs • Microscopic examinations of coke deposits
2Q82	<ul style="list-style-type: none"> • Proposed mechanism for coke formation in ECLP slurry preheater • Study of solvency effect by model solvents • Mapping of SQI/tube temperature for Illinois and Wyodak coal slurries with bottoms recycle by CCLU tests • Microscopic examination of coke desposits
3Q83	<ul style="list-style-type: none"> • Study of solvency effect on coking severity with model solvents by coking bomb tests • Mapping of SQI/tube temperature for Burning Star coal slurry on CCLU tests • Laboratory studies on ECLP hot separator deposits
4Q82	<ul style="list-style-type: none"> • Study of donor hydrogen and solvency effect on coking of coal derived asphalthenic materials • Study of temperature effect on hot separator deposits • CCLU runs on Ireland, Wandoan and Burning Star coal slurries

FIGURE 6-2

83B-2-117

FLOW UNIT FOR PREHEATER COKING STUDIES

in the flow unit were Illinois No. 6 (Monterey and Burning Star No. 2 mines), Pittsburgh No. 8 (Ireland mine), Wyoming subbituminous (Wyodak mine), Texas lignite (Martin Lake mine), and Australian black (Wandoan mine). A list of the various studies undertaken and the appropriate references are given in Table 6-6.

Data obtained from polarized light microscopic analysis of each flow unit preheater tube were used to define the coking and non-coking regions of each coal as functions of tube temperature and solvent quality index. The coking maps for the EDS coals tested in the flow unit are given in Figures 6-3 through 6-7.

- Monterey Coal

Coking with Monterey slurries (Figure 6-3) begins at 875°F at low (< 3.5) SQI. At higher SQI, the temperature required to produce coking increases dramatically. Coking with Monterey slurries is characterized by a rapid, complete plugging of the flow unit preheater tube.

- Wyodak Coal

The coking behavior of Wyodak slurries (Figure 6-4) is also a strong function of SQI. At low (< 3.0) SQI, Wyodak slurries begin to coke at 800°F. As the SQI is increased, the maximum allowable tube temperature rises to 900°F at 4.5 SQI. Coking with Wyodak slurries is characterized by the formation of annular deposits, which build to form complete cross-sectional plugs at severe (> 900°F, low SQI) conditions.

- Martin Lake Lignite

Coking with Martin Lake slurries is unique. Two coking regions have been defined for this coal, both of which are invariant with SQI (Figure 6-5). The partial coking region (> 920°F tube temperature) is similar to Wyodak coking in that annular deposits were formed. However, catastrophic coking was not observed with Martin Lake slurries. The minimal coking region (825-920°F) is unique to Martin Lake lignite. In this region, the coke formed is thin, an order of magnitude or less in thickness than in the partial coking region, and is limited to the first third of the flow-unit preheater tube. The exact impact of operating in the minimal coking region in a large unit is not clear.

- Ireland Coal

A short study (11 tests) was conducted to determine the coking behavior of Ireland coal slurries (Figure 6-6). Ireland slurries begin to coke when the tube temperature reaches 950-975°F. Because the study was short, the effect of high SQI on coking was not determined. However, given the high maximum allowable tube temperature (950°F), the response of the coking boundary to SQI is of less importance than it is with coals such as Wyodak or Martin Lake.

Table 6-6

SUMMARY OF FLOW UNIT PREHEATER COKING STUDIES

<u>Coal</u>	<u>Reference</u>	
Wyodak	4Q1981 1Q1982	FE-2893-83 FE-2893-89
Monterey	4Q1981 1Q1982	FE-2893-83 FE-2893-89
Martin Lake	1Q1982 2Q1982	FE-2893-89 FE-2893-93
Burning Star	3Q1982 4Q1982	FE-2893-99 FE-2893-103
Ireland	4Q1982	FE-2893-103
Wandoan	4Q1982	FE-2893-103

FIGURE 6-3

MONTEREY COKING MAP

FIGURE 6-4

WYODAK COKING MAP

FIGURE 6-5
MARTIN LAKE COKING MAP

FIGURE 6-6

83B-3-8

IRELAND COKING MAP

FIGURE 6-7

WANDOAN COKING MAP

83B-3-9

- Burning Star Coal

Burning Star coal slurries showed the least coking tendency of any coal studied. Only one condition studied showed any coke formation (975°F, 2.6 SQI). Therefore, it appears that Burning Star slurries only begin to coke at film temperatures of 975°F or higher and a low SQI (< 2.6).

- Wandoan Coal

The last coal tested in the flow unit was Wandoan coal (Figure 6-7). Although the tests showed considerable scatter (coking and non-coking points intermixed), the results are qualitatively similar to Wyodak coal in that coking was observed as low as 800°F.

From these studies, the relative coking tendency of each coal in the bottoms recycle mode has been established as: Wyodak $\approx$ Wandoan > Martin Lake > Monterey > Ireland > Burning Star.

The flow unit tests have been a cost effective and successful method of determining the relative coking tendencies of coal slurries and have provided valuable guidance and understanding during ECLP slurry preheater operations. This tool will play a role in the EDS licensing program to qualitatively assess slurry preheater coking risk for non-program coals.

6.4 EDS Bottoms Characterization

6.4.1 Introduction

Characterization of physical and chemical properties of EDS bottoms are required to provide a basis for bottoms utilization. Technical issues involved in each bottoms processing option can be better addressed with a complete understanding of bottoms structure and properties. Also, a detailed characterization and understanding is needed to establish a relationship between the bottoms properties and liquefaction conditions. This understanding, coupled with a knowledge of the coal structure, would help in understanding the coal liquefaction mechanism and thus impact on process improvements.

This characterization is carried out first by the inspection of pilot conditions, which can be correlated with bottoms properties, and then by systematic laboratory analyses. These analyses address both the chemical and physical natures of the bottoms, with measurements being both quantitative and qualitative.

6.4.2 Major Considerations

This report reviews bottoms characterization studies and documents current understanding of bottoms properties. Table 6-7 contains references for more detailed information. The analytical techniques used for bottoms characterization, the effect of liquefaction conditions on bottoms properties, and the chemical interactions which alter bottoms viscosity were studied and the major conclusions are summarized below.

- Bottoms Recycle Effects

Recycling the vacuum bottoms to the liquefaction reactor in the EDS process produced improvements in at least three major areas as reported in the EDS Annual Technical Progress Report, July 1, 1980-June 30, 1981 (FE-2893-74).

Table 6-7

EDS Bottoms Characterization Studies

<u>Reference</u>	<u>Topic</u>
1980 Annual (FE-2893-53)	<ul style="list-style-type: none">• Discussion of the viscosity and storage stability of once-through bottoms• Analyses of Illinois No. 6 (Monterey) bottoms by mass spectrometry and FTIR
3Q81 (FE-2893-78)	<ul style="list-style-type: none">• Differences between Monterey once-through and recycle bottoms
4Q81 (FE-2893-83)	<ul style="list-style-type: none">• Characterization of Wyodak recycle bottoms• Comparison of ECLP and CLPP bottoms for Wyodak bottoms• Correlation of solubility characteristics with overall conversion
1981 Annual (FE-2893-74)	<ul style="list-style-type: none">• DSC analyses of Wyodak bottoms demonstrates thermal differences between once-through and recycle bottoms• Thermal stability of once-through versus recycle bottoms• Analyses of Wyodak bottoms by mass spectrometry
3Q82 (FE-2893-99)	<ul style="list-style-type: none">• Characterization of Texas lignite (Martin Lake) recycle bottoms• Comparison of hydrogen to carbon and heteroatom to carbon ratios• Regressive reactions of the bottoms• Results of bottoms combustability by TGA

These improvements include a lighter product slate, lower bottoms viscosity and bottoms with improved thermal stability. Much of this improvement is a result of the longer reaction time, which allows for additional bond breaking and reduction of molecular size.

When the liquefaction bottoms samples from CLPP operations on Illinois No. 6 (Monterey mine), Wyoming (Wyodak), and Texas (Big Brown) lignite coals were analyzed, substantial differences were noted for the once-through and the recycle mode. One obvious difference was the higher ash content of the recycle bottoms resulting from the overall increase in conversion. The recycled bottoms have improved solubility, lower heteroatom contents and lower viscosities. The lower viscosity probably results from the reduction of aromatic sidechains and oxygen functionalities.

The viscosity of the recycled bottoms also is more shear rate-dependent (shear thinning) and less temperature-dependent than once-through bottoms. The decrease in temperature dependency is important because the recycle bottoms have less tendency for degradation during upsets or extended residence times.

- Elemental Analyses

Elemental analyses is one method used for comparing properties of the bottoms. Graphs presenting the H/C ratios and heteroatom ratios can be found in the EDS Quarterly Technical Progress Report July 1-September 30, 1982 (FE-2893-99). A low H/C ratio is characteristic of bottoms that are high in aromatics and very condensed. A high H/C ratio of approximately 2.0 is indicative of long sidechain aliphatics. The bottoms generated from ECLP had H/C ratios that ranged from 0.7 to 1.0, generally lower than the parent feed coal. The atomic H/C ratio in the bottoms typically decreases with increasing temperature and residence time, but increases with increasing hydrogen partial pressure.

Many of the physical characteristics of the bottoms are also affected by high atomic ratios of heteroatoms in the sample. These include oxygen-, nitrogen-, and sulfur-to-carbon atomic ratios. High heteroatomic ratios would be typical of polar bottoms which have a high melting range and a high viscosity. The O/C and S/C atomic ratios in bottoms are substantially lower than in the feed coal. Furthermore, these ratios decrease with increasing liquefaction severity. It is notable that the N/C ratio of the bottoms is very close to the ratio existing in the parent coal. This condition would indicate that the nitrogen is incorporated into the aromatic ring structure, which would add to the polarity of the bottoms.

- Solubility

Solubility of the bottoms is generally characterized by the extractability of four fractions. Oils, which generally consist of the 1000°F material, can be separated from the bottoms by cyclohexane extraction. The asphaltene fraction of the bottoms is toluene or benzene soluble, but cyclohexane insoluble. This bottoms fraction is low melting and has a relatively

low viscosity.. The preasphaltenes consist of pyridine solubles but toluene insolubles. This fraction has a higher melting point and is considerably more viscous as compared to the asphaltenes. The pyridine insolubles are characterized by their high ash levels and highly crosslinked organics. The pyridine insolubles can remain unmolten in the bottoms during normal bottoms processing and contributes to high bottoms viscosity.

The October 1-December 31, 1981 EDS Quarterly Technical Progress Report reports the asphaltenes and preasphaltenes as being directly proportional to the amount of conversion. However, the scatter in the data suggest that operational factors also influence the solubility character.

- Regressive Reactions

Regressive reactions occur in the bottoms to different degrees, and are dependent upon the severity of the temperature, coal type (chemical functionalities present), unit residence time and the liquefaction conditions. The regressive reaction of asphaltenes to preasphaltenes and pyridine insolubles was investigated by analyzing the solubilities of atmospheric (or S-2 separator) bottoms and vacuum bottoms obtained from CLPP and ECLP. There were 64 of these sample sets (consisting of the atmospheric and vacuum bottoms) taken from CLPP and 9 taken from ECLP. Analyses on these samples show that the atmospheric bottoms asphaltenes are deconverted to preasphaltenes or pyridine insolubles in the vacuum bottoms. Analyses indicated a deconversion of $15.5 \pm 12.2\%$ for CLPP and a $21.9 \pm 13.7\%$ for ECLP.

It is suspected that the vacuum tower temperature and residence time are the primary factors in the amount of regressive reaction. These correlations, however, have been difficult to make without better data on the thermal history of the bottoms.

- Viscosities

When the bottoms viscosity was measured with different levels of solids (ash and pyridine insolubles), effects were observed in temperature and shear dependency. As the solids level increases there is less change in the viscosity resulting from variations in temperature. This non-Newtonian behavior of the bottoms is thixotropic, a condition where the viscosity decreases with increasing shear rate. Bottoms with lower levels of solids also show a much higher shear dependency at 600°F.

- Thermal Characterization

Thermal characterization of the bottoms has been conducted in three areas. Thermogravimetric (TGA) analyses provide information on the weight lost as vacuum bottoms are heated at a specified rate over a predetermined temperature range. The Differential Scanning Calorimetry (DSC) provides information on phase transitions of the bottoms over different temperature ranges and in different gaseous environments. The Thermomechanical Analysis (TMA) is typically used to obtain the melting range of the bottoms. With the

collective use of these tools it has been possible to gain an understanding of the physical changes occurring in the bottoms at process temperatures.

TGA's were conducted on the weekly composites generated from ECLP. The results indicated that there is little difference in the thermal decomposition of the bottoms. However, when each of the solubility fractions were separated from the vacuum bottoms and analyzed, the thermal fractions were found to be in consistent ratios for each of the solubility fractions. The feed coals and the unit size had no apparent effect on the ratios of the thermal fractions for each soluble fraction. The asphaltene fractions contained from 50 to 55% volatiles and 45 to 50% fixed carbon. These volatiles were evolved over a range of 150 to 600°C. By comparison, the preasphaltenes had 20 to 25% volatiles and 75 to 80% fixed carbon. The pyridine insolubles maintained a volatile to fixed carbon ratio of 2:3. Because the ratio of the solids (ash and fixed carbon)-to-volatiles is a major factor in determining bottoms viscosity, the TGA can give an approximation of the bottoms viscosity range.

The DSC is used to detect both physical and chemical changes in the bottoms such as melting. Samples of the thermograms produced from DSC are reported in the July 1-June 30, 1981 EDS Annual Technical Progress Report (FE-2893-84). An exothermic peak that is characteristic of once-through bottoms can be observed above 140°C in the DSC thermogram. It is believed that this exothermic transition is the result of chemical condensation of the sample. When the sample was heated to 250°C and cooled back to 50°C for three cycles, the exotherm decreased with each cycle. This would indicate that the functionalities involved in the condensation reactions are slowly being consumed by the reaction. Experiences with heat soaking the bottoms over 24 hours at 600°F demonstrate the thermal instability of once-through bottoms and agree with the DSC findings.

Analyses by TMA show that the bottoms melt over a wide temperature range, normally between 160 and 300°C. By placing loads on the TMA probe, correlations can be made between the probe penetration and the pumpability of the bottoms at a given temperature.

● Bottoms Combustion

A study was conducted to determine the feasibility of providing process heat to the feed slurry or for steam generation by burning the vacuum bottoms. It was reported in the July 1-September 30, 1982 EDS Quarterly Technical Progress Report (FE-2893-99) that the bottoms burned at a slower rate and had a higher ignition temperature than the parent coal. Tests made on all of the coals processed in ECLP indicate the same results. The difficulty in burning the bottoms is proportional to the increases in conversion which result in high percentages of asphaltenes. It should be noted, however, that the laboratory tests were conducted at very low heating rates compared to the actual heating rates in a commercial furnace.

Fouling studies show that both the recycle and once-through bottoms had fouling rates that were close to that of the parent coal. This was supported in the tests made by Combustion Engineering where an Illinois once-through (ECLP) sample proved to be slightly less prone to fouling than would have been expected from the parent coal.

Sulfur emissions in the Solid Fuels Evaluation Unit (SFEU) suggest that controls to meet the 90% reduction criterion will be required, but SO₂ emissions will not approach the absolute limit. The data also suggest that NO_x reduction practices will be required.

ECLP PROJECT MANAGEMENT, DETAILED ENGINEERING,
PROCUREMENT, CONSTRUCTION, AND OPERATIONS

1. PROJECT MANAGEMENT

This task was completed in 1980 and has been summarized in the Construction of EDS Coal Liquefaction Pilot Plant Final Report (FE-2893-66).

2. ENGINEERING AND PROCUREMENT

This task was completed in 1980 and has been summarized in the Construction of EDS Coal Liquefaction Pilot Plant Final Report (FE-2893-66).

3. CONSTRUCTION

This task was completed in 1980 and has been summarized in the Construction of EDS Coal Liquefaction Pilot Plant Final Report (FE-2893-66).

4. PREPARATION FOR OPERATIONS

This task was completed in 1980 and has been summarized in the Construction of EDS Coal Liquefaction Pilot Plant Final Report (FE-2893-66).

5. OPERATIONS

5.1 ECLP Simplified Flow Plan

A simplified flow plan of the ECLP plant is shown in Figure 5-1. A more detailed flow plan is included in Appendix A, Figure A-1. The plant had four major sections -- coal receipt/preparation, coal liquefaction, product distillation, and solvent hydrogenation.

Mined coal was transported to the plant by rail in a 30-car unit train. Coal was stored in a silo of 5,000-ton capacity and was prepared by crushing and drying in either a gas-swept mill or an impact mill plus slurry drier. The prepared coal was slurried with hot, hydrogenated recycle solvent in the slurry drier and was pumped in two stages to a pressure of about 2500 pounds per square inch. Hydrogen-rich recycle gas was added to the slurry and the mixture was then heated to 780°F to 810°F in a commercial-type furnace using vertical serpentine coils. The mixture passed through a series of two to four vertical liquefaction reactors which provided nominal residence times of 40 to 90 minutes. Exotherms from the reaction increased the average liquefaction temperature to about 830°F to 850°F.

After liquefaction, the three-phase mixture passed into a separator drum. The vapors from the separator were sent through hot and cold separators for additional condensation. The slurry from the separator was sent through a single-stage pressure letdown valve and fed, after mixing with the hot and

FIGURE 5-1

ECLP SIMPLIFIED FLOW PLAN

cold separator liquids, to an atmospheric tower. The slurry was fractionated into a naphtha stream, two distillate streams, and a bottoms stream containing the original coal ash. These atmospheric bottoms were sent through a preheat furnace into a vacuum tower where light and heavy vacuum gas oil streams were stripped from the vacuum bottoms stream. The distillate sidestreams from the atmospheric tower and the overhead from the vacuum tower were combined, hydrotreated to replenish donor hydrogen, and returned to the slurry drier as recycle solvent. A slipstream of net solvent was directed to product tankage. The gas oil sidestreams from the vacuum tower were at various times taken as product, recycled to the slurry drier, or recycled to the solvent hydrotreater. The vacuum bottoms contained hydrocarbons boiling above 1000°F, plus the original ash in the coal and any unconverted coal. During bottoms recycle operations, a portion of the bottoms was recycled to the slurry drier and fed to the liquefaction reactors. The remaining portion of the bottoms was solidified on a cooling belt and stored in a building onsite for further upgrading tests.

5.2 Summary of ECLP Operations

5.2.1 ECLP Start-up and Shakedown

Mechanical completion of ECLP was achieved on March 21, 1980 with the turnover of the Liquefaction Distillation Unit (LDU) to Exxon Company, U.S.A. Following mechanical completion, all plant equipment was checked out for proper operation, pressure tested and run in. Also, the Solvent Hydrogenation Unit (SHU) catalyst was activated and a supply of creosote oil was hydrogenated for a start-up solvent.

Initial coal operations were achieved on June 24, 1980. During the three and a half month shakedown period that followed, Illinois No. 6 coal from the Monterey No. 1 mine was fed to the plant for a total of 1245 hours in eight individual runs. A detailed tabulation of each run is included in Appendix B. As shown in Figure 5-2, the coal-in percentage for this time was 51 percent. This period consisted of shaking down the plant, learning how to run it, detecting problems and potential problem areas, and developing changes to correct any deficiencies found. Some of the problems encountered during the shakedown were the short packing life of the slurry reciprocating pumps, the plugging of process piping due to the solidification of heavy coal liquids, slurry piping erosion, which resulted in failure of an elbow in the vacuum furnace transfer line, and plugging of the slurry feed heat exchanger (E-102) due to saltation of coal solids.

5.2.2 First Turnaround - October, 1980

In October 1980, a turnaround was conducted to allow equipment inspection to determine the effect of operation on plant internals and to make modifications to remedy the problems detected during shakedown. The major findings of this turnaround were:

- Plugging and disruption of the distributor trays in the two liquefaction reactors which were used during shakedown. The trays were removed for the next operating period.

Figure 5-2 ECLP OPERATING HISTORY

- Slight erosion/corrosion in the upper section of the atmospheric tower (T-201).
- Erosion in the inlet area of the vacuum tower (T-204).
- Erosion of the transfer line from the vacuum furnace (F-201) to T-204. It was replaced with a refractory-lined line and elbow.
- Erosion of the cyclones in the gas-swept mill.

Additional turnaround information is contained in the July 1, 1980 - June 30, 1981 EDS Annual Technical Progress Report (FE-2893-74).

5.2.3 Illinois Coal Testing Operation

Following completion of the turnaround at the end of November 1980, start-up activities were commenced. Coal-in operations resumed on December 30, 1980 beginning a five-month testing program. During both the shakedown and testing periods, the operation was in a once-through mode, that is, without the recycle of vacuum bottoms to the liquefaction section of the plant.

During the testing operation, the coal-in factor was improved to 72 percent. A total of 2658 hours of operations on Illinois No. 6 coal from the Monterey No. 1 mine were achieved in nine individual runs (Fig. 5-2 plus details in Appendix B).

In general, operations during this period were hampered by low coal conversion, poor solvent quality and hot spot formation in the slurry preheat furnaces. Other major learnings were:

- Corrosion in the upper section of the atmospheric tower shell resulted in its holing-through near Tray No. 23. Temporary stainless steel slab latches were welded on the shell between four trays.
- Wear-life of the main slurry letdown valve (L-106CV) was excellent. A life of 128 days was achieved with one valve.
- A rotary-valve coal feeder to the slurry drier gave much better service than the original gate-lock feeder.

Additional information concerning this operation is contained in the July 1, 1980 - June 30, 1981 EDS Annual Technical Progress Report, FE-2893-74.

5.2.4 Second ECLP Turnaround - June 1981

The second ECLP turnaround occurred during June 1981 to quantify further the effects of the Illinois coal operation on plant equipment. The major findings of this turnaround were:

- Major erosion of some flooded tees in the slurry pumparound piping. All tees of this type were replaced with long-radius elbows.
- Coke deposits in the atmospheric tower feed preheat exchanger (E-105).

- Hard coke-like deposits in the liquefaction reactor effluent separator (D-103).
- Severe spalling of the atmospheric tower feed mix chamber (MC-203).
- Fouling of the stripping baffles in the vacuum tower (T-204).
- Severe erosion at the tangential inlet to the vacuum tower (T-204).
- Ammonium chloride deposition in the solvent hydrogenation cold separator condenser (E-302).

Additionally, part of the upper section of the atmospheric tower was replaced with a 321 stainless-steel-lined section in a five-tray zone. The tangential inlet section of the vacuum tower (T-204) was lined with alumina bricks for better erosion resistance. Redesigned stuffing boxes were installed on the atmospheric bottoms pump (P-204A) to extend packing life. Redesigned distributor trays were installed in the first two liquefaction reactors (R-101A/B). R-101C and D were placed in the operating reactor train and were left without trays.

More detailed information about this turnaround is contained in the July 1, 1980 - June 30, 1981 EDS Annual Technical Progress Report, FE-2893-74.

Following completion of this turnaround, the installation of the facilities to recycle a portion of the vacuum bottoms stream to liquefaction was completed. All subsequent ECLP operations were carried out in this bottoms recycle mode.

5.2.5 First Wyoming Coal Operation

On July 31, 1981, operations began in a bottoms recycle mode. Operations continued through August 7 when a switch was made to a Wyoming subbituminous coal from the Wyodak mine. During this operating period, 1842 hours of coal-in operation were completed in two runs (Figure 5-2 plus details in Appendix B). The coal-in factor was improved to 85 percent.

Highlights of the first Wyoming coal bottoms recycle operation were:

- Completion of Run 18 which lasted for 57.9 days. This was the longest run during ECLP operations.
- Successful commissioning of the vacuum bottoms recycle facilities.
- Reduction of the solvent hydrogenation unit catalyst volume to improve solvent quality.
- Completion of radioactive tracer tests to determine gas holdups in the liquefaction reactors.
- Improvement in solvent quality by removing additional light-boiling saturates from the solvent by distillation.

- Improved packing life of the atmospheric bottoms pump (P-204A).

As in the previous operation, low coal conversion, formation of hot spots in the slurry preheat furnace, and poor solvent quality were encountered during this operation. Some improvement in solvent quality was made because of the above changes in operations.

Additional information on this operation is contained in the July 1,-September 30, 1981 and the October 1-December 31, 1981 EDS Quarterly Technical Progress Reports, FE-2893-78 and FE-2893-83, respectively.

5.2.6 Third ECLP Turnaround - November, 1981

Following a completion of the Wyoming coal bottoms recycle operations in October 1981, a turnaround inspection was conducted. During this turnaround, an equipment inspection was completed, the slurry preheat furnace was modified into a two-zone (high-flux/low flux) design to lower the slurry film temperatures, and redesigned stuffing boxes were installed on the slurry feed pump (P-102B). The major findings during the equipment inspections were:

- The long-radius elbows in the slurry pumparound piping were in good condition. Minor erosion was noted downstream of weld intrusions.
- A minor accumulation of solids was left in the liquefaction reactors (R-101A/B/C/D) after draining. Only minimal plugging has occurred on the R-101 A/B distributor trays.
- Deposits of soft solids were noted in the liquefaction reactor effluent separator (D-103).
- No erosion or corrosion was detected in the atmospheric tower (T-201).
- Minor erosion had occurred in the transfer line from the vacuum furnace to the vacuum tower (T-204).
- Significant thinning of the chimneys on the vacuum overflash and heavy vacuum gas oil trays in the vacuum tower (T-204) had occurred. The chimneys were sleeve-lined to repair them.

Additional details of this turnaround are contained in the October 1-December 31, 1981, EDS Quarterly Technical Progress Report (FE-2893-83).

5.2.7 Illinois Coal Bottoms Recycle Operation

Following completion of the turnaround, a three-month Illinois No. 6 (Monterey No. 1 mine) bituminous coal bottoms recycle operation was started on November 28, 1981. During the operating period, 2024 hours of coal-in operation were achieved in four runs (Figure 5-2 plus details in Appendix B). Two of these runs were terminated because of extremely cold weather in January, 1982. The coal-in factor was 91 percent.

Highlights of the Illinois coal bottoms recycle operations were:

- Attainment of design points for a commercial-sized plant at solvent-to-coal-to-bottoms (S/C/B) ratios of 2.3/1/0.5 and 1.6/1/0.5.
- Trouble-free operation of the modified slurry preheat furnace. There were no indications of hot spot or coke formation at S/C/B ratios as low as 1.6/1/0.5.
- Demonstration of a coal conversion level of 60 percent 1000°F⁻ on a dry and ash-free coal basis.
- Improved solvent quality. Higher donor hydrogen, lower saturates and higher 600°F⁺ contents were obtained.
- Installation and operation of slurry drier screw feeders (CO-101, 102) to inject the feed coal below the slurry drier liquid level.
- Installation and operation of the redesigned, vertical slurry heat exchangers (E-102A/B). Plugging of these exchangers continued but was caused by oversize coal rather than saltation.
- Installation and operation of the modified slurry letdown valve (L-106B-CV). The valve was streamlined to improve its wear life during bottoms recycle operations.

Further information on this operating period is contained in the October 1-December 31, 1981 and January 1-March 31, 1982, EDS Quarterly Technical Progress Reports, FE-2893-83 and FE-2893-89, respectively.

5.2.8 Second Wyoming Coal Bottoms Recycle Operation

On March 1, 1982, the on-site supply of Illinois coal was used up and operations continued on Wyoming subbituminous coal from the Wyodak mine in a bottoms recycle mode. There was no coal outage between these operations. During this Wyoming coal operating period, 862 hours of coal-in operations were achieved in six runs (Figure 5-2 plus details in Appendix B). Mechanical problems, not specifically related to coal type, dropped the coal-in factor to 72 percent during this operation.

Highlights of the second Wyoming coal bottoms recycle operations were:

- Attainment of a design point for a commercial-sized plant at a solvent-to-coal-to-bottoms (S/C/B) ratio of 2.0/1/0.5.
- Trouble-free operation of the modified slurry preheat furnace (F-102B) with no indications of hot-spot formation at a S/C/B ratio of 2.0/1/0.5. Operations at lower S/C/B ratios did result in some increases in tube metal temperatures.
- Demonstration of a coal conversion of 66 percent 1000°F⁻ on a dry and ash-free coal basis.

- Production of high-quality donor solvent.
- Completion of a record run on the atmospheric bottoms pump (P-204A) with redesigned stuffing boxes. During this run, a packing life of 88 days (79 days on slurry) was achieved.
- Successful withdrawal of solids from the liquefaction reactors using the high-pressure letdown system.
- Installation and operation of the slurry drier vapor disengagement drum (D-122). This drum was designed to allow water vapor disengagement from the feed slurry before it entered the suction of the slurry feed booster pumps (P-101 A/B).
- Installation of smaller diameter tubes in the outlet row of the modified slurry preheat furnace (F-102A).

Additional information about this operation is contained in the January 1-March 31, 1982 EDS Quarterly Technical Progress Report (FE-2893-89) and in the July 1 1981 - June 30, 1982 EDS Annual Technical Progress Report, FE-2893-93.

5.2.9 Fourth ECLP Turnaround

The second Wyoming coal operation was discontinued on April 19, 1982, when a hole was eroded in the shell of the atmospheric tower feed preheat exchanger (E-105). A mini-turnaround was conducted to:

- Repair the atmospheric tower feed preheat exchanger (E-105).
- Inspect the vacuum tower (T-204).
- Clean the effluent separator (D-103) and hot separator (D-104) drums.
- Skim a catalyst restriction from the first solvent hydrogenation reactor (R-301).

Turnaround inspection results were:

- Extensive, hard, coke-like deposits in the effluent separator (D-103).
- Hard, coke-like deposits in the atmospheric tower feed preheater exchanger (E-105) shell.
- Misplaced chimney hats in the vacuum tower trays for light and heavy vacuum gas oils.
- Moderate erosion of the refractory-lined transfer line from the vacuum furnace to the vacuum tower (T-204).

Additional turnaround information is contained in the July 1, 1981 - June 30, 1982 EDS Annual Technical Progress Report, FE-2893-93.

5.2.10 Texas Lignite Bottoms Recycle Operations

Following completion of the turnaround, operations were resumed on May 2, 1982, with some Wyoming coal remaining from the previous operation. With operations continuing, a switch was made on May 12, 1982 to a Texas lignite from the Martin Lake mine. During this operating period, 2061 hours of coal-in operations were achieved in six separate runs (Figure 5-2 plus details in Appendix B). The overall coal-in factor was 78 percent.

Highlights of the Texas lignite bottoms recycle operation were:

- Attainment of a design point for a commercial-sized plant at a solvent-to-coal-to-bottoms (S/C/B) ratio of 1.6/1/0.5.
- Completion of 28 days of operation at a S/C/B ratio of 1.6/1/0.5 with no indication of hot spot formation in the modified slurry preheat furnace (F-102A) with smaller diameter tubes in the last half of the outlet row. Lower S/C/B ratios (down to 1.2/1/0.5) were tested for shorter time periods. Also, higher slurry film temperatures were demonstrated at a 2.0/1/0.8 S/C/B ratio.
- Demonstration of a coal conversion level of 66 percent 1000°F⁻ on a dry and ash-free coal basis.
- Production of high-quality donor solvent. Although the 600°F⁻ content of the lignite solvent was slightly higher than the two previous operations, the donor hydrogen and saturates contents were similar. The lighter solvent was caused by lower vacuum tower severity necessitated by the high lignite bottoms viscosity.
- Demonstration of the EDS process with feed coal ash contents of 9 to 20 weight percent (a maximum of 23 weight percent).
- Slurry drying of high-moisture lignite.
- Control of liquefaction reactor solids buildup by high-pressure letdown solids withdrawal.
- Further improvement in the packing life of the slurry reciprocating pumps.

Additional details of this Texas lignite bottoms recycle operation are contained in the July 1, 1981 - June 30, 1982 EDS Annual Technical Progress Report, FE-2893-93, and in the July 1- September 30, 1982 EDS Quarterly Technical Progress Report, FE-2893-99.

5.2.11 Final ECLP Inspection

ECLP operations were terminated on August 20, 1982 to begin the final ECLP inspection. During this inspection, all major pieces of equipment were opened or disassembled for inspection. Notable inspection results were:

- Severe erosion of the casings and impellers of the gas-swept mill venturi scrubber circulation (P-1101) and blowdown (P-1510A/B) pumps.
- Severe fouling of the distributor trays in the lead liquefaction reactors (R-101A/B). Some hard, coke-like deposits were found in all liquefaction reactors.
- Severe plugging of R-101D. Drilling and hydroblasting were required to remove the plug. The plug may have resulted from operational difficulties during the final shutdown.
- Hard coke-like deposits in one-half of the bottom head of the liquefaction reactor effluent separator (D-103). The upper cartridge-tray section was clean.
- Heavy wear of the main slurry letdown valve (L-106ACV) plug tip and seat. Both were made of tungsten carbide with a titanium diboride coating.
- Moderate erosion of the atmospheric tower (T-201) inlet transfer line.
- Moderate corrosion of the carbon steel shell of the atmospheric tower (T-201) below the stainless steel-lined section (Tray No. 19).
- Cracking of some stainless steel hardware in the area of Tray Nos. 20 to 26 in the atmospheric tower (T-201).
- Moderate erosion of the refractory-lined vacuum tower (T-204) transfer line and flash zone ceramic brick.
- Moderate erosion of the carbon steel chimneys on the vacuum tower (T-204) overflash and heavy vacuum gas oil trays.
- Moderate corrosion of the carbon steel trays and internals in the upper section of the solvent fractionator (Tray Nos. 27 to 33).

Additional details of the results of this inspection are contained in the July 1-June 30, 1982 EDS Quarterly Technical Progress Report, FE-2893-99.

5.3 ECLP Equipment Performance

This section presents a brief summary of the performance of the major ECLP equipment during total operations.

5.3.1 Drums

- Slurry Drier (D101) -- There were initial operating problems with D-101 caused by the inadvertent setting of its mixer speed at 28 rpm, which did not suspend all of the coal. At mixer speeds of 68 or 84 rpm, there were no problems.

During slurry drying operations, problems were encountered with the slurry feed booster pumps (P-101) because of entrained water vapor

bubbles in the pump suction. An additional drum (D-122) was placed in the pump suction to allow vapor disengagement. This drum allowed higher feed rates of wet coal but did not completely eliminate pumping problems during slurry drying. However, sufficient data for design of a commercial-size slurry drier were obtained.

Liquefaction Reactor Effluent Separator (D-103) -- During Operations, there was a general difficulty in detecting the precise liquid level in D-103. Nuclear level detectors (continuous level) and point source alarm level) were used to detect level but a head-type meter was used to control the level. Overflow of D-103 into the hot separator drum (D-104) was caused both by inaccuracies in determining level and by sudden increases in gas rates which "burped" solids from the liquefaction reactors into D-103.

During turnaround inspections, hard coke-like deposits were generally found in the bottom of D-103 due to high drum temperatures (above 800°F). Similar deposits were found in the upper cartridge section when the overhead wash system was not used. After wash oil, addition to the top of D-103 was commenced in May 1982, fouling and coking in this cartridge section were minimal.

- Liquefaction Hot Separator Drum (D-104) -- This horizontal drum trapped loose reactor solids which were carried over from D-103 overflows during upsets. These solids fouled the displacement-type level detector and severely eroded the hot separator letdown valve (L-108CV).
- Solvent Hydrogenation Unit Feed Filter (D-308) -- Pressure drop increases across D-308 occurred on several occasions during ECLP operations. The cause of these increases was solids carry-over into liquefaction product solvent streams. At times, normal pressure drops could be restored by backflushing D-308 to slop tankage with solvent. If this was not successful, catalyst bed replacement in the drum was necessary.

5.3.2 Towers

- Atmospheric Tower (T-201) -- The upper, carbon-steel section of T-201 corroded through the tower wall during the Illinois coal once-through testing period. Replacement of the affected section with a stainless steel-lined section controlled the corrosion. Similar corrosion was found in the atmospheric Tower No. 1 sidestream stripper (T-202), but to a lesser extent.

During operations, overflow of the T-201 bottoms into the atmospheric Tower No. 2 sidestream caused pump mechanical seal failures and solvent hydrogenation unit feed filter (D-308) plugging.

During the final inspection, moderate erosion was detected in the T-201 inlet transfer line.

- Vacuum Tower (T-204) -- Erosion of the T-204 inlet transfer line initially was severe. The line was replaced with a fiber-reinforced, refractory-lined one during the first turnaround. This new line

controlled the erosion but did not totally eliminate it. Erosion of the thermowells in this transfer line, especially those near the tower, was very severe. Similar erosion occurred in the T-204 flashzone area and was controlled by lining this area with ceramic bricks.

Corrosion of the carbon-steel chimneys occurred on the trays for the vacuum overflash and heavy vacuum gas oil drawoffs. Sleeve lining with stainless steel was used to extend their lives.

- Solvent Fractionator (T-303) -- During the final inspection, corrosion similar to that in T-201 was found in the upper section of T-303 and in the solvent fractionator No. 1 sidestream stripper (T-304).

5.3.3 Slurry Pumps

- Slurry Feed Booster Pumps (P-101) -- The P-101 pumps generally performed well. The single mechanical seals used in these pumps were adequate. Erosion in these pumps generally occurred in the outwater area. Erosion in other areas was highly specific to pump design.
- Slurry Feed Pumps (P-102) -- Although the P-102 pumps performed well generally, early operations were hampered by short packing life and pumping problems due to large coal particles. Packing life was greatly improved through the use of different packing schemes (type, material, arrangement, etc.) and redesigned stuffing boxes. Also, coal preparation operations were adjusted to produce coal with no more than one weight percent larger than eight mesh.

A pulsation dampener, which used recycle gas injection, dampened the pump discharge pulsations much more effectively than the original liquid-filled dampener.

- Atmospheric Bottoms Pumps (P-204) -- These vertical reciprocating pumps also performed well, in general, during ECLP operations. Although early packing life was very short, it was improved by using alternate packing schemes and redesigning the stuffing box. Packing life was improved from one to two days up to 131⁺ days at the end of operations.

Pump performance was reduced, at times, by refractory particles which had spalled from upstream equipment. In-line filters were installed to keep this material out of the P-204 suction.

- Atmospheric Bottoms Test Pump (P-216) -- Although the operating time of this pump, which was in a recycle test loop, was very limited due to its system design deficiencies, its performance was adequate to generate the necessary data.
- Vacuum Bottoms Pump (P-210) -- The performance of this screw pump was satisfactory, in general, but poor at times; however, it was difficult to determine its pumping rate due to continuous use of an unmetered recycle from discharge to suction. During the 1982 ECLP operation, performance deteriorated because of wear of the screw flights and casing.

A clean, high-pressure flush oil supply was critical to achieving long packing life in this pump. Leaking of the light vacuum gas oil through the packing into the pumpage affected solvent balance and solvent quality. After leakage of bottoms into the packing began, packing life was very short.

- Vacuum Bottoms Recycle Pumps (P-222) -- These centrifugal pumps performed well but were generally operated at low speed due to low flows and heads required. Their double mechanical seals and flush oil supply system worked well.

5.3.4 Reactors

- Liquefaction Reactors (R-101) -- The R-101 reactors had a lower liquid holdup than the smaller EDS pilot plants (CLPP and RCLU). This lower holdup was confirmed by pressure drop and radioactive tracer testing. It resulted in lower coal conversions than had been achieved in the smaller pilot plants at the same "nominal residence time."⁽¹⁾ Acceptable conversions were eventually obtained by using all four reactors in series and operating them at higher temperatures.

Temporary loss of flow in the reactors caused the bed of reactor solids to slump and partially plug the distributor trays in the reactor. This plugging resulted in the disruption of the inlet distributor trays or the formation of hard, coke-like deposits. Redesigned supports with greater strength were needed to keep the trays in place if plugging occurred. Performance in the two foot diameter ECLP reactors was not affected by the absence or presence of the distributor trays.

The original systems for withdrawing liquefaction reactor solids were not operable chiefly due to flow control difficulties and plugging of piping. The cycling-valve system was modified to allow its operation as a high-pressure letdown system. This system was used to successfully remove solids from all four reactors during the ECLP Texas lignite operations.

- Solvent Hydrogenation Reactor (R-301) -- The only operating problem associated with R-301 was periodic pressure drop increases across its catalyst bed. These increases were caused both by carry-over of liquefaction reactor solids into clean solvent streams and the deposition of a heavy, organic, iron-rich phase from the solvent or from tank scale. R-301 catalyst bed skimmings or replacements were performed in August 1980, and during the turnarounds of October 1980, June 1981, and April 1982.

5.3.5 Valves

- Slurry Block Valves -- Through conduit gate valves worked well during ECLP operations. These valves needed to be flushed during each cycle to remove coal solids from the body cavity.

(1) Defined as reactor volume divided by slurry volumetric rate at 600°F.

Plug valves also performed well. Regular lubrication was required to maintain performance. Some stem system failures occurred when proper lubrication was not provided.

- Slurry Letdown Valve -- The original design slurry letdown valve, a sweep-flow angle valve with tungsten carbide internals, had a long life (128 days) during once-through operations.

The valve was redesigned to handle the higher ash slurries during bottoms recycle operations. A life of 79⁺ days was obtained during the Illinois and Wyoming coal bottoms recycle operations.

Valve wear accelerated during the high-ash Texas lignite operations. The valve life of 24 days was adequate to avoid operational problems. There was no apparent benefit in using a titanium boride coating over the base tungsten carbide.

5.3.6 Miscellaneous Equipment

- Coal Feed System -- The original gatelock feeder (GL-101) for the slurry drier gave many operational problems due to its mechanical complexity and unreliability. A replacement rotary valve (RV-101) gave much better service but did allow gas blow-by except at very low slurry drier pressures. This resulted in carry-over of coal fines into the slurry drier overhead system.

Both of these problems were solved by using screw feeders (CO-101/102) to feed the coal into the slurry drier below the slurry level. Flush solvent injection was required at critical locations on these feeders to keep the coal moving into the slurry drier.

- Slurry Feed Heat Exchangers (E-102A/B) -- The original E-102 design was a horizontal, multipass exchanger. Although the tubes were designed for velocities above the saltation velocity, saltation occurred in the channel heads where there were much lower velocities. These exchangers were completely redesigned to vertical down-flow, single-pass ones. This eliminated the saltation problem.

Trash material and oversize coal particles did plug these exchangers on occasion. Back flushing or mechanical cleaning were required to remove the plugging material.

- Flushing Systems -- The flushing systems at ECLP worked well, especially in emergency situations. The biggest problem in this area was the carry-over of solids into clean solvent streams and then into the flushing system. These solids caused packing and seal failures and erosion in equipment which was not designed for slurries. Another problem in the vacuum bottoms area was that the 400°F flush oil was too cold to adequately flush high-melt-point bottoms.

- Blowdown System -- The blowdown system at ECLP worked well as long as the blowdown piping was flushed after use. Erosion of the piping did occur when high-pressure equipment containing slurry was discharged into the low-pressure blowdown system.

Rerunning of the slop solvent from the blowdown system was a general consideration during routine operations. Slop was rerun into the slurry drier (D-101). The need to maintain high coal concentrations in D-101 for testing purposes generally allowed only a small amount of slop to be rerun.

- Coal Crushing

- Impact Mill (CR-1102) -- CR-1102 operations were very limited because of problems in slurry drying. Special care was taken during the start-up of the mill to keep oversize coal out of the slurry drier system where it could clog the slurry heat exchangers. Wear and breakage of its internals was high during the high-ash Texas lignite operations due to the presence of petrified wood and rocks.
- Gas-Swept Mill (CR-1101) -- CR-1101 was used to crush coal during most of ECLP operations and operated well. Some erosion and corrosion occurred in the overhead cyclone and venturi scrubber system but was easily controlled.

- Slurry Flowmeter -- Venturi meters were used almost exclusively for slurry flow measurements. Although affected by the non-Newtonian slurry, their accuracy was adequate for control purposes. A reliable high-pressure flush oil supply was necessary to prevent impulse line plugging and ensure continual operation.

- Vacuum Bottoms Solidification Belt (CO-1901) -- Operating problems with CO-1901 were chiefly caused by poor distribution of vacuum bottoms across the width of the belt. This was caused by an inadequate bottoms distributor design which allowed bottoms to solidify at the ends of the distributor. The resulting sheet of bottoms on the belt was thicker than necessary and more difficult to completely solidify. Additional water was sprayed directly onto the bottoms sheet to aid in solidification.

Control of fugitive fume emissions from the belt was also difficult at times because the venturi scrubbing system was not always adequate to keep a negative pressure inside the belt enclosure. The problem was compounded by the need to open the enclosure to observe or correct bottoms distribution, and by southerly winds which created a "wind tunnel" inside the enclosure. Emissions were minimized by installing internal curtains to break the wind and minimizing opening of the enclosure.

5.4 ECLP Safety and Occupational Health Programs

During the Preparation for Operation Phase of the ECLP project, a 22-point Safety and Occupational Health Program was instituted. The components of this program were:

- Safety Policy Statement
- Plant Safety Steering Committee
- Special Task Committee on Employees
- Accident/Disability Reporting and Investigation
- Safety Performance Indices
- Safe Operation Committee
- Emergency Organization Plans
- Risk Management
- OSHA Compliance
- Safety Awareness
- Basic Safety Training
- Equipment Identification
- Task Books
- Operating Procedures
- Interactions with Maintenance and Other Contractors
- Housekeeping
- Buildings Safety Plans
- Equipment Designs
- Safety and Operability Audits
- General Inspection Program
- Equipment Inspection Program
- Carcinogenic Materials Protection Program

Additional information on these components is contained in the Appendix. A separate report, ECLP Industrial Hygiene - II, FE-2893-119, summarizes the results of the Occupational Health Program.

Table 5-1 briefly summarizes the ECLP safety performance during ECLP operations.

5.5 ECLP Operating Data

Table 5-2 briefly summarizes yield test data from operations during the Illinois coal bottoms recycle, the second Wyoming coal bottoms recycle and the Texas lignite bottoms recycle operating periods.

TABLE 5-1

ECLP SAFETY SUMMARY

	<u>1980</u>				
	<u>EXXON</u>			<u>CONTRACTORS</u>	
	<u>Process</u>	<u>Others</u>	<u>Total</u>	<u>Mechanical</u>	<u>Instrument/ Electrical</u>
On-Job Hours	99,821	180,055	279,876	558,556	36,514
Off-Job Hours	179,677	324,197	503,874	558,600	39,492
AII or RII ¹	2.38 (AII)	1.8 (AII)	2.04 (AII)	2.5 (AII)	0 (RII)
Target AII or RII	1.0 (AII)	0 (AII)	1.0 (AII)	4.0 (AII)	4.0 (RII)
On-Job Disabling Injuries	0	0	0	1	0
	<u>1981</u>				
	<u>EXXON</u>			<u>CONTRACTORS</u>	
	<u>Process</u>	<u>Others</u>	<u>Total</u>	<u>Mechanical</u>	<u>Instrument/ Electrical</u>
On-Job Hours	109,200	175,310	284,510	456,398	28,565
Off-Job Hours	181,920	315,619	497,539	664,711	37,880
AII or RII	2.75 (AII)	0.63 (AII)	1.45 (AII)	2.2 (RII)	0 (RII)
Target AII or RII	1.2 (AII)	NA	1.0 (AII)	3.0 (RII)	3.0 (RII)
On-Job Disabling Injuries	0	0	0	1	0
	<u>1982</u>				
	<u>EXXON</u>			<u>CONTRACTORS</u>	
	<u>Process</u>	<u>Others</u>	<u>Total</u>	<u>Mechanical</u>	<u>Instrument/ Electrical</u>
On-Job Hours	72,254	104,106	176,270	196,733	16,332
Off-Job Hours	120,425	187,272	307,697	NA	NA
AII or RII	0 (AII)	2.1 (AII)	1.3 (AII)	7.1 (RII)	0 (RII)
Target AII or RII	1.7 (AII)	0.9 (AII)	1.3 (AII)	2.5 (RII)	2.5 (RII)
On-Job Disabling Injuries	0	0	0	2	0

¹ AII - All Injury Index; RII - Recordable Injury Index

TABLE 5-2

ECLP Operating Data

Coal Type Mine	Illinois No. 6 Bituminous <u>Monterey No. 1</u>	Wyoming Subbituminous <u>Wyodak</u>	Texas Lignite <u>Martin Lake</u>
Yield Test Date	1/28/82	3/22/82	6/23/82
Liquefaction Temperature, °F	846	855	845
Liquefaction Pressure, psig	2520	2493	2512
Liquefaction Hydrogen Rate lbs/100 lbs dry coal	4.7	6.9	5.3
Nominal Liquefaction Residence Time, Minutes	81	85	88
Solvent-to-coal Ratio	1.6	2.0	1.55
Recycle Bottoms-to-coal Ratio	0.6	0.5	0.5
Yields, lbs/100 lbs dry ash-free coal			
H ₂	-4.8	-4.9	-4.5
C ₁ - C ₃	11.0	10.4	10.3
C ₄ - 400°F	23.3	25.0	23.9
400-1000°F	14.8	15.7	15.4
1000°F ⁺	39.2	34.0	33.8

Additional and more detailed information is contained in Appendix C, Tables C-1 through C-7.

Table 5-3 summarizes the overall consumption of coal and production of coal liquids for the different ECLP operating periods. The "yields" calculable from these numbers will not be the same as the above yield pattern due to coal and liquid losses in the plant and to operations at different conditions.

TABLE 5-3

ECLP Production Summary

	<u>Illinois Coal Once-Through</u>	<u>Illinois Coal Bottoms Recycle</u>	<u>Wyoming Coal Bottoms Recycle</u>	<u>Texas Lignite Bottoms Recycle</u>
Coal Processed, tons	36255	13717	21894	19422
Naphtha Produced, barrels	17919	11780	14963	11763
Solvent Produced, barrels	-514	4727	3910	5079
Heavy Vacuum Gas Oil Produced, barrels	5096	0	0	0
Vacuum Bottoms Produced, tons	14868	4947	6965	4887

5.6 ECLP Product Shipments

Tables 5-4 to 5-7 summarize the disposal of naphtha, solvent, heavy vacuum gas oil (HVG0) and vacuum bottoms produced at ECLP. Additionally, 3474 barrels of HVG0 were sent to the Exxon Baytown Refinery for blending with an asphalt stream; 21974 barrels of naphtha were sent to the Exxon Baytown Chemical Plant for furnace fuel and 30214 barrels of naphtha were sent to the Exxon Baytown Refinery for blending with catalytic reformer feed as a test.

6.0 ECLP Environmental Assessment

An environmental assessment of ECLP was completed in 1977 and has been documented in Environmental Assessment of the Exxon Coal Liquefaction Pilot Plant, Baytown, Texas, prepared by the United States Energy Research and Development Administration, September, 1977.

ECLP TERMINATION OF OPERATION

1.0 Dismantling

Following completion of the final ECLP turnaround, all toxic materials were removed from the plant and surplus material and equipment were disposed of. The plant was then turned over to a contractor for dismantling.

TABLE 5-4

SUMMARY OF SAMPLE SHIPMENTS OF ILLINOIS COAL ONCE-THROUGH PRODUCTS

<u>Samples Shipped</u>	<u>Naphtha (Barrels)</u>	<u>Solvent (Barrels)</u>	<u>HVGO (Barrels)</u>	<u>Vacuum Bottoms (Tons)</u>	<u>Other (1) (Barrels)</u>
Project	6.25	207.0	54.0	233.0	304.0*
EPRI	0.0	686.0	315.0	0.0	0.0
DOE	22.0	22.0	22.0	0.0	615.0**
Exxon	0.1	0.1	20.0	0.2	0.1***
Phillips	60.0	60.0	60.0	6.0	0.0
Anaconda	13.0	13.0	13.0	2.0	0.0
RAG	46.0	16.0	1.0	0.0	0.0
ENI	54.0	200.0	96.0	4.0	0.0
JCLD	0.0	500.0	225.0	0.0	0.0
TOTAL	241.35	1704.1	806.0	245.2	919.1

(1) Samples included under "Other":

* 69 Barrels of 600°F+ solvent for testing as a feed to a partial oxidation gasification process; 32 gallons of various streams for material testing; 220 barrels of fuel oil for PNA emission testing; 500 gallons of 350-430°F oil for engine tests.

** 275 gallons of T-303 No. 1 sidestream, 330 gallons of T-303 bottoms, 600 barrels of 750°F- solvent.

*** Five gallons of 750°F- solvent.

TABLE 5-5

SUMMARY OF SAMPLE SHIPMENTS OF ILLINOIS COAL BOTTOMS RECYCLE PRODUCTS

<u>Samples Shipped</u>	<u>Naphtha (Barrels)</u>	<u>Solvent (Barrels)</u>	<u>HVGO (Barrels)</u>	<u>Vacuum Bottoms (Tons)</u>	<u>Other (1) (Barrels)</u>
Project	246.5	542.0	0.1	306.4	6.0*
EPRI	0.0	4648.0(2)	0.0	160.0	0.0
DOE	0.0	4.4	0.0	0.0	0.0
JCLD	0.0	0.0	0.0	20.0	0.0
Exxon	15.0	40.0	0.0	0.0	0.0
Anaconda	<u>0.0</u>	<u>65.0</u>	<u>0.0</u>	<u>0.0</u>	<u>0.0</u>
TOTAL	261.5	5299.4	0.1	486.4	6.0

(1) Samples included under "Other":

* 220 gallons of hydrotreated creosote oil, one gallon of sour water from D-105, one gallon of solvent from Tray 23 of Fractionator T-201, nine gallons of LVGO, and six gallons of HAGO.

(2) Includes some Wyoming solvent.

TABLE 5-6

SUMMARY OF SAMPLE SHIPMENTS OF WYOMING COAL BOTTOMS RECYCLE PRODUCTS

<u>Samples Shipped</u>	<u>Naphtha (Barrels)</u>	<u>Solvent (Barrels)</u>	<u>HVGO (Barrels)</u>	<u>Vacuum Bottoms (Tons)</u>	<u>Other (1) (Barrels)</u>
Project	20.0	187.0	1.3	136.0	3.0*
JCLD	0.0	0.0	0.0	30 lbs.	0.0
EPRI	0.0	1976.0	0.0	0.0	0.0
ENI	13.0	26.0	0.02	0.2	0.0
Anaconda	6.5	6.5	0.0	0.8	0.0
Phillips	6.6	6.5	0.0	8.3	0.0
DOE	0.0	13.0	0.0	0.0	0.0
RAG	<u>1.3</u>	<u>1.3</u>	<u>0.0</u>	<u>0.0</u>	<u>0.0</u>
TOTAL	47.4	2216.3	1.32	145.3	3.0

(1) Samples included under "Other":

* One gallon of solvent from Tray 23 of Fractionator T-201, six gallons of LVGO, 2.6 barrels of hydrotreated creosote oil, 10 gallons of slop oil.

TABLE 5-7

SUMMARY OF SAMPLE SHIPMENTS OF TEXAS LIGNITE BOTTOMS RECYCLE PRODUCTS

<u>Samples Shipped</u>	<u>Naphtha (Barrels)</u>	<u>Solvent (Barrels)</u>	<u>HVGO (Barrels)</u>	<u>Vacuum Bottoms (Tons)</u>	<u>Other (1) (Barrels)</u>
Project	13.1	172.4	0.0	32.0	5.0*
DOE	0.0	235.7	0.0	0.0	0.0
EPRI	0.0	5079.0(2)	0.0	0.0	0.0
RAG	1.3	1.3	0.0	0.0	0.0
Phillips	170.2	276.3	0.2	7.5	0.0
Anaconda	6.5	6.5	0.0	0.0	0.0
ENI	<u>13.0</u>	<u>25.0</u>	<u>0.2</u>	<u>0.2</u>	<u>0.0</u>
TOTAL	202.8	5796.2	0.4	39.7	5.0

(1) Samples included under "Other":

* 220 gallons of hydrotreated creosote oil.

(2) Also includes some solvent produced from Illinois and Wyoming coals and small amount of hydrotreated creosote.

APPENDIX A

ECLP Flow Plan

APPENDIX B

This Appendix presents detailed tabulations of time on coal and causes for coal outages for each of the ECLP operating periods.

TABLE B-1
ECLP OPERATING HISTORY
ILLINOIS ONCE-THROUGH
SHAKEDOWN

Run	In/ Out	Date	Time	Hours	Run Coal-In Hours	Cumulative			Remarks
						Coal-In Hours	Total Hours	% Coal-In	
1	In	6/24/80	2135	-	-	-	-	-	P-204, P-102, T-204 plugging.
	Out	6/30/80	0530	128	128	128	128	100	
2	In	7/10/80	1600	250	-	128	378	34	T-204 transfer line erosion.
	Out	7/31/80	2100	509	509	637	887	72	
3	In	8/15/80	1400	353	-	637	1,240	51	Includes 120 hours for hurricane plant shutdown; P-204 and P-210 plugging.
	Out	8/16/80	2200	32	32	669	1,272	53	
4	In	8/24/80	1600	186	-	669	1,458	46	FE-1104 failure.
	Out	8/30/80	0600	134	134	803	1,592	50	
5	In	9/9/80	0100	235	-	803	1,827	44	FE-1104 failure and P-210 problem.
	Out	9/9/80	2200	21	-	824	1,848	45	
	In	9/10/80	0600	8	-	824	1,856	44	P-210 motor loss.
	Out	9/12/80	1400	56	77	880	1,912	46	
6	In	9/16/80	2200	104	-	880	2,016	44	HVG0 plugging.
	Out	9/20/80	0300	77	77	957	2,093	46	
7	In	9/24/80	1600	109	-	957	2,202	43	Instrument tubing failure.
	Out	9/25/80	0900	17	-	974	2,219	44	
	In	9/25/80	1300	4	-	974	2,223	44	C-701 recycle valve, Sandvik stopping, P-101 plug.
	Out	10/2/80	0100	156	173	1,130	2,379	47	
8	In	10/6/80	0900	104	-	1,130	2,483	46	D-103 carryover.
	Out	10/11/80	0400	115	115	1,245	2,598	48	

TABLE B-2
ECLP OPERATING HISTORY
ILLINOIS ONCE-THROUGH (TEST)

Run	In/ Out	Date	Time	Hours	Run Coal-In Hours	Cumulative			Remarks
						Coal-In Hours	Total Hours	% Coal-In	
9	In	12/30/80	1000	-	29	29	29	100	Sandvik belt trip-out.
	Out	12/31/80	1500	29					
10	In	1/3/81	0100	58	226	29	87	33	RV-1101 failure.
	Out	1/6/81	0600	77		106	164	65	
	In	1/6/81	1300	7		106	171	62	
	Out	1/12/81	1800	149		255	320	80	
11	In	1/17/81	1900	121	317	255	441	58	F-102B hot spots.
	Out	1/30/81	2400	317		572	758	75	
12	In	2/2/81	1900	67	49	572	825	69	F-102A hot spots.
	Out	2/4/81	2000	49		621	874	71	
13	In	2/15/81	1000	254	6	621	1,128	55	P-204 suction refractory plug.
	Out	2/15/81	1600	6		627	1,134	55	
14	In	2/19/81	1200	92	738	627	1,226	51	Sandvik belt gear box failure.
	Out	2/22/81	0400	64		691	1,290	54	
	In	2/22/81	1200	8		691	1,298	53	
	Out	3/22/81	0200	662		1,353	1,960	69	
	In	3/22/81	1000	8		1,353	1,968	68	
	Out	3/22/81	2200	12		1,365	1,980	69	
15	In	4/1/81	1000	228	398	1,365	2,208	62	Hole in T-201 shell.
	Out	4/17/81	2400	398		1,763	2,606	68	

TABLE B-2 (Continued)

ECLP OPERATING HISTORY

ILLINOIS ONCE-THROUGH (TEST)--CONTINUED

Run	In/ Out	Date	Time	Hours	Run Coal-In Hours	Cumulative			Remarks
						Coal-In Hours	Total Hours	% Coal-In	
16	In	4/24/81	1700	161	39	1,763	2,767	64	P-204 suction refractory plug.
	Out	4/26/81	0800	39		1,802	2,806	64	
17	In	4/28/81	0300	43	856	1,802	2,849	63	P-102 packing.
	Out	5/8/81	1800	255		2,057	3,104	66	
	In	5/8/81	2000	2		2,057	3,106	66	End of operation (planned).
	Out	6/2/81	2100	601		2,658	3,707	72	

TABLE B-3

ECLP OPERATING HISTORY

WYOMING COAL, BOTTOMS RECYCLE

Run	In/ Out	Date	Time	Hours	Run Coal-In Hours	Cumulative			Remarks
						Coal-In Hours	Total Hours	% Coal-In	
Illinois									
18I	In	7/31/81	1500	-	168	168	168	100	Continuing--swung to Wyoming.
Wyoming									
18W	In	8/7/81	1500	-		168	168	100	Swung to Wyoming.
	Out	8/21/81	0800	329		497	497	100	FE-1104 plugging.
	In	8/21/81	1400	6		497	503	99	P-210 packing--actually out 0700, 0800, 1100.
	Out	8/27/81	0700	137		634	640	99	
	In	8/27/81	1000	3		634	643	99	P-210 packing--actually out 1400, 1500, 2200, 2300.
	Out	8/29/81	1400	52		686	695	99	
	In	8/29/81	1800	4		686	699	98	P-210 packing--actually out 1500, 1900-2400.
	Out	8/30/81	1500	21		707	720	98	
	In	8/30/81	2100	6		707	726	97	P-210 packing-- actually out 0000-0400, 1400, 1500.
	Out	8/31/81	0000	3		710	729	97	
	In	8/31/81	0600	6		710	735	97	RV-101 plugging--actually out 1400-2300.
	Out	9/2/81	1400	56		766	791	97	
19	In	9/2/81	2300	9		766	800	96	T-204 shed plug--due to solids withdrawal.
	Out	9/28/81	2200	623	1,321	1,389	1,423	98	
19	In	10/11/81	0100	291		1,389	1,714	81	F-102 swing/backflow of solids.
	Out	10/29/81	2200	453	453	1,842	2,167	85	F-102 swing/backflow of solids.
NOTE: Excluding Illinois Portion:						1,674	1,999	84	

TABLE B-4

ECLP OPERATING HISTORY
ILLINOIS COAL, BOTTOMS RECYCLE

Run	In/ Out	Date	Time	Hours	Run Coal-In Hours	Cumulative			Remarks
						Coal-In Hours	Total Hours	% Coal-In	
20	In	11/28/81	1600	-					
	Out	12/2/81	2100	101		101	101	100	P-204 plugging.
	In	12/3/81	0500	8		101	109	93	
	Out	12/18/81	1600	371		472	480	98	H ₂ loss from Baytown Refinery.
	In	12/18/81	2100	5		472	485	97	
21	Out	1/11/82	0400	559	1,031	1,031	1,044	99	Freeze-ups--15°F.
	In	1/15/82	1600	108		1,031	1,152	89	
	Out	1/16/82	1200	20	20	1,051	1,172	90	Freeze--voluntary.
	In	1/17/82	1000	22		1,051	1,194	88	
	Out	1/29/82	0300	281	281	1,332	1,475	90	Plug between MC-101 and E-105.
22	In	1/17/82	1000	22		1,051	1,194	88	
	Out	1/29/82	0300	281	281	1,332	1,475	90	
23	In	1/31/82	0400	49		1,332	1,524	87	Terminated Illinois run
	Out	2/28/82	2400	692	692	2,024	2,216	91	(planned).

TABLE B-5

ECLP OPERATING HISTORY

WYOMING COAL, BOTTOMS RECYCLE

Run	In/ Out	Date	Time	Hours	Run Coal-In Hours	Cumulative			Remarks
						Coal-In Hours	Total Hours	% Coal-In	
24	In	2/28/82	2400	-					
	Out	3/1/82	0600	6		6	6	100	Plugged barometric leg.
	In	3/1/82	0700	1		6	7	86	P-101/102 coal chunks plug
	Out	3/3/82	1900	60		66	67	99	impact.
	In	3/3/82	2300	4		66	71	93	
	Out	3/5/82	0700	32	98	98	103	95	Plug valves at P-102 failed.
25	In	3/8/82	1300	78		98	181	54	
	Out	3/10/82	0700	42	42	140	223	63	P-210 packing--replaced pump.
26	In	3/11/82	1100	28		140	251	56	
	Out	3/23/82	1400	291	291	431	542	80	Seal weld leak--L-1C8 bypass.
27	In	3/26/82	1200	70		431	612	70	
	Out	4/8/82	1600	316		747	928	80	Plugged screw feeder RV-101.
	In	4/9/82	1300	21		747	949	79	
	Out	4/9/82	1400	1	317	748	950	79	Plugged barometric leg.
28	In	4/10/82	1530	26		748	976	77	
	Out	4/11/82	0100	9	9	757	985	77	P-102 valve plug and crank- case failure.
29	In	4/15/82	0100	96		757	1,081	70	
	Out	4/19/82	1000	105	105	862	1,186	73	E-105 hole.
	Out	4/19/82	2400	14		862	1,200	72	Start turnaround.

TABLE B-6
ECLP OPERATING HISTROY
TEXAS LIGNITE COAL, BOTTOMS RECYCLE

Run	In/ Out	Date	Time	Hours	Run Coal-In Hours	Cumulative			Remarks
						Coal-In Hours	Total Hours	% Coal-In	
<u>Wyoming</u>									
30W	In	5/2/82	2200	-	218	218	218	100	Continuing--swung to lignite.
<u>Lignite</u>									
30L	In	5/12/82	0000	-		218	218	100	1.6/1.0/0.5 (5/14--1200).
	Out	5/22/82	1300	253	253	471	471	100	Cable failure to Substation 4.
31	In	5/31/82	1300	216		471	687	68	
	Out	5/31/82	2300	10		481	697	69	T-204 upset due D-108.
	In	6/1/82	1300	14		481	711	68	
	Out	6/3/82	0900	43	53	524	754	69	FE-1104 failure--E-102 plug.
32	In	6/4/82	1300	29		524	783	67	
	Out	6/6/82	0200	37	37	561	820	68	Liquefaction exotherm.
33	In	6/10/82	0200	96		561	916	61	1.6/1.0/0.5 (6/12--1700).
	Out	7/12/82	1400	780		1,341	1,696	79	Install screen--impact
	In	7/12/82	1700	3		1,341	1,699	79	Slurry drying.
	Out	7/18/82	1800	145	925	1,486	1,844	80	Explosion at CXI.
34	In	7/19/82	1700	23		1,486	1,867	80	1.2/1.0/0.4 (7/29--1000).
	Out	8/1/82	1400	309	309	1,795	2,176	82	Sandvik belt (C0-1901) failure aborted restart.
35	In	8/9/82	1000	188		1,795	2,364	76	
	Out	8/20/82	1200	266	266	2,061	2,630	78	THE END (PLANNED)
NOTE: Excluding Wyoming Portion						1,843	2,412	76	
TOTAL (EXCLUDING TURNAROUND)						10,692	14,518	74	
TOTAL						10,692	18,878	57	

APPENDIX C

ECLP Tabulated Yield Period Data

This Appendix provides tabulated yield test data for ECLP during bottoms recycle operation on Illinois coal, Wyoming coal (second run) and Texas lignite

TABLE C-1
ECLP Yield Test Data
Feed Coal Analyses

<u>Coal Type</u>	<u>Illinois Coal</u>	<u>Wyoming Coal</u>	<u>Texas Lignite</u>
Composition, wt% feed coal			
• Moisture***	1.77	4.70	7.10
• Ash	10.08	9.77	13.33
• Dry ash-free coal*	88.15	85.53	79.57
Elements of dry coal, wt%			
• Carbon	69.44	67.07	63.99
• Hydrogen	4.95	4.80	4.63
• Oxygen*	9.62	17.90	16.70
• Nitrogen	1.11	0.92	1.32
• Sulfur	4.95	0.76	1.71
• Ash**	9.93	8.55	11.65
Ash Elements, wt% ash			
• P ₂ O ₅	0.36	1.01	0.37
• SiO ₂	49.00	34.29	40.47
• Fe ₂ O ₃	20.47	7.79	7.40
• Al ₂ O ₃	16.91	16.41	11.15
• TiO ₂	1.00	1.11	1.19
• CaO	4.63	16.88	15.34
• MgO	0.95	4.33	3.98
• K ₂ O	2.12	0.55	0.32
• NaO	1.42	1.05	0.93
• SO ₃	3.14	16.57	18.85

All properties normalized

*By difference

**Does not include SO₃

***After drying in gas-swept mill

TABLE C-2
ECLP Yield Test Data
Vacuum Bottoms Analyses

<u>Coal Type</u>	<u>Illinois Coal</u>	<u>Wyoming Coal</u>	<u>Texas Lignite</u>
<u>Composition, wt% bottoms</u>			
• Ash	21.53	22.22	28.15
• Ash-free bottoms	78.47	77.78	71.85
<u>Elements of bottoms, wt%</u>			
• Carbon	68.55	68.99	63.21
• Hydrogen	4.15	3.94	3.73
• Oxygen [*]	2.61	4.97	5.05
• Nitrogen	1.20	0.89	1.28
• Sulfur	2.66	0.51	0.94
• Ash ^{**}	20.83	20.70	25.79
<u>Ash Elements, wt% ash</u>			
• P ₂ O ₅	0.43	1.03	0.41
• SiO ₂	47.99	41.68	46.98
• Fe ₂ O ₃	21.13	6.08	7.24
• Al ₂ O ₃	16.42	19.11	13.28
• TiO ₂	0.96	1.22	1.40
• CaO	5.50	17.68	16.43
• MgO	0.94	4.51	4.43
• K ₂ O	2.05	0.64	0.39
• NaO	1.31	1.18	1.06
• SO ₃	3.27	6.87	8.38
Viscosity @ 550°F, 21 sec ⁻¹ , poise	19.48	28.53	19.37
1000°F- content, wt% (by microlube distillation)	6.1	5.6	10.6

All properties normalized

*By difference

**Does not include any SO₃

TABLE C-3
ECLP Yield Test Data
Naphtha Analyses

<u>Coal Type</u>	<u>Illinois Coal</u>	<u>Wyoming Coal</u>	<u>Texas Lignite</u>
<u>Composition, wt%</u>			
● Carbon	85.40	85.34	84.93
● Hydrogen	12.70	12.65	12.97
● Oxygen*	1.55	1.81	1.79
● Nitrogen	0.13	0.15	0.18
● Sulfur	0.22	0.05	0.13
 <u>Specific gravity @ 60°F</u>			
	0.8217	0.8204	0.8050
 <u>Distillation**</u>			
IBP, °F	112	90	93
5 LV %, °F	168	150	148
10 LV %, °F	192	176	178
20 LV %, °F	224	214	214
30 LV %, °F	253	244	243
40 LV %, °F	279	273	267
50 LV %, °F	307	302	291
60 LV %, °F	330	328	314
70 LV %, °F	349	350	332
80 LV %, °F	371	373	354
90 LV %, °F	390	394	379
95 LV %, °F	407	413	395
FBP, °F	435	444	425

*By difference

**D-86 data corrected to a true boiling point basis

TABLE C-4

ECLP Yield Test Data

Solvent Analyses

<u>Coal Type</u>	<u>Illinois Coal</u>	<u>Wyoming Coal</u>	<u>Texas Lignite</u>
<u>Composition, wt%</u>			
• Carbon	89.36	89.72	89.05
• Hydrogen	9.59	9.62	10.22
• Oxygen*	0.62	0.47	0.57
• Nitrogen	0.24	0.19	0.16
• Sulfur	0.19	0.003	0.004
<u>Donor Hydrogen, wt%</u>	1.68xRV	1.72xRV	1.91xRV
<u>Specific gravity at 60°F</u>	0.9928	0.9807	0.9549
<u>Distillation**</u>			
IBP, °F	322	380	368
5 LV%, °F	415	438	418
10 LV%, °F	433	453	437
20 LV%, °F	462	479	461
30 LV%, °F	492	507	488
40 LV%, °F	531	538	509
50 LV%, °F	572	571	535
60 LV%, °F	616	613	576
70 LV%, °F	669	659	625
80 LV%, °F	731	712	699
90 LV%, °F	826	810	813
95 LV%, °F	897	872	909
FBP, °F	979	948	1002

*By Difference

**D-1160 data corrected to a true boiling point basis.

TABLE C-5

ECLP Yield Test Data

Sour Water Analyses

<u>Coal Type</u>	<u>Illinois Coal</u>		<u>Wyoming Coal</u>		<u>Texas Lignite</u>	
<u>Contaminants in water make*, ppm</u>	<u>LDU</u>	<u>SHU</u>	<u>LDU</u>	<u>SHU</u>	<u>LDU</u>	<u>SHU</u>
H ₂ S	8569	10105	4069	1817	5557	38675
NH ₃	3690	5178	2833	5081	2964	6275
CO ₂	5100	11700	18600	800	27900	6400
<u>Contaminants in other process water streams, ppm</u>						
H ₂ S	----		40		10	
NH ₃	----		--		41	
CO ₂	----		30		2100	
<u>Atmospheric Fractionator</u>						
● Reflux Drum						
H ₂ S	1254		90		250	
NH ₃	1326		56		1338	
CO ₂	200		20		2300	
● Distillate Drum						
H ₂ S	13000		5060		4700	
NH ₃	4114		2807		1569	
CO ₂	1300		7200		10400	
<u>Vacuum Fractionator</u>						
H ₂ S	595		290		180	
NH ₃	88		1808		68	
CO ₂	100		900		2000	
<u>Solvent Hydro Fractionator</u>						
● Reflux Drum						
H ₂ S	9680		----		----	
NH ₃	6358		----		----	
CO ₂	340		----		----	
● Distillate Drum						
H ₂ S	11400		1930		6890	
NH ₃	7290		2871		3554	
CO ₂	400		200		3800	

*High-pressure cold separators

TABLE C-6

ECLP Yield Test Data

Coal Type	Feed/Product Rates					
	1/28/82 Illinois Coal		3/22/82 Wyoming Coal		6/23/82 Texas Lignite	
Feed Rates, lb/hr	Raw ⁺	DRS ⁺⁺	Raw ⁺	DRS ⁺⁺	Raw ⁺	DRS ⁺⁺
• Coal ^{***}	12517	11882	11185	11710	13034	12745
• Make up hydrogen gas	1172	1248	787	717	752	762
TOTAL	13689	13130	11972	12427	13786	13507
Product Rates, lb/hr						
• Purge Gas						
- LDU	UNM	790	538	523	733	664
- SHU	206	299	67	67	124	117
• Fuel Gas						
- LDU	1287	1339	1206	1260	1496	1515
- SHU	182	184	100	96	151	151
• Acid Gas [*]	269	263	506	452	457	441
• Sour Water ^{**}						
- LDU	1098	1308	1616	1830	1924	2193
- SHU	UNM	279	UNM	344	UNM	230
• Naphtha	2030	2043	2292	2376	1683	2014
• Solvent	950	1148	973	1094	833	1031
• Bottoms	5904	5607	4599	4744	5750	5491
• Process Drum Level Changes	~(130)	(130)	(368)	(368)	~(340)	(340)
TOTAL	~12945	13130	11873	12427	13041	13507
Balance Closure (Products/Feed) x 100	94.6	100.0	99.2	100.0	94.6	100.0

⁺As measured rates⁺⁺As corrected by the Data Reconciliation System computer program^{*}That fraction of the acid gas which was dissolved in water, assumed to be 58%^{**}Process Water rates discounted^{***}As received from the Gas-Swept Mill Drier.

UNM = Unmeasured. DRS values used in summing totals in Raw column.

TABLE C-7

ECLP Yield Test Data

Operating Conditions and Yields

<u>Coal Type</u>	<u>Illinois Coal</u>	<u>Wyoming Coal</u>	<u>Texas Lignite</u>
<u>LDU Operating Conditions</u>			
Average Liquefaction Temperature, °F	846	855	845
Pressure, psig	2520	2493	2512
Nominal Residence time, minutes	81	85	88
Treat Gas			
• Rate, KSCFD	3277	3897	3463
• H ₂ purity, mole %	80	86	84
Solvent-to-Coal Ratio	1.6	2.0	1.55
Bottoms-to-Coal Ratio	0.6	0.5	0.5
Solvent Quality Index	3.41	4.37	3.75
<u>SHU Operating Conditions</u>			
EIT**, °F	112+RV	93+RV	99+RV
Pressure, psig	1845	1798	1827
Weight Hourly Space Velocity, hour ⁻¹	1.66xRV	1.96xRV	1.58xRV
Treat gas			
• Rate, SCF of H ₂ /Bbl of feed solvent	0.77xRV	0.74xRV	0.85xRV
• Gas purity, mole % H ₂	81	98	93
<u>Yields, wt % DAF Coal*</u>	<u>1/28/82</u>	<u>3/22/82</u>	<u>6/23/82</u>
H ₂	-4.8	-4.9	-4.5
H ₂ O	10.1	12.9	12.0
H ₂ S	4.3	0.6	1.5
NH ₃	0.5	0.6	0.8
CO	0.3	0.6	0.9
CO ₂	1.3	5.1	5.9
CH ₄	4.0	4.0	4.1
C ₂	3.2	3.5	3.3
C ₃	3.8	2.9	2.9
C ₄	1.6	1.5	1.5
C ₅ /400 °F	21.7	23.5	22.4
400/700 °F	8.8	10.3	7.9
700/1000 °F	6.0	5.4	7.5
1000 °F+	39.2	34.0	33.8
Naphtha	22.2	24.8	22.7
Solvent	10.3	11.1	9.2

*Does not include SO₃

**Equivalent Isothermal Temperature

LIST OF ABBREVIATIONS

API	American Petroleum Institute
APS	Atmospheric Pipe Still
ART	Actual (Slurry) Residence Time
ASTM	American Society for Testing and Materials
BARD	Baytown Research and Development Division (Baytown, TX)
B/CD	Barrels per Calendar Day
B/SD	Barrels Per Stream Day
BTX	Benzene Toluene Xylenes
CCLU	Continuous Coking Liquefaction Unit
C-E	Combustion Engineering, Inc.
CLPP	Coal Liquefaction Pilot Plant (One Ton Per Day Unit)
Co/Mo	Cobalt/Molybdenum
COD	Chemical Oxygen Demand
COT	Coal Outlet Temperature
CSCU	Continuous Stirred Coking Unit
DAF	Dry, Ash-Free
DBM	Design Basis Memorandum
DC	Direct Combustion
DCF	Discounted Cash Flow
DEA	Diethanolamine
DMMF	Dry Mineral Matter-Free
DOE	Department of Energy
DRS	Data Reconciliation System
DSC	Differential Scanning Calorimetry
ECLP	EDS Coal Liquefaction Pilot Plant (250 Tons Per Day)

LIST OF ABBREVIATIONS (Continued)

EDS-FPU	EDS - FLEXICOKING Prototype-Unit
EEPM	Exxon Engineering Project Management
EETD	Exxon Engineering Technology Department (Florham Park, NJ)
EOR	End-of-Run
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ERDL	Exxon Research and Development Laboratories (Baton Rouge, LA)
ER&E	Exxon Research and Engineering Company
FBG	Fluid Bed Gasifier
FBU	Fluidized Bed Unit
FCBU	Fluid Coker Bogging Unit
FSBF	Full Scale Burner Facility
FTIR	Fourier Transform Infra Red
GC	Gas Chromatography
GPM	Gallons Per Minute
GSM	Gas Swept Mill
HB	Hybrid Boiler
HBG	High Btu Gas
HCO	Hydrogenated Cresote Oil
HVGO	Heavy Vacuum Gas Oil
IBG	Intermediate Btu Gas
IKG	Integrated Coking/Casification Pilot Plant
k	Thousand
LBG	Low Btu Gas
LDU	Liquefaction/Distillation Unit

LIST OF ABBREVIATIONS (Continued)

LHV	Lower Heating Value
LP	Linear Program
LPG	Liquefied Petroleum Gas
LSCU	Large Stirred Coker Unit
LSFO	Low Sulfur Fuel Oil
M	Million
MBG	Moving-Bed Coal Gasification
MPSS	Multi-Pass Spent Solvent
NDIR	Non-Dispersive Infrared
NDT	Non-Destructive Testing
Ni/Mo	Nickel Molybdenum
NPSH	Net Positive Suction Head
NRT	Nominal Residence Time
OTCLU	Once-Through Coal Liquefaction Unit
PACT	Powered Activated Carbon Treatment
PAM	Process Alternatives LP Model
PDA	Process Development Allowance
P&ID	Piping and Instrument Diagram
PNA	Polynuclear Aromatics
POX	Partial Oxidation
PRD	Product Research Division (Linden, NJ)
psig	pounds per square inch, gauge
RCLU-1	Recycle Coal Liquefaction Unit with Nominal Coal Feed Rates of 75 Pounds-Per-Day

LIST OF ABBREVIATIONS (Continued)

RCLU-2	Recycle Coal Liquefaction Unit with Nominal Coal Feed Rates of 75 Pounds-Per-Day
RCO	Raw Creosote Oil
RISP	Required Initial Selling Price
RV	Reference Value - Code to prevent disclosure of non-program data.
SASS	Source Assessment Sampling System
S/C	Solvent/Coal
S/C/B	Solvent/Coal/Bottoms
SCF	Standard Cubic Feet
SDU	Study Design Update
SEM	Scanning Electron Microscope
SFEU	Solid Fuels Evaluation Unit
SFU	Small Fluidized Bed Unit (for coke gasification)
SHU	Solvent Hydrogenation Unit
SOR	Start-of-Run
SQI	Solvent Quality Index
TDS	Total Dissolved Solids
T/D	Tons Per Day
TEC	Total Erected Cost
TGA	Thermal Gravimetric Analysis
TIR	Temperature Increase Required
TMA	Thermomechanical Analysis
TOC	Total Organic Carbon
T/SD	Tons Per Stream Day
UOP, Inc	Union Oil Products, Inc.

LIST OF ABBREVIATIONS (Continued)

VB	Vacuum Bottoms
VGO	Vacuum Gas Oil
VLE	Vapor Liquid Equilibrium
VPS	Vacuum Pipe Still
V/Hr/V	Volumetric Hourly Space Velocity, ft^3 feed per hour per ft^3 of reactor volume.
WWT	Wastewater Treatment
YP	Yield Period