EDS COAL LIQUEFACTION PROCESS DEVELOPMENT: PHASE V. FINAL TECHNICAL PROGRESS REPORT, VOLUME I

EXXON RESEARCH AND ENGINEERING CO.
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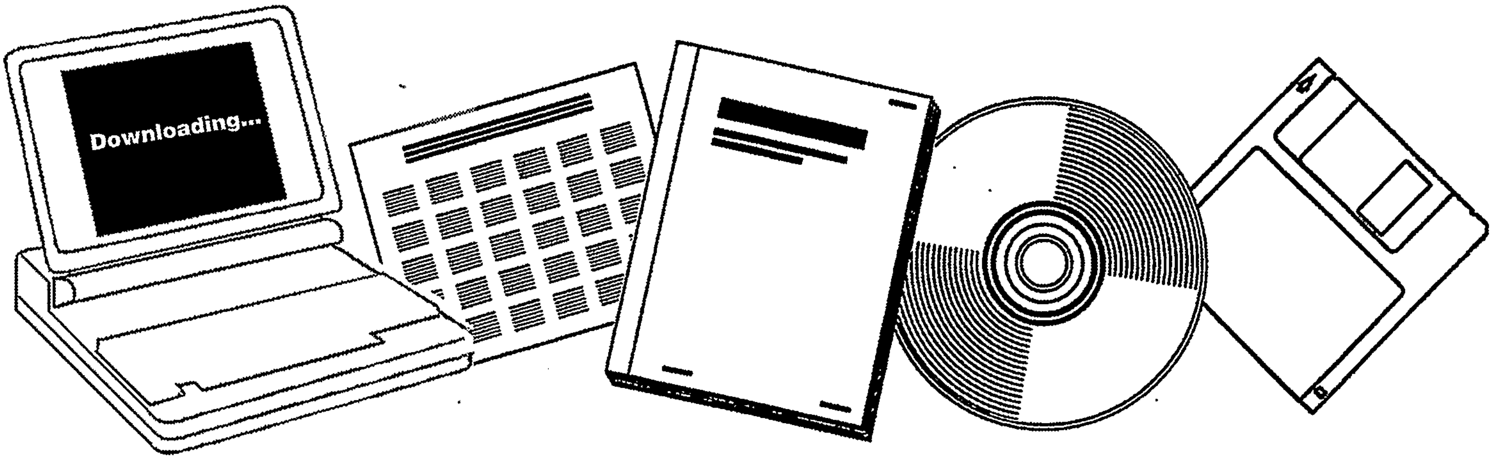

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EDS COAL LIQUEFACTION PROCESS DEVELOPMENT

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

A Project Jointly Sponsored By
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
ENI

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 hytdrotreating. 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 physcial 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. COSTRUCTION

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 RLCUs. 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 Wandoan 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

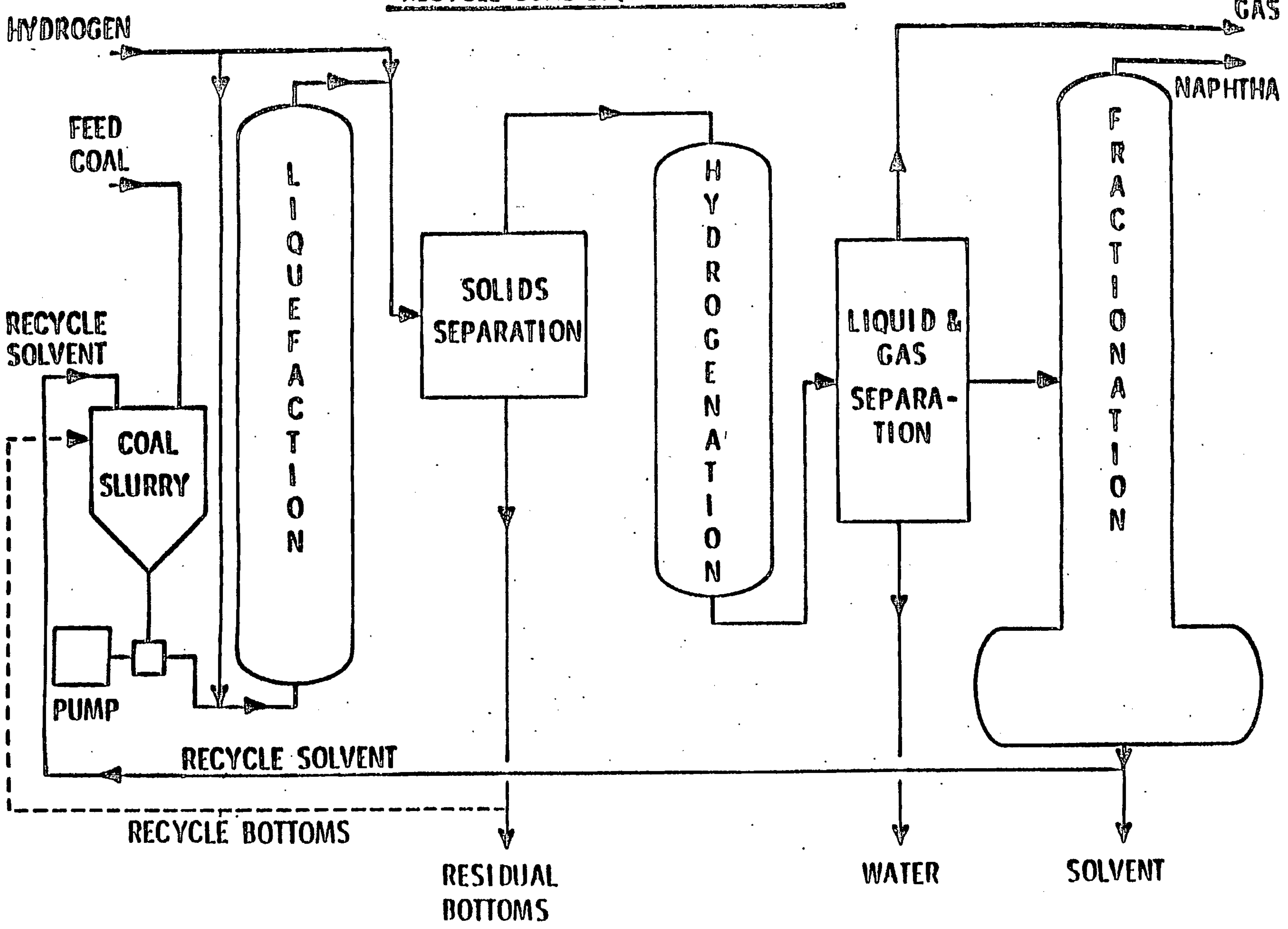


Table 1-1

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	RCLU 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. • Liquid yield improvements of up to 14 wt % DAF coal were noted with once-through bottoms. • Second pass bottoms yielded lower gains in conversion and liquid yield than once-through bottoms.
				1	CV	555-556	
				1	CW	557-558	
				1	CX	559-560	
				1	CW	561-563	
				1	CY	567-568	
				1	C	564-566	
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 RCLU results. • RCLU screening of CLPP coal and bottoms showed no quality problems. • CLPP bottoms recycle contacting facilities were modified to provide better contact beteen solvent and bottoms.
				1	CV	678-680	
				1	CW	699-701	
				1	V	675-677	
				1	V	681-682	
				1	EC	697-698	
2nd	1980	FE-2893-53	Illinois (Monterey mine) coal bottoms recycle studies	1	EI	733-736	• Continuous bottoms recycle on RCLU continued to exhibit increased yields, economic incentive defined. • High pressure bottoms recycle operations improved yield structure.
				1	EJ	737-743	
				1	EK	744-746	
				2	EN	106-110	
				2	EO	111-114	
3rd	1980	FE-2893-57	Illinois (Monterey) coal bottoms recycle studies	2	EW	134-139	• Studies at high pressure, high bottoms-to-coal ratio provide understanding of bottoms composition relative to conversion. • Continued process variables studies define economically preferred conditions.
				2	EX	140-144	
				2	EY	145-149	
				2	FA	150-156	
				2	FC	157-161	
4th	1980	FE-2893-64	Illinois (Monterey) coal bottoms recycle studies	2	FH	169-172	• Lowering solvent-to-solids ratio had little effect on total liquid yield. Shifts product slate toward heavier liquids. • High pressure coal-only experiments define the effect of pressure on coal conversion.
				2	FJ	173-176	
				2	FD	162-165	
				2	FE	166-168	
3rd	1981	FE-2893-78	ECLP support studies ECLP support for HVGO feed	1	GM	863-866	• ECLP support studies indicated conversion was lower than RCLU data base for SQI <3.5. • Experiments demonstrated that solvent composition was a function of both liquefaction and hydrotreater conditions.
				1	GK	860-862	
				1	GN	868-869	
				1	GH	852-854	
				1	GK	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	GI	855-858	
				1	GW	898	
				1	GX	899-901	
				1	GV	893-897	
				1	GY	902-904	
				1	GZ	905-909	
				1	HB	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
1st	1979	FE-2893-29	Burning Star coal screening study	1	DA	580-583	• 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	• 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	• 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 1-1 (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	
				1	DV	655-657	
				1	CG	658-660	• Unlike Monterey coal, total liquid yields increased monotonically with increasing residence time.
				1	DW	661-663	
				1	CH	664-667	
				1	CL	668-671	
				1	DX	672	
				1	CK	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 750-2500 psig.
				1	EA	693-695	
				1	EB	696,702-704	
				1	ED	705-707	• 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	EE	708-710	
				1	EF	711-713	
				1	EF	714-717	
				1	EF	718-719	• Significant increases in conversion and yields similar to the effects previously demonstrated for Monterey and Wyodak coals were noted over the range of SQI 2 to 4.
				1	CL	720-721	
1st	1980	FE-2893-49	Pittsburgh No. 8 coal process variable studies	1	EG	722-726	• Continuous bottoms recycle greatly improved conversion and liquid yields at high pressure compared to coal-only operations.
				1	CL	727-729	
				1	EH	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	
				1	JR	1057-1059	• Hydrodynamic studies established the effect of gas velocity on gas phase holdup.
				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 MINE) 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	SR	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 Liquefaction temperature effect on Wyoming coal yields	1	ST	442-447	• Wyoming coal liquid yields at 840°F increases continually with increasing residence time. • 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.
				1	SU	448-451	
				1	SV	452-455	
1st	1978	FE-2893-12	Wyoming coal solvent quality Wyoming coal hydrogen treat rate study Sulfur dioxide pretreatment of Wyoming coal	1	SH	456-459	• With coal-only operations, conversion and liquid yield are independent of solvent quality above an SQI of 4.0. • Reducing hydrogen treat rate from 4 wt % on dry coal to 2 wt % has no significant effect on products. • Sulfur dioxide pretreatment of Wyodak coal was unsuccessful in reducing reactor solids accumulation.
				1	SH	460-463	
				1	SH	464-467	
				1	SH	468-472	
				1	SX	473-476	
				1	SZ	477-480	
				1	SU	481-484	
				1	SZ	485-488	
				2	BY	79-82	
				2	CC	85-88	
				2	CA	83,89-90	
				2	CB	84	
				2	BT	91-93	
2nd	1978	FE-2893-17	Wyoming coal process variable study	1	CF	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 times and low temperatures (120 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	SU	575-579	
2nd	1979	FE-2893-35	Liquefaction bottoms recycle studies	1	DH	603-605	• Simulated bottoms recycle experiment indicated increased conversion and liquid yields with subbituminous Wyodak coal. • More solvent required for Wyodak bottoms to convert to lighter liquids than required for Illinois Monterey bottoms.
				1	DI	610-613	
				1	DJ	617-620	
				1	DL	621-624	
				1	SU	606-608	
				1	SS	609	
				1	SS	614-616	
				1	DK	621-622	
3rd	1980	FE-2893-57	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. • Conversion and liquid yields were increased significantly with the use of bottoms recycle. • Higher solvent-to-coal ratio had litle effect on conversions. Higher pressure accounted for approximately 5 wt % DAF increase in conversion.
				1	EQ	759-764	
				1	EU	770-772	
				1	EZ	773-777	
				1	EH	754-758	
				1	ES	765-769	
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	FH	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 SQI range of 3-8.
				2	FX	211-215	
				2	FZ	216-219	
				2	GC	220-222	
				2	FU	245-249	
				2	GU	250-254	
				2	GC	255-260	
				2	FX	261-263	
				1	FX	845-848	
				1	CF	849-851	
4th	1981	FE-2893-83	ECLP support studies for Wyodak bottoms recycle operations	2	HF	278-282	• Gas Swept Mill processing of Wyodak coal reduced liquefaction conversion 4 wt % DAF. • Hydrodynamic tests showed that ECLP actual liquid residence time was approximately 55% that of RCLU.
				2	HH	283-288	
				2	HJ	289-290	
				1	HV	965-968	
				1	HX	969-972	
				1	HZ	975-976	
				1	IB	973-974	

Table 1-1 (Continued)

SUMMARY OF AUSTRALIAN (WANDOAN MINE) STUDIES

Coal: Australian
Rank: Subbituminous
Mine: Wandoan

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	• Liquid yield at 840°F peaked at a relatively short residence time of 40 minutes with Wandoan coal in the once-through mode.
				1	DN	629-631	
				1	DO	632-634	
				1	DP	635-637	• Solvent balance problems were encountered at high severity temperature-residence time combinations such as 840°F/100 minutes and 880°F/25 minutes.
				1	DQ	638-640	
				1	DR	641-642	
				1	DS	643-647	
							• Unit operability was comparable to other subbituminous coals such as Wyodak.
1st	1981	FE-2893-70	Wandoan coal studies	2	FN	184-188	• Bottoms recycle resulted in increased total liquid yields of up to 9 wt % on a DAF coal basis.
				2	FP	189-193	
				2	FR	198-201	
				2	FS	202-205	• High pressure studies showed improved unit operability due to lower bottoms viscosities.
				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	DCLU No.	Series Designation	Yield Periods Reported	Results
3rd	1978	FE-2893-21	Texas lignite study	1	CP	532-536	• 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	FE	778-784	• Increases in C_4-1000°F liquid yields of 10 wt % (DAF coal basis) were obtained with bottoms recycle operations as compared to once-through operations. • An DQI 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	FG	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	RCLU No.	Series Designation	Yield Periods Reported	Results
1st	1982	FE-2893-89	Texas lignite (Martin Lake mine) bottoms recycle studies	1	IF	979-982	• 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.
				1	IH	983-986	
				1	II	987-990	
				1	IJ	991-994	• High bottoms ash content resulted in high viscosities.
				1	IE	995-996	
3rd	1982	FE-2893-99	Martin Lake lignite screening study	1	IK	997-998	• Experiments demonstrated that changes in hydrogen pressure over the range of 1500-2500 psig had an insignificant effect on conversion with Martin Lake.
				1	IK	1012-1014	
				1	JD	1015-1018	
				1	JF	1019-1022	• 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 % DAF).
				1	JG	1023-1027	
				1	JI	1028-1032	
				1	JJ	1033-1037	• Solvent quality experiments showed that Martin Lake was insensitive to SQI in the range of SQI from 2.8 to 4.8.
				1	JL	1038-1040	
				1	JM	1041-1044	
				1	JN	1045-1047	• Lower ash feed coal resulted in lower viscosity bottoms.

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 C_4-1000°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.

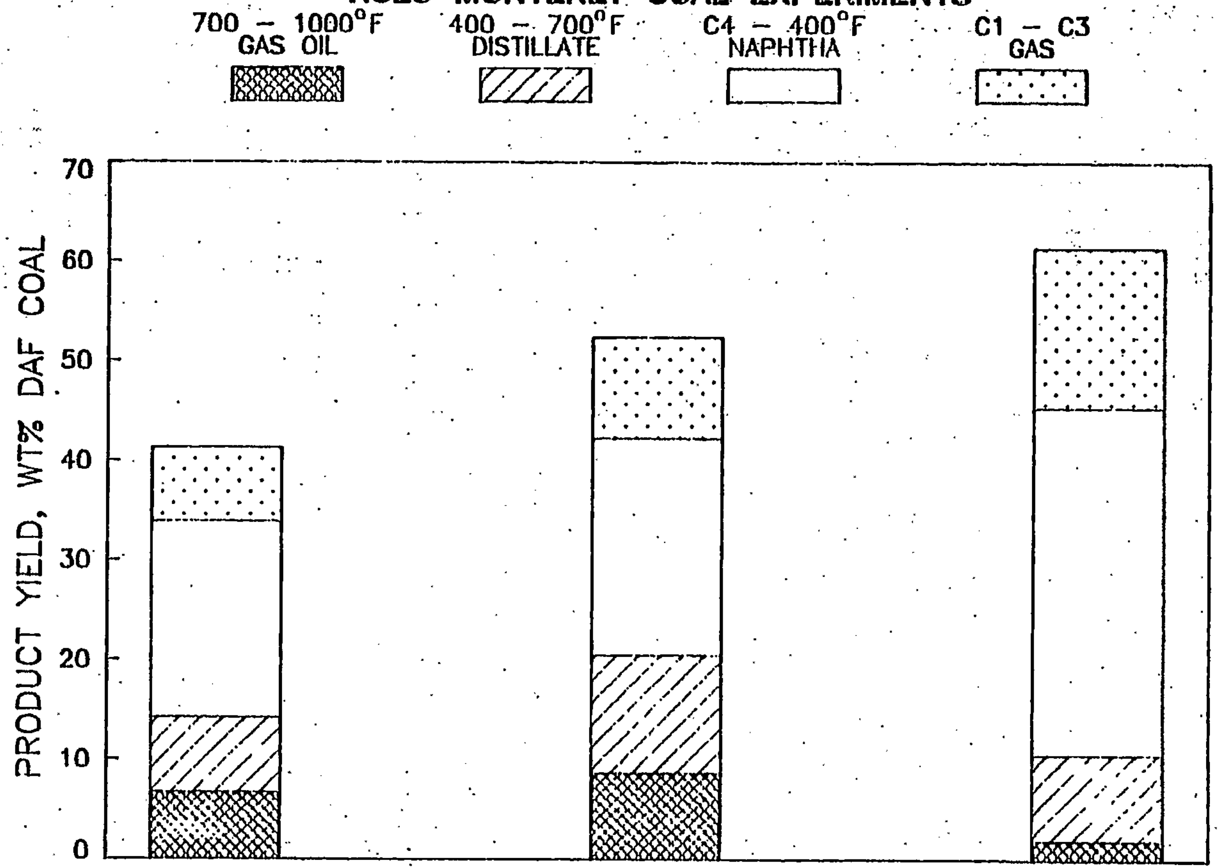
Continuous bottoms recycle operations with Monterey No. 1 coal were concluded in RCLU during the second quarter of 1980. The final experiment examined the effect of low solvent-to-solids ration (1.2/1/0.5 solvent-to-coal-to-bottoms proportions). The primary result of the lower solvent-to-solids ratio 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



DAF CONVERSION	53	64	72
LIQUEFACTION CONDITIONS			
TEMPERATURE,°F	840	800	840
H2 PRESSURE, PSIG	1500	2000	2000
NRT, MINUTES	40	100	60
S/C/B, BY WT.	1.6/1/0	1.2/1/0.5	2.5/1/1
H2 TREAT, WT% ON COAL	4	6	6
RCLU NO.	1	2	2
YIELD PERIODS	863–866	173–176	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 C_4-1000°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, C_4-1000°F total liquid yield decreased due to increased product cracking to C_1-C_3 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

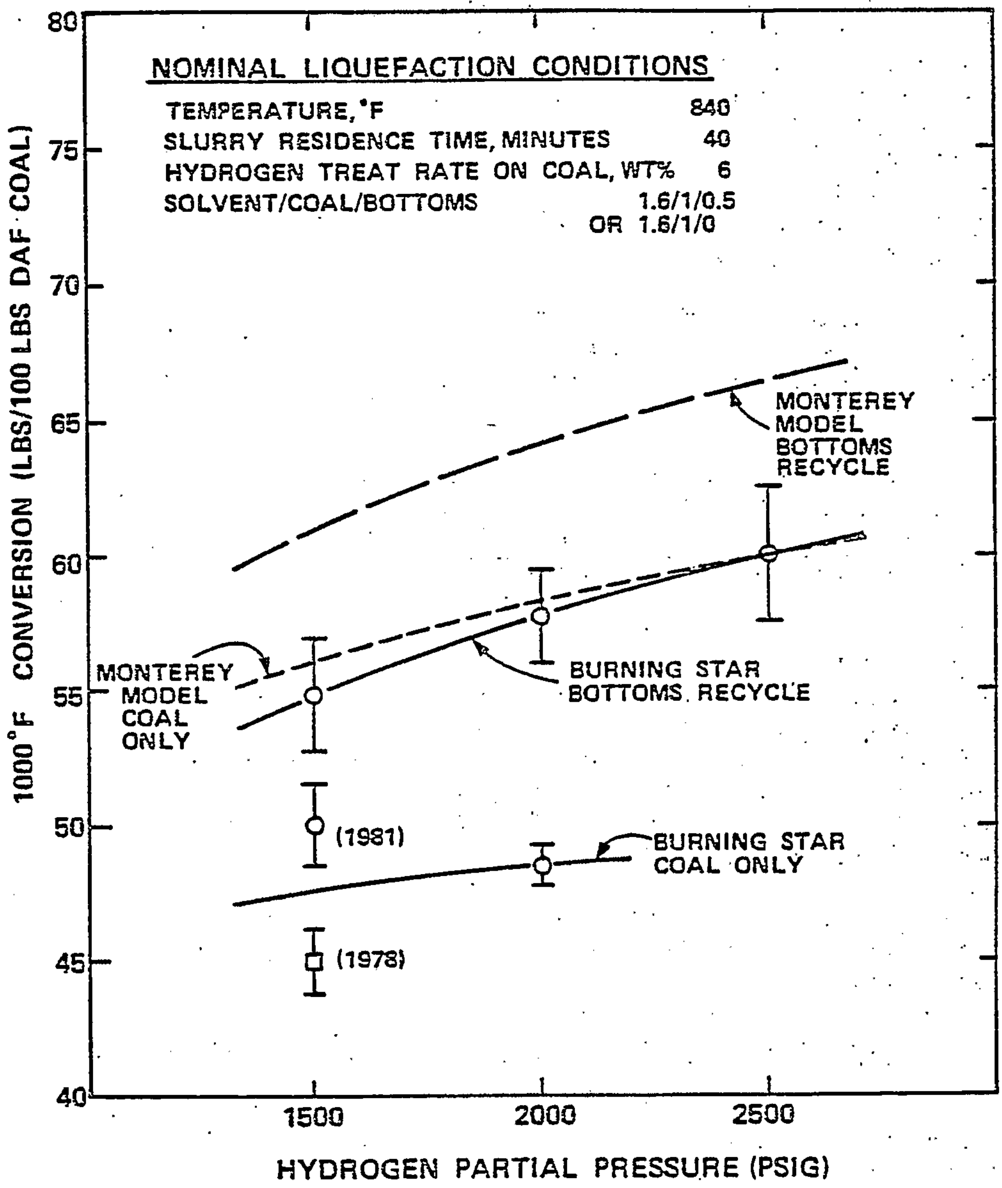
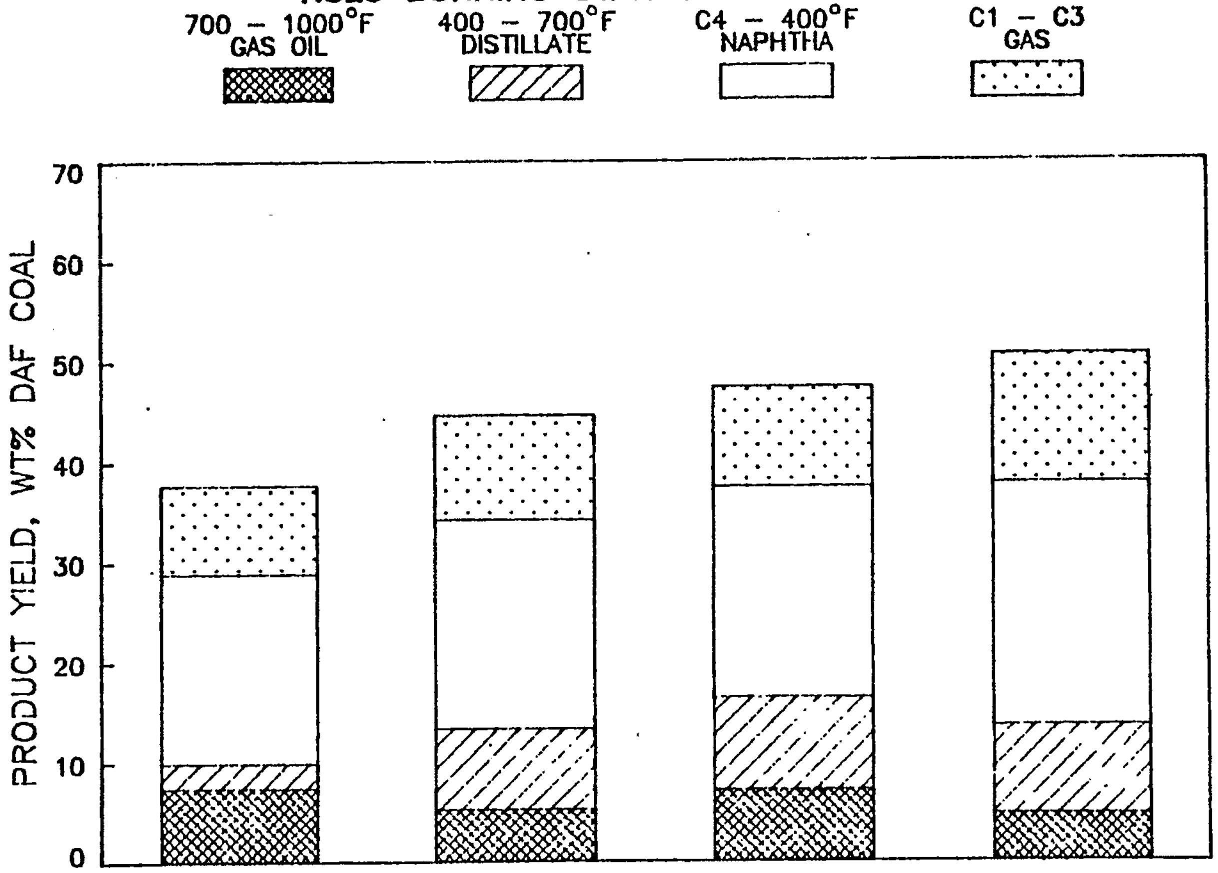


FIGURE 1-4
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED RCLU BURNING STAR COAL EXPERIMENTS



DAF CONVERSION	48	55	58	60
LIQUEFACTION CONDITIONS				
TEMPERATURE, °F	840	840	840	840
H2 PRESSURE, PSIG	1500	1500	2000	2000
NRT, MINUTES	40	40	40	40
S/C/B, BY WT.	1.6/1/0	1.6/1/0.5	1.6/1/0.5	1.6/1/1
H2 TREAT, WT% ON COAL	4	6	6	6
RCLU NO.	1	1	1	1
YIELD PERIODS	580–583;931–935	946–950	936–940	951–955

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 C_1-C_3 gas make and hydrogen consumption, were similar to trends previously observed for Monterey coal.

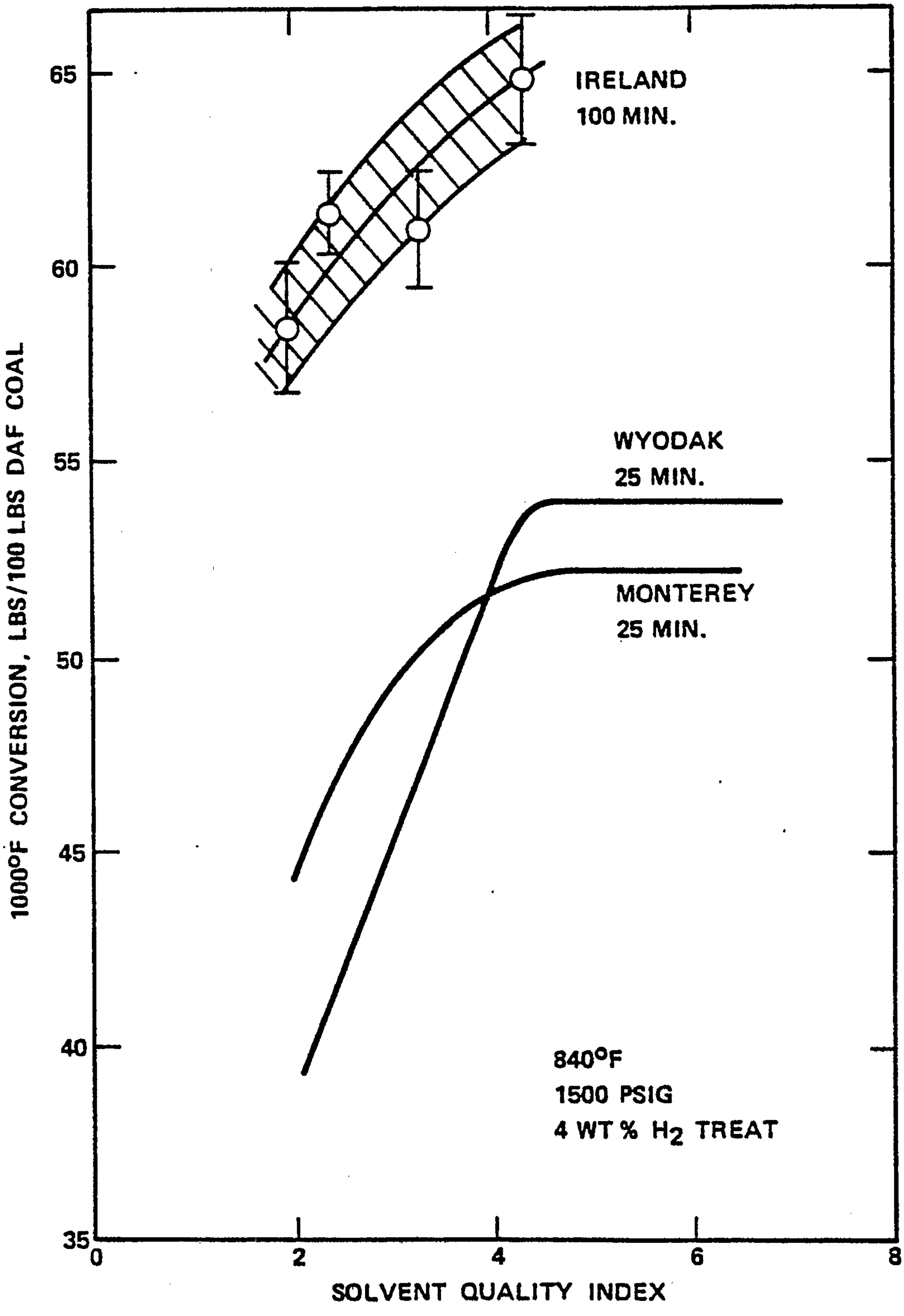
Studies in the final quarter of 1979 thoroughly examined the effects of liquefaction pressure (750, 1000, 1500 and 2500 psig), hydrogen treat rate (2, 4 and 6 wt% on coal), and solvent quality index (1.9, 2.4, 3.3, and 4.3 SQI). Variations in hydrogen pressure were found to have significant effects on 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 C_4-1000°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 C_1-C_3 gas, C_4-1000°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 (C_4-400°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% H_2 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 (C_1-C_3), naphtha (C_4-400°F), total liquid (C_4-1000°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 C_1-1000°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

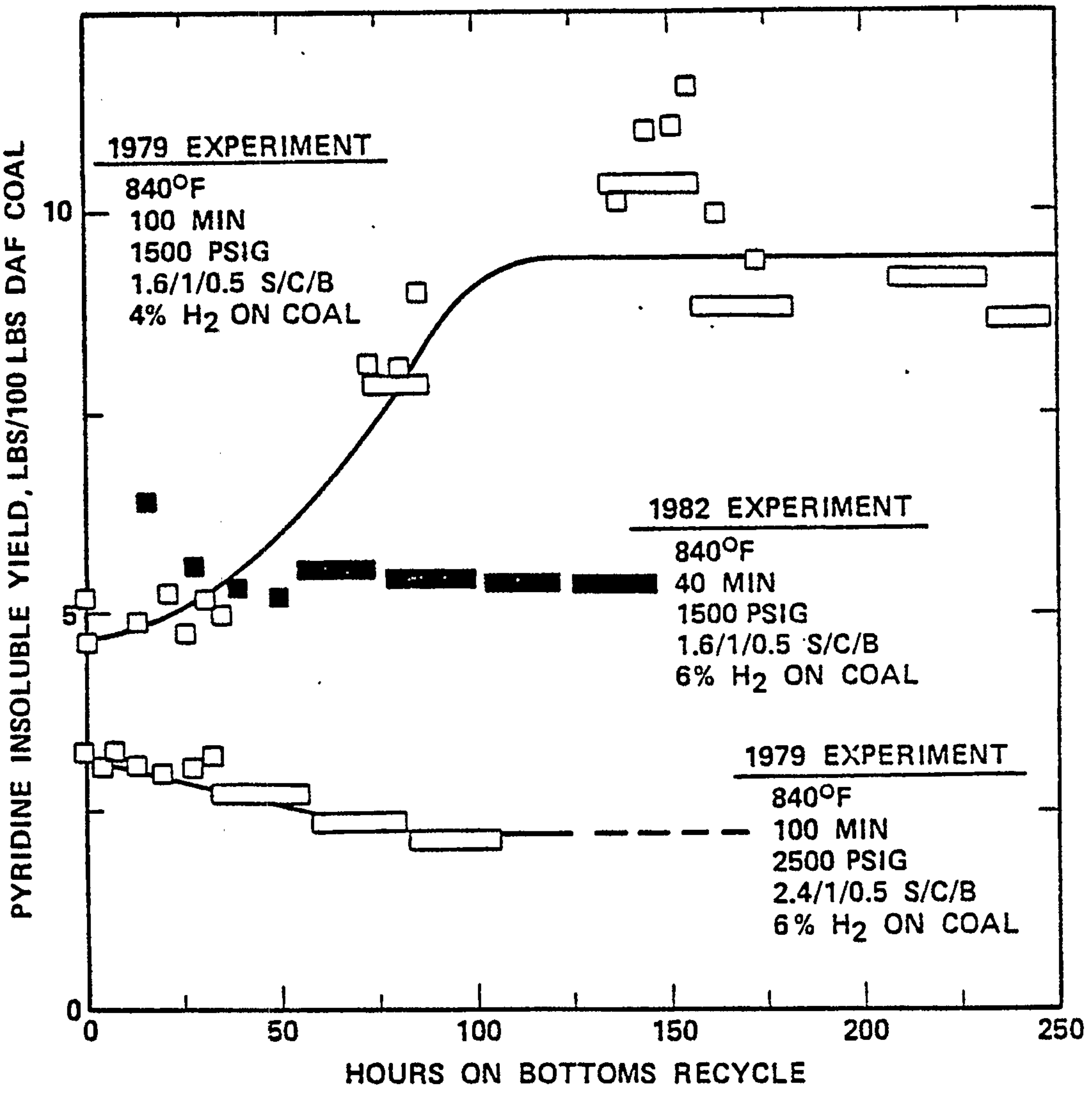
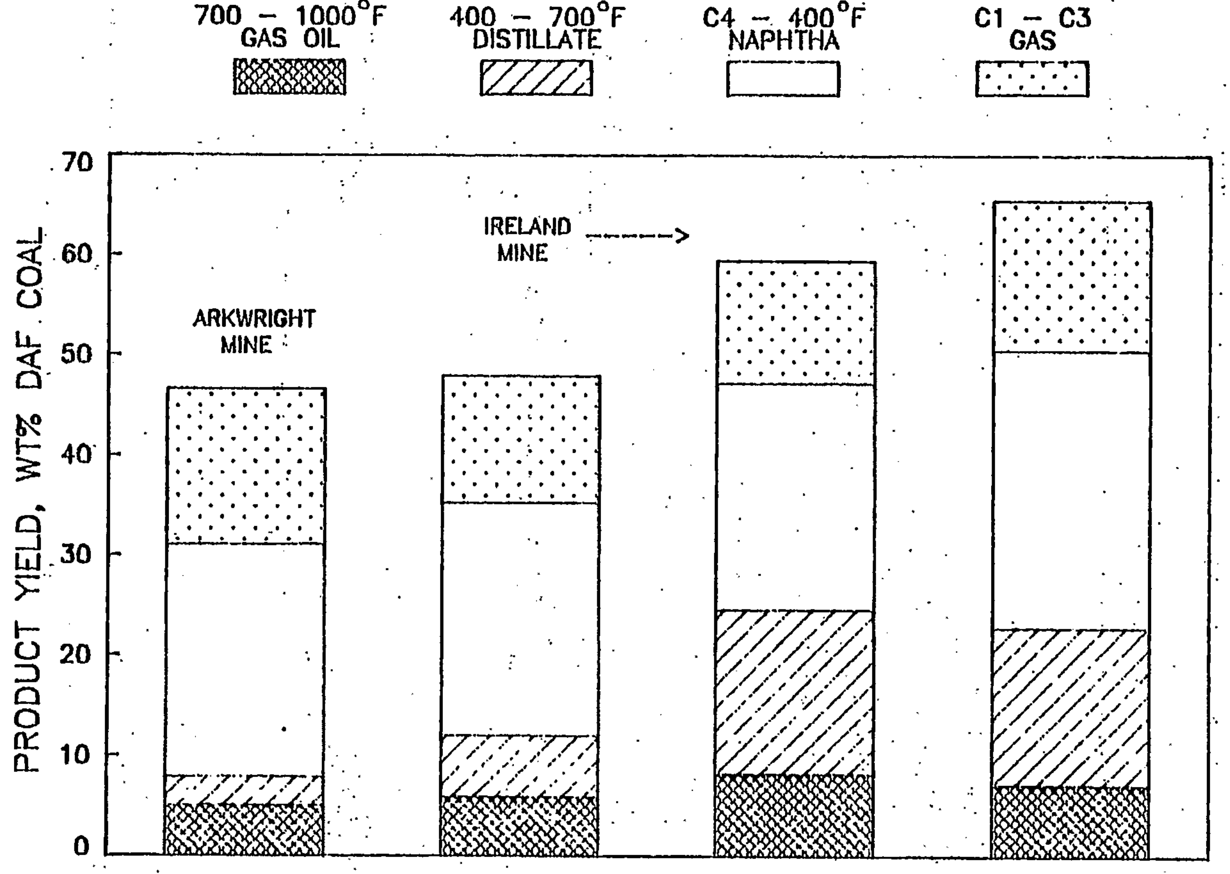


FIGURE 1—7
HYDROCARBON YIELD DISTRIBUTIONS FOR SELECTED RCLU IRELAND AND ARKWRIGHT EXPERIMENTS



DAF CONVERSION	50	55	66	72
LIQUEFACTION CONDITIONS				
TEMPERATURE, °F	840	840	840	840
H2 PRESSURE, PSIG	1500	1500	2000	2000
NRT, MINUTES	60	60	60	60
S/C/B, BY WT.	1.6/1	1.6/1	1.2/1/0.5	1.2/1/1
H2 TREAT, WT% ON COAL	4	4	6	6
RCLU NO.	1	1	1	1
YIELD PERIODS	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, C_4-1000°F liquid yield for Wyodak coal was lower than for Illinois coal at equivalent conditions. However, C_4-1000°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% H_2 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 ligher 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 C_1-C_3 hydrocarbon gas and C_4-400°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% H_2 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.

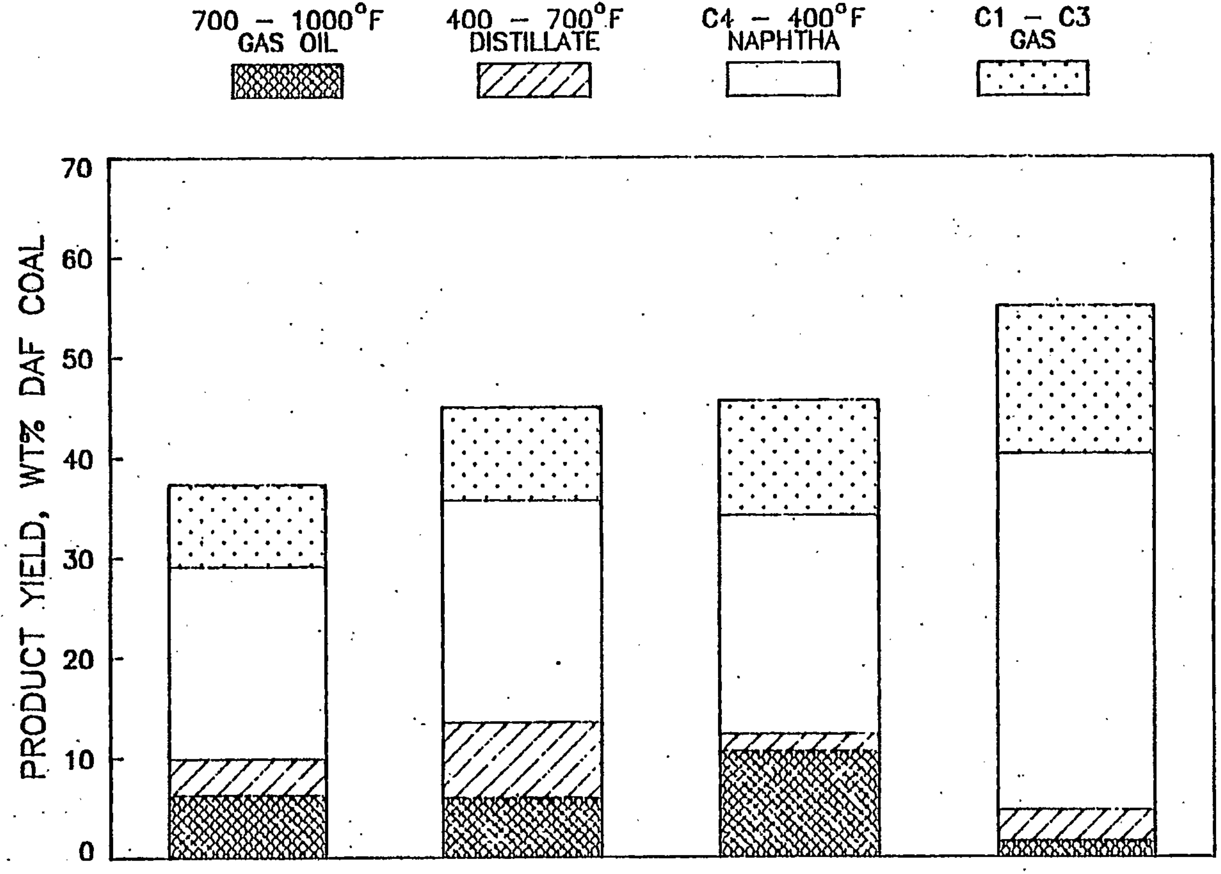
Figure 1-8 shows hydrocarbon yield distributions for selected Wyodak coal experiments illustrating the effect of key process variables on product distributions.

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



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.

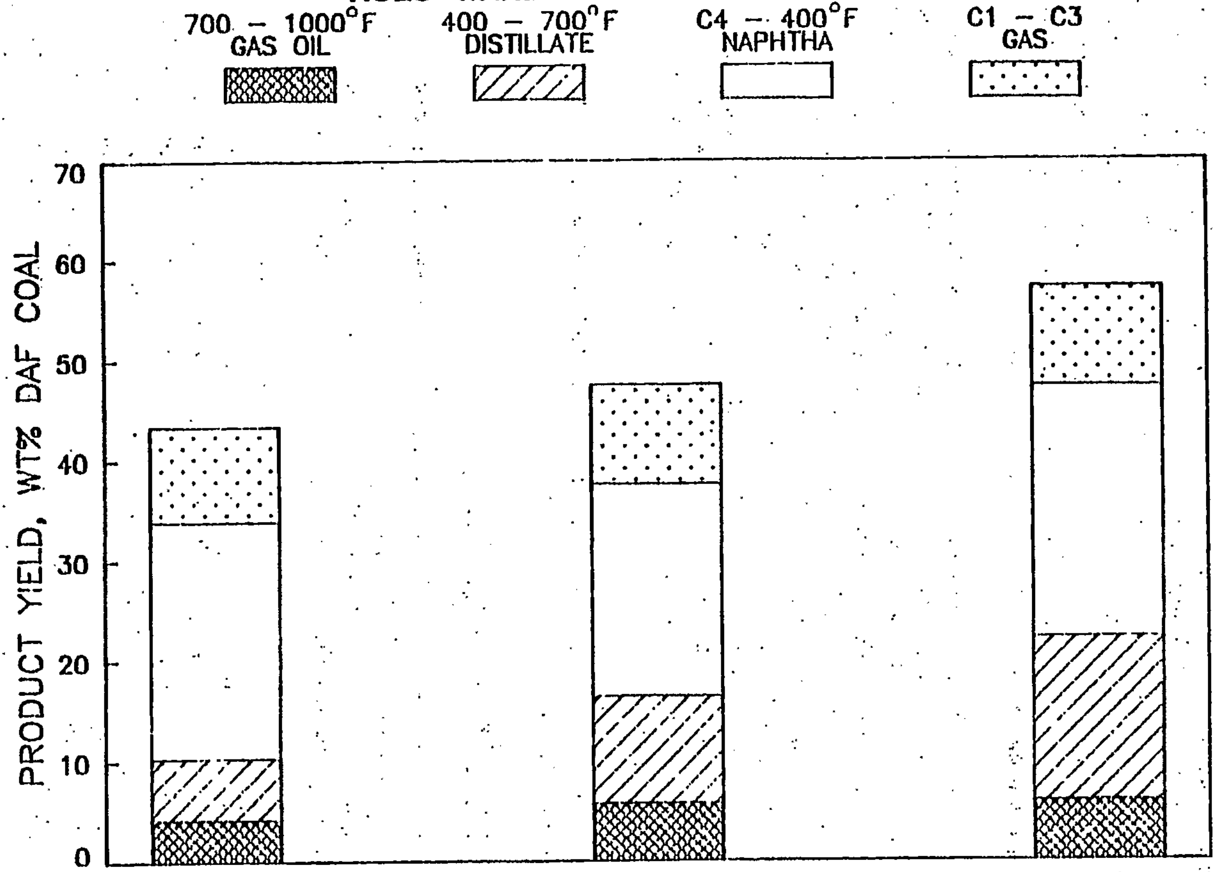
Figure 1-9 compares hydrocarbon yield distributions for related Wandoan coal experiments.

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 C_4-1000°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 C_1-C_3 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	57	60	68
LIQUEFACTION CONDITIONS			
TEMPERATURE, °F	840	840	800
H2 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
H2 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°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.

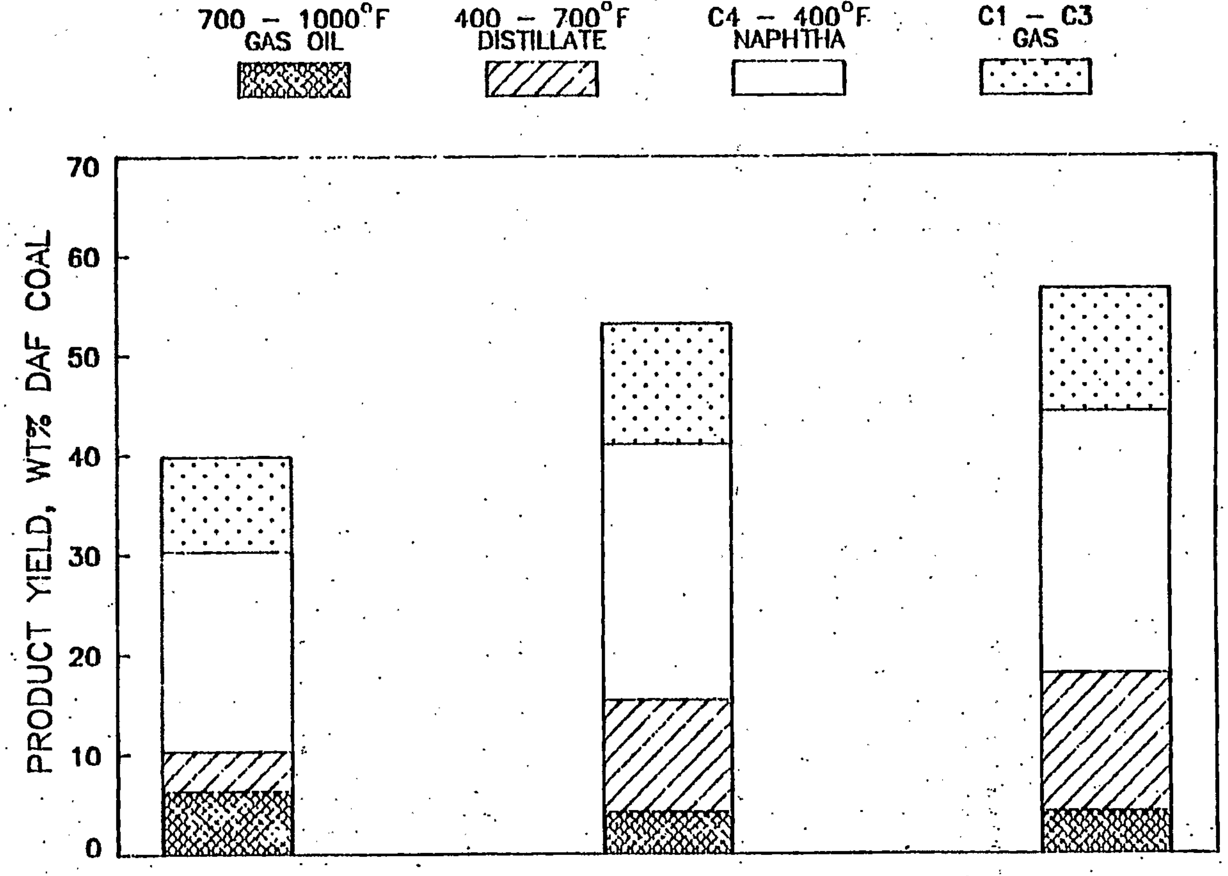
1.2.8 Texas Lignite (Martin Lake Mine)

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



DAF CONVERSION	59	71	75
LIQUEFACTION CONDITIONS			
TEMPERATURE, °F	840	840	840
H2 PRESSURE, PSIG	1500	2000	2000
NRT, MINUTES	40	40	40
S/C/B, BY WT.	1.6/1/0	1.35/1/0.5	1.6/1/1
H2 TREAT, WT% ON COAL	4	6	6
RCLU NO.	1	1	1
YIELD PERIODS	532–536	816–820	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.

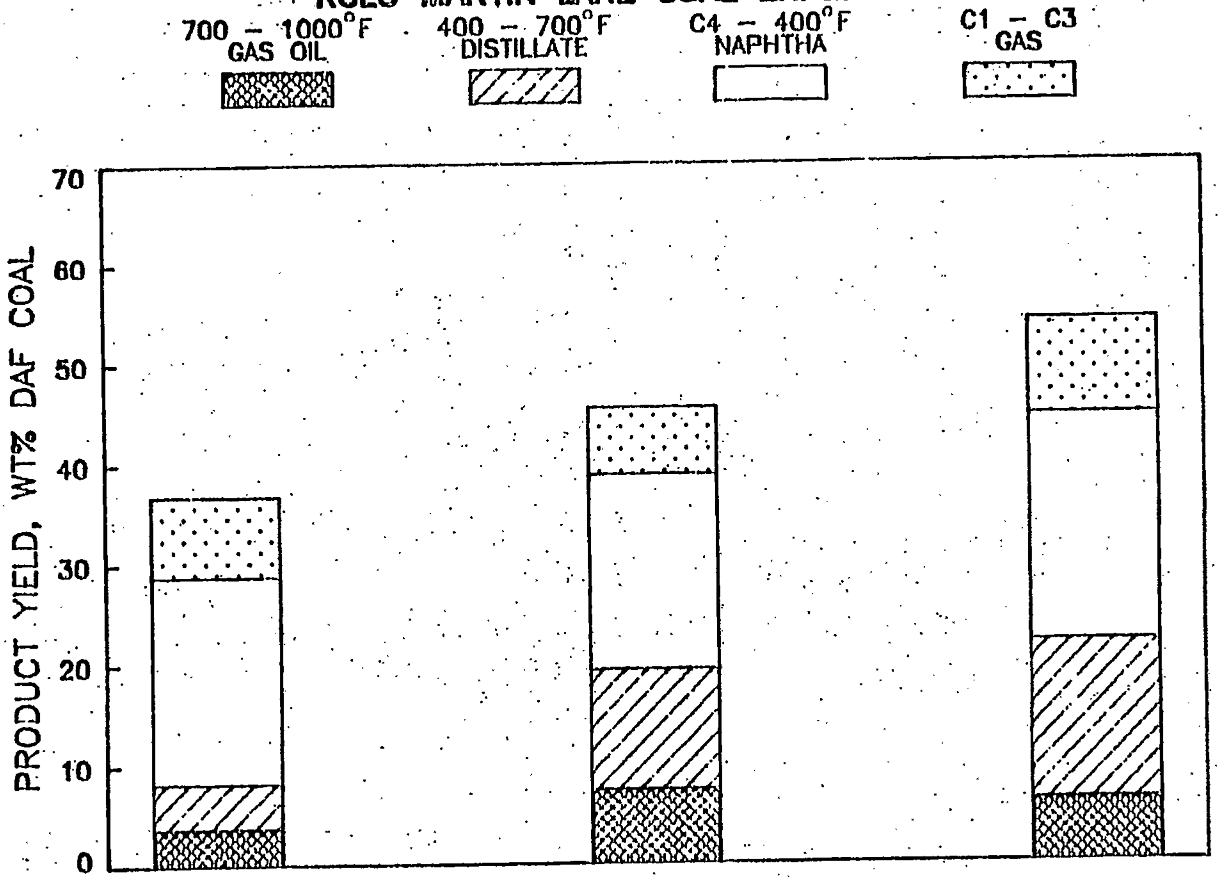
1.3 Bottoms Recycle

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



DAF CONVERSION	55	64	72
LIQUEFACTION CONDITIONS			
TEMPERATURE, °F	820	820	820
H2 PRESSURE, PSIG	1500	2000	2000
NRT, MINUTES	40	40	40
S/C/B, BY WT.	1.6/1/0	1.6/1/0.5	1.6/1/1
H2 TREAT, WT% ON COAL	4	6	6
RCLU NO.	1	1	1
YIELD PERIODS	1038–1040	991–994	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% H_2 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 C_1-1000°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 C_1-C_3 gas and naphtha (C_4-400°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 C_1-1000°F total hydrocarbon, C_4-1000°F liquid, C_1-C_3 gas and C_4-400°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 C_1-C_3 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% H_2 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 hydrotreater 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 acctual 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		Wyodak	
Nominal Liquefaction Conditions			
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
Unit Conditions			
Phase Holdup, vol%	RCLU	CLPP	ECLP
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

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* 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	Ireland	Ireland	Ireland	Wyodak
Liquefaction Conditions				
Temperature, ^oF	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
Average Velocities (Ft/Sec)				
Gas	0.019	0.046	0.075	0.028
Slurry	0.0073	0.0062	0.0050	0.0069
Holdups (Volume %)				
E_g	8	21	27	16
E_1	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 $Na_2Mg(CO_3)_2$ 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
Reactor Solids[1]								
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
Composition, Ranges, Wt %								
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
Major Crystalline Species	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 $Na_2Mg(CO_3)_2$ FeS SiO_2

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[1] Toluene 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
Mine	Monterey No. 1	Burning Star No. 2	Ireland	Arkwright	Wandoan	Wyodak	Big Brown	Indian Head
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)	61-96	69-93	78-86	47-61	56-74	59-63	52-86	57-80
$CaCO_3$ (by TGA)	5-14	8-25	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 Analyzed	0.1-5	Not Analyzed
Ca	2-7	0.1-13	17-34	3-43	0.5-30		0.8-38	
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
Total Solids Accumulation										
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
Composition Ranges, Wt%										
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
Major Crystalline Species	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.

FIGURE 2-1

CLPP FLOW DIAGRAM

83B-1-9

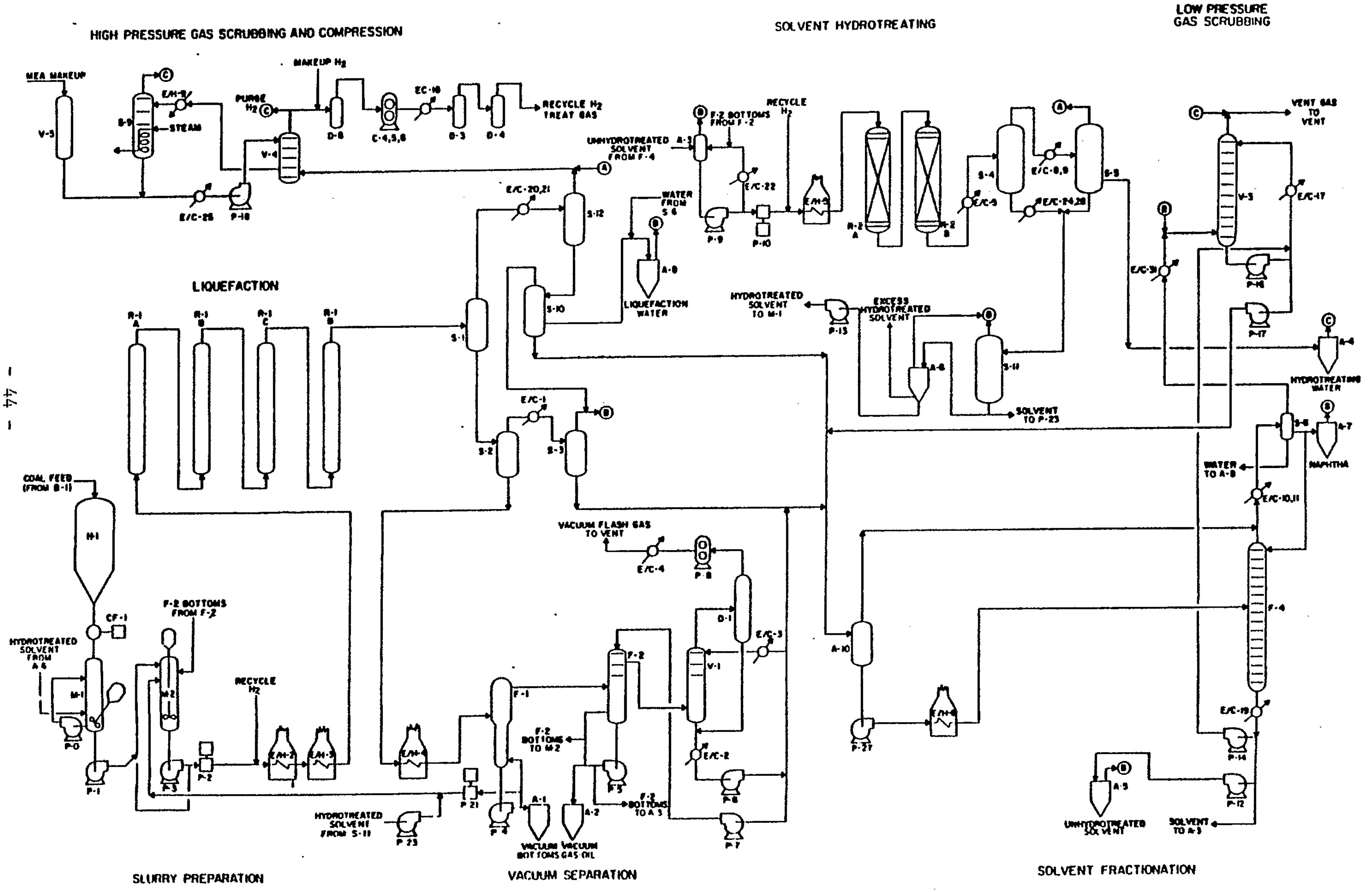


Table 2-1

SUMMARY OF CLPP STUDIES

Coal Rank Mine	Illinois No. 6 Bituminous Monterey No. 1	Illinois No. 6 Bituminous Burning Star No. 2	Pittsburgh No. 8 Bituminous Ireland	Wyoming Subbituminous Wyodak	Wandoan Black Subbituminous Queensland, Australia	Texas Lignite Big Brown	Texas Lignite Martin Lake
Liquefaction Modes	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
VGO Disposition	Product, Hydrotreating	Product, Liquefaction, Hydrotreating	Product, Liquefaction, Hydrotreating	Product, Liquefaction, Hydrotreating	Product, Liquefaction	Product, Hydrotreating	Hydrotreating
Yield Periods	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
Results Reported 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				
KCLP 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 microlube 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 Hydrodynamic Studies						X
10. Liquefaction Temperature 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, C_1-1000°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 undersirably high C_1-C_3 gas yield of 16 wt% on DAF coal.

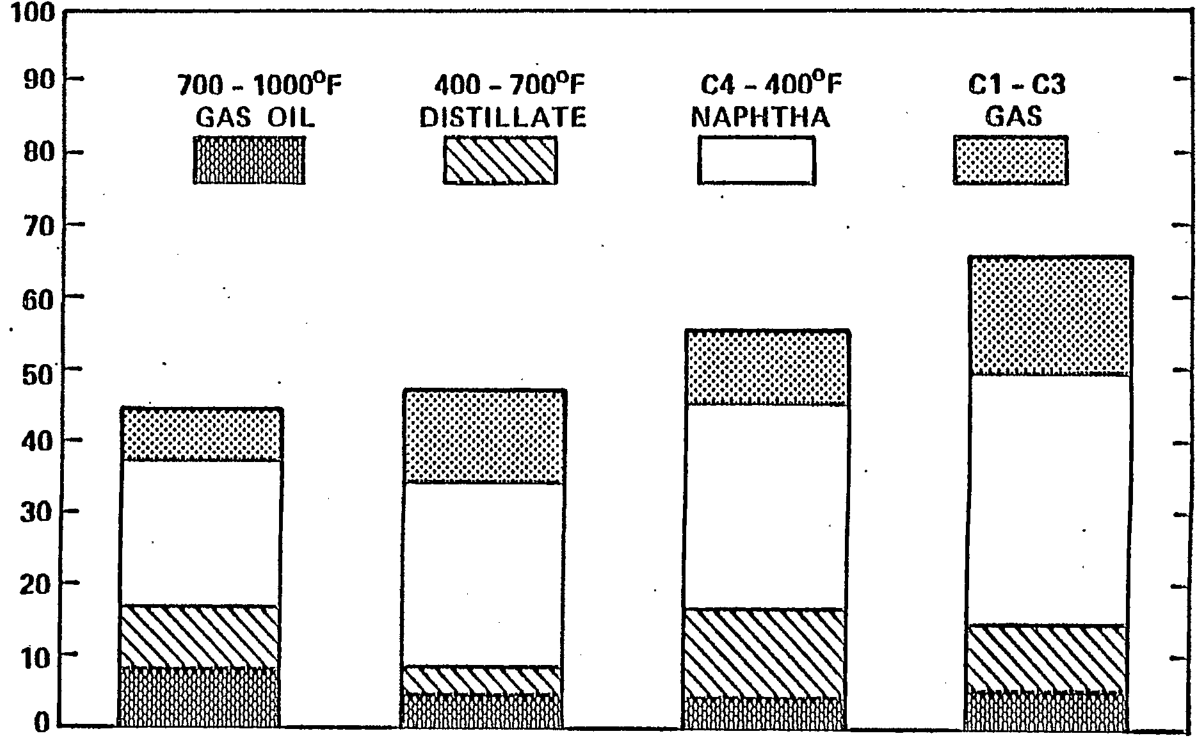
High pressure coal-only operations did not show significant conversion increases over low pressure coal-only operations. The conversion enhancement of about 2 wt% for YPs 320 and 321 can be accounted for by the increased nominal residence time (60 vs 40 minutes). However, a substantial shift toward lighter products occurs in high pressure coal-only operations. C_1-C_3 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

HYDROCARBON YIELD DISTRIBUTIONS FOR CLPP MONTEREY COAL OPERATIONS



DAF CONVERSION	57	59	69	77
LIQUEFACTION CONDITIONS				
TEMPERATURE, F	840	840	840	840
H2 PRESSURE, PSIG	1500	2000	2000	2000
NRT, MINUTES	40	60	60	60
S/C/B, BY WT.	1.2/1/0	1.2/1/0	1.6/1/0.5	1.8/1/1
H2 TREAT, WT% ON COAL	4	4	6	8
VGO DISPOSITION	PROD.	PROD.	HYT.	PROD.
YIELD PERIODS	256-258, 260-264	320, 321	346-350	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

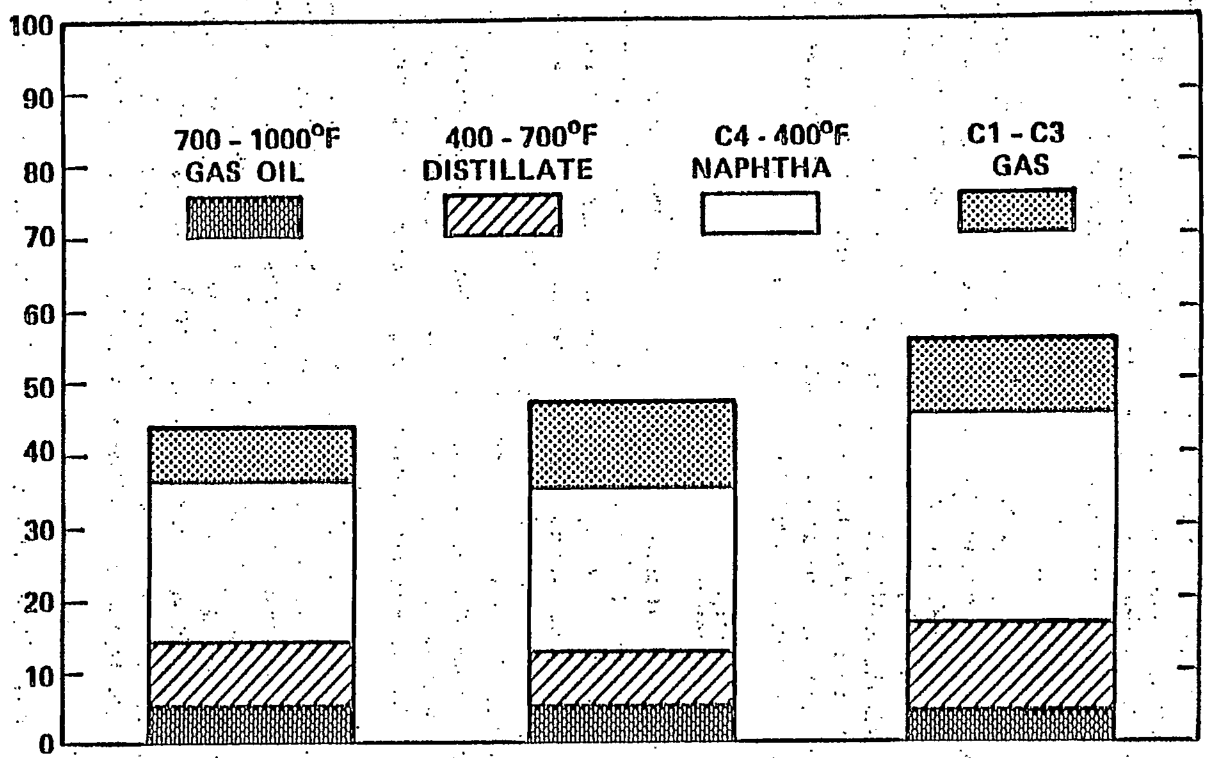
Once-through and bottoms recycle operations were conducted on the CLPP using Pittsburgh No. 8 coal from the Ireland mine. Once-through operations were conducted in September, 1979, and were aimed at assessing yields and operability at base case conditions. Conditions selected were 840°F liquefaction 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	BURNING STAR		MONTEREY
DAF CONVERSION	52	56	69
LIQUEFACTION CONDITIONS			
TEMPERATURE, F	840	840	840
H2 PRESSURE, PSIG	2000	2000	2000
NRT, MINUTES	60	80	60
S/C/B, BY WT.	1.6/1/0.5	1.6/1/0.5	1.6/1/0.5
H2 TREAT, WT% ON COAL	6	6	6
VGO DISPOSITION	HYT.	HYT.	HYT.
YIELD PERIODS	393-395	390-392	346-350

FIGURE 2-4

VACUUM BOTTOMS VISCOSITIES FROM CLPP BOTTOMS RECYCLE BITUMINOUS COAL OPERATIONS

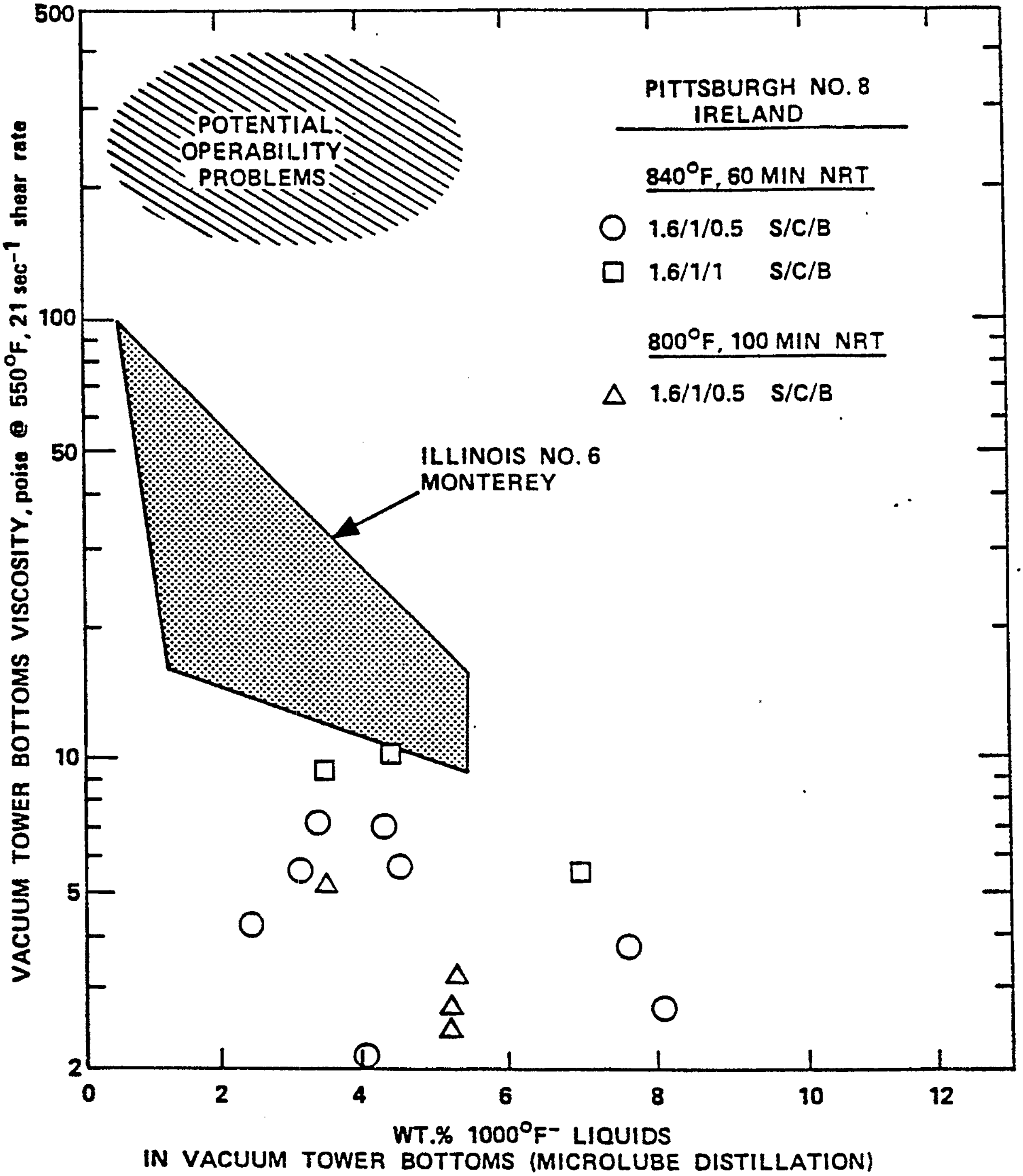
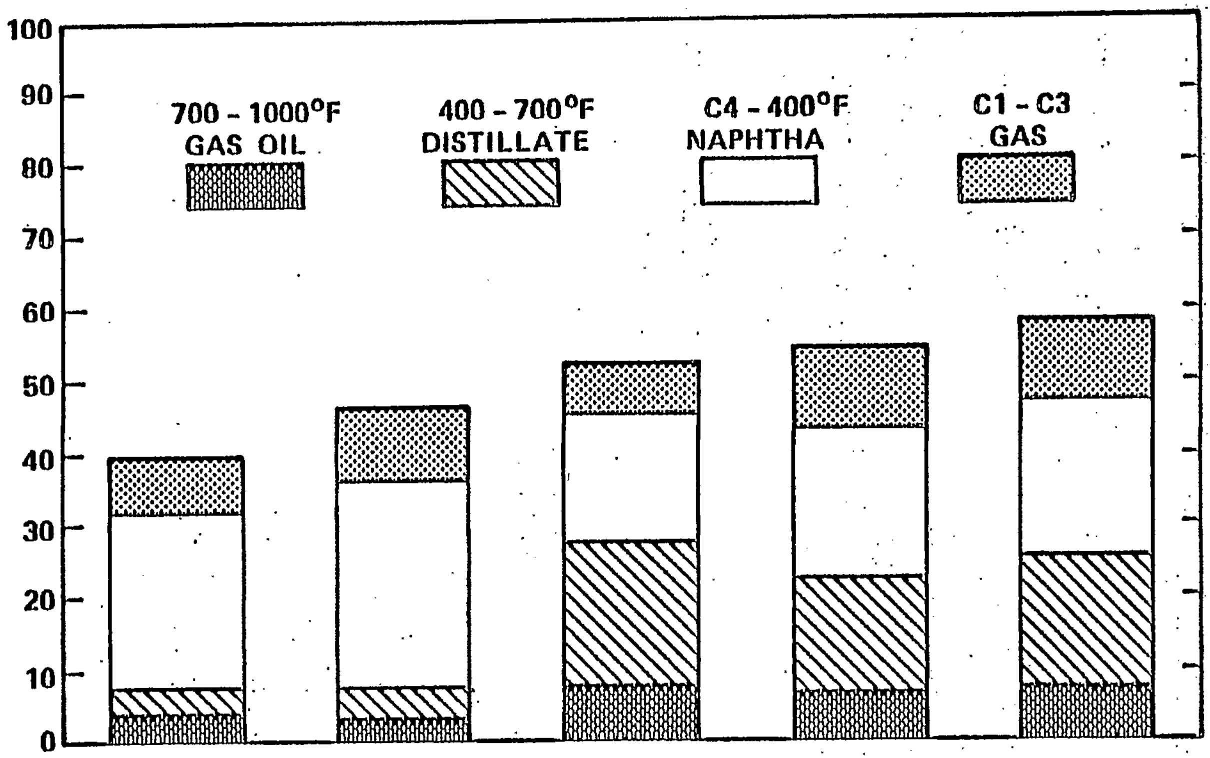


FIGURE 2-5

HYDROCARBON YIELD DISTRIBUTIONS FOR CLPP IRELAND COAL OPERATIONS



DAF CONVERSION	47	55	59	62	66
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/coal/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 convertability 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/coal/bottoms proportions. VGO was recycled directly to liquefaction and taken as product in these runs.

Table 2-3

CLPP OPERATIONS WITH WYODAK MINE COAL

Operating Period	July, 1977	May, 1978- Nov., 1978	January, 1980	April, 1980	December, 1980- February, 1981	September, 1981- November, 1981
Liquefaction Mode	Once-Through	Once-Through	Bottoms Recycle	Once-Through, Bottoms Recycle	Bottoms Recycle	Bottoms Recycle
VGO Disposition	Product	Product	Product	Hydrotreating	Liquefaction, Product	Liquefaction, Hydrotreating
Yield Periods Obtained	245-249	266-284	312-319	320-325	351-357	MB 8-12 385-388
Nominal Liquefaction Conditions						
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
Major Objectives						
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 Hydrodynamic 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, C_1-1000°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 C_1-C_3 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 C_1-1000°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.

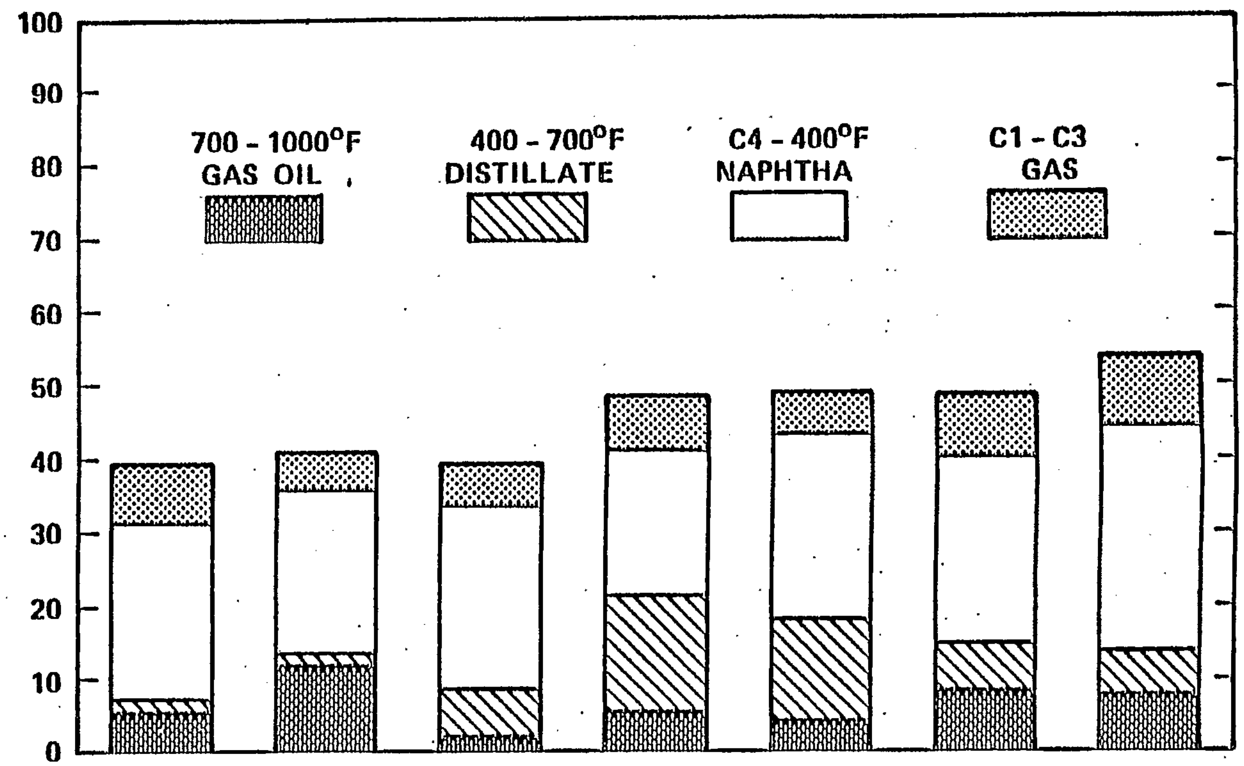
2.1.5 Wandoan Coal Evaluation

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 C_4-1000°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 opeations.

As shown in Figure 2-7, C_1-1000°F yield for Wandoan coal liquefaction was 49 wt% in 840°F, 60 minute NRT operations versus 43 wt% for

FIGURE 2-6

HYDROCARBON YIELD DISTRIBUTIONS FOR CLPP WYODAK COAL OPERATIONS

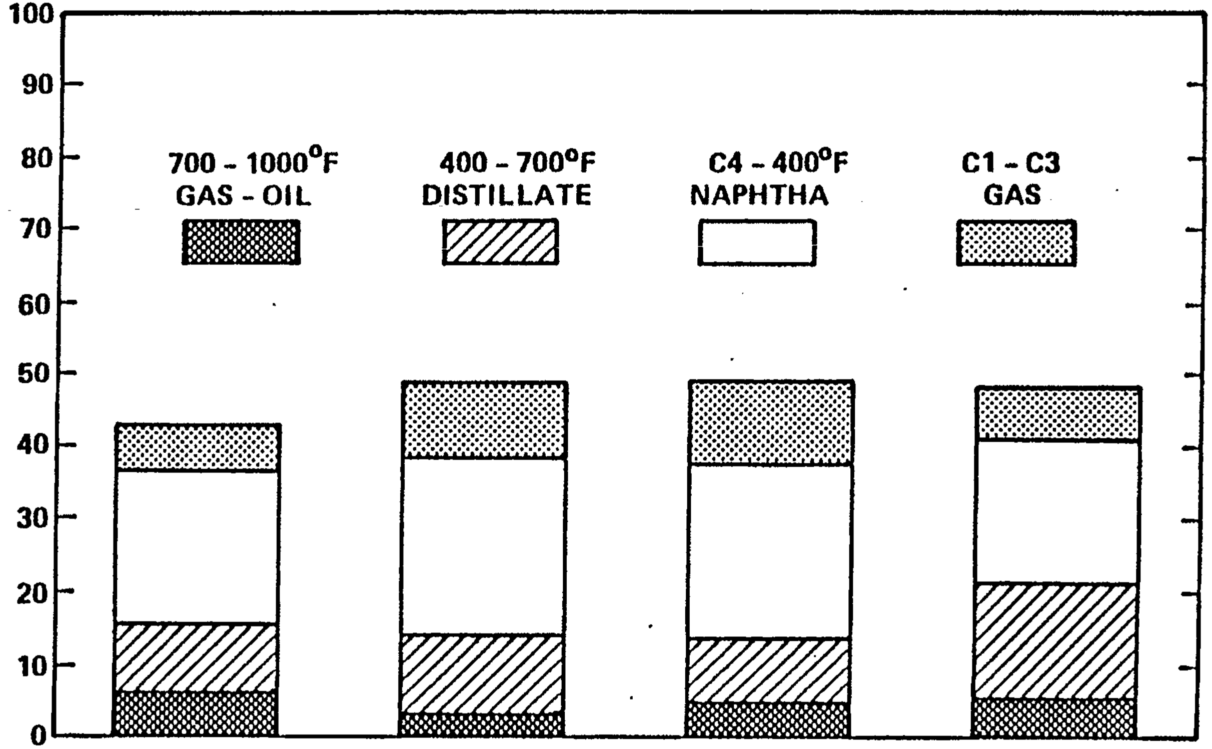


DAF CONVERSION	58	58	59	67	68	67	72
LIQUEFACTION CONDITIONS							
TEMPERATURE, F	840	800	800	840	800	800	800
H2 PRESSURE, PSIG	1500	1500	2000	2000	2000	2000	2000
NRT, MINUTES	60	100	100	60	100	100	100
S/C/B, BY WT.	1.6/1/0	1.6/1/0	1.6/1/0	1.6/1/0.5	2/1/0.5	2/1/1	2.5/1/1
H2 TREAT, WT% ON COAL	4	4	4	6	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

82B-11-154

FIGURE 2-7

HYDROCARBON YIELD DISTRIBUTIONS FOR CLPP SUBBITUMINOUS COAL OPERATIONS



MINE	WANDOAN			WYODAK
DAF CONVERSION	54	63	63	67
LIQUEFACTION CONDITIONS				
TEMPERATURE	800	840	840	840
H2 PRESSURE, PSIG	2000	2000	2000	2000
NRT, MINUTES	100	60	60	60
S/C/B, BY WT.	1.6/1/0.5	1.6/1/0.5	1.6/1/0.5	1.6/1/0.5
H2 TREAT, WT% ON COAL	6	6	6	6
VGO DISPOSITION	LIQ.	LIQ.	PROD.	LIQ.
YIELD PERIODS	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 C_1-1000°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 C_4-1000°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.

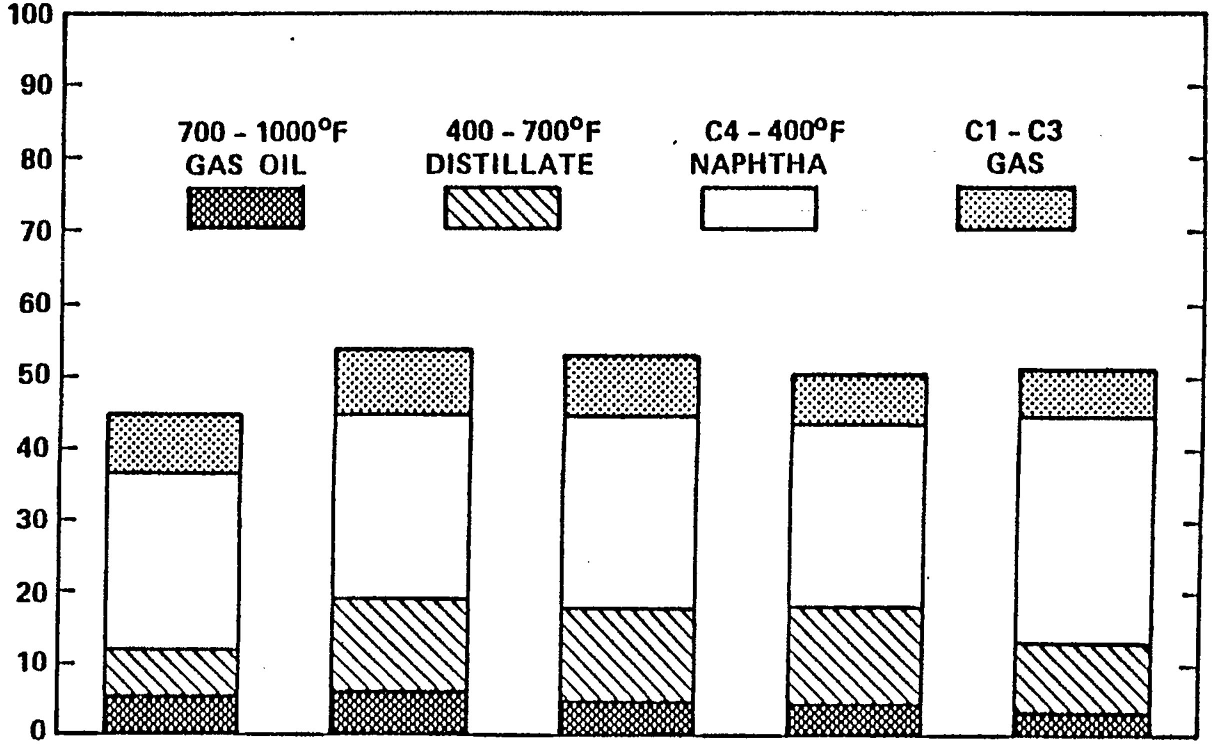
As shown in Figure 2-8, total C_1-1000°F hydrocarbon yield was approximately constant for Big Brown bottoms recycle operations. There were no significant effects of solvent-to-coal or bottoms-to-coal ratios on C_1-1000°F liquid yield or conversion at the conditions examined. However, liquid yield distribution was affected by slurry feed proportions. Naphtha (C_4-400°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 C_1-1000°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

HYDROCARBON YIELD DISTRIBUTIONS FOR CLPP BIG BROWN LIGNITE OPERATIONS



DAF CONVERSION	59	70	69	69	69
LIQUEFACTION CONDITIONS					
TEMPERATURE, F	840	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 diminsihed 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.

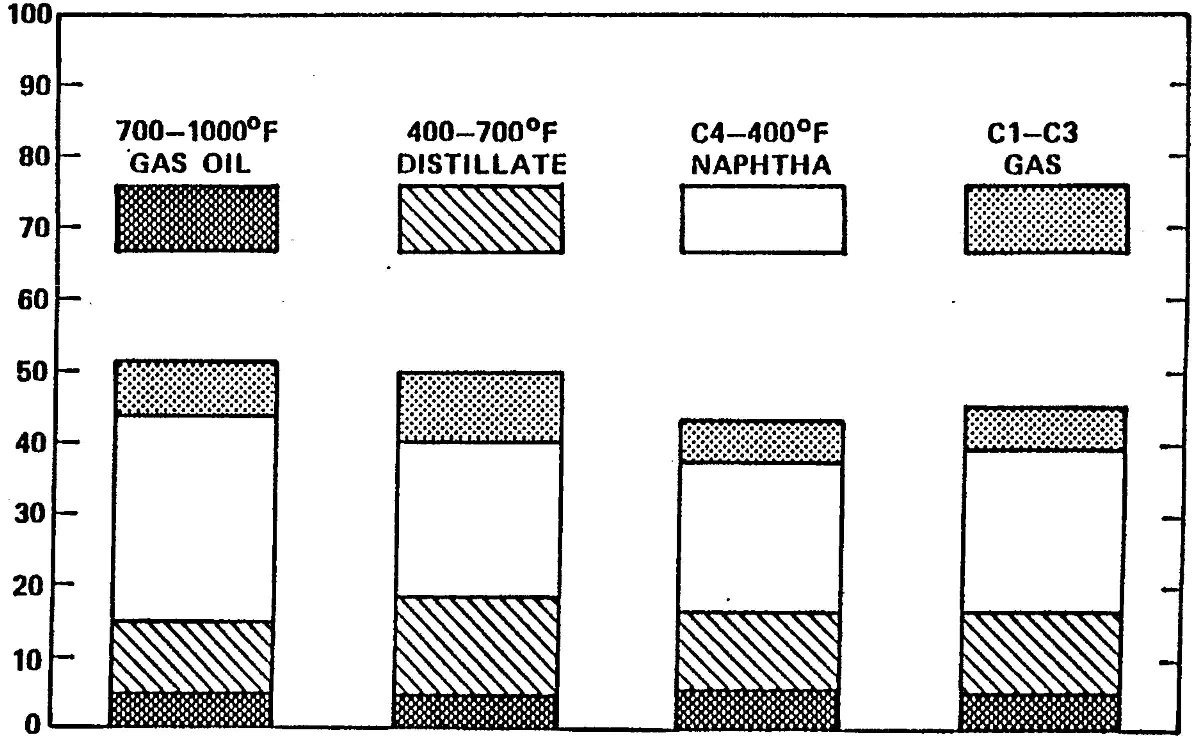
2.2 Evaluation of Bottoms Recycle

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

HYDROCARBON YIELD DISTRIBUTION FOR CLPP MARTIN LAKE LIGNITE OPERATIONS

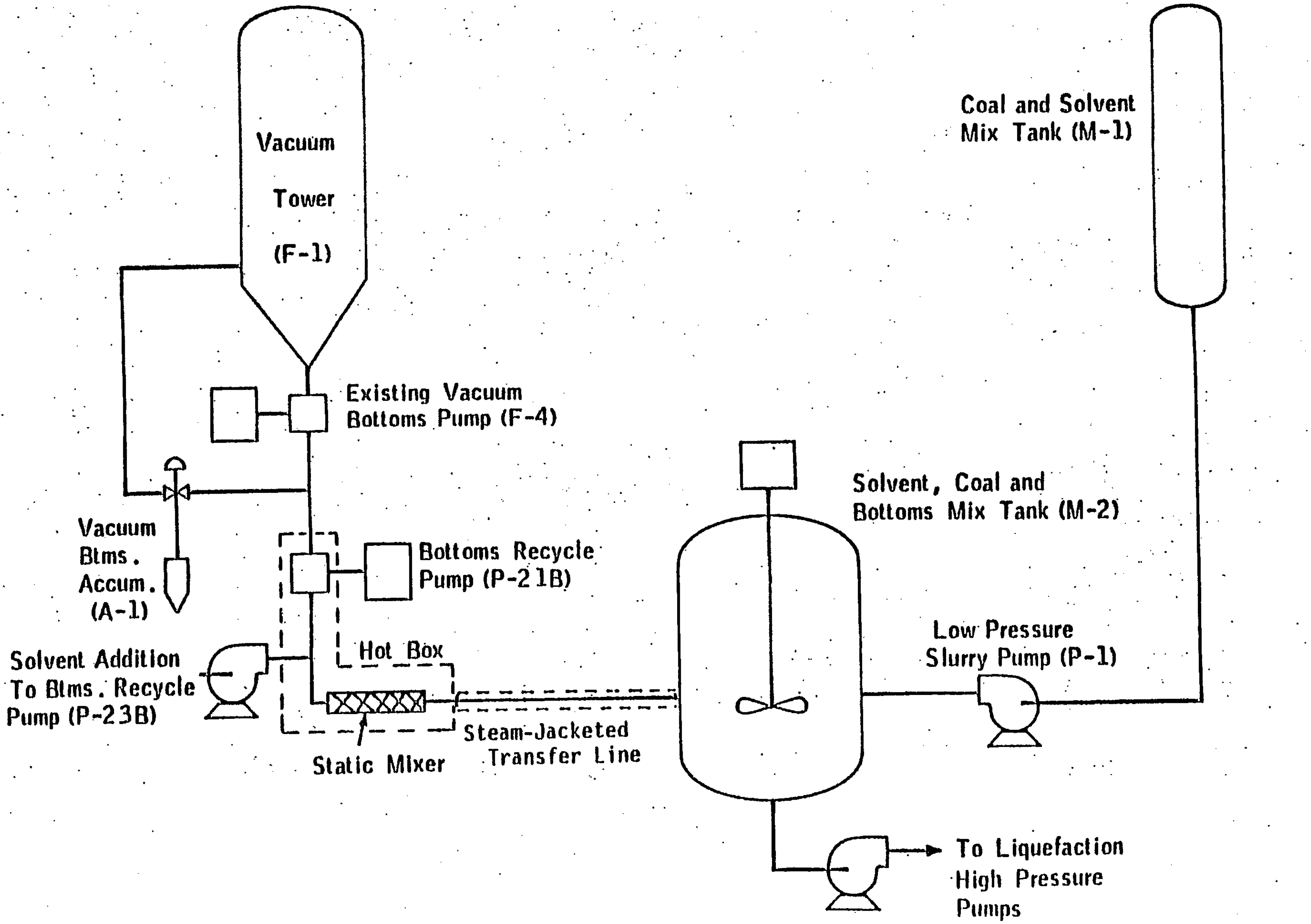


FEED	WHOLE COAL		HIGH ASH FRACTION	
DAF CONVERSION	67	65	61	62
LIQUEFACTION CONDITIONS				
TEMPERATURE, F	850	830	820	820
H2 PRESSURE, PSIG	2000	2000	2000	2000
NRT, MINUTES	40	40	60	60
S/C/B, BY WT.	1.6/1/0.5	1.6/1/0.5	1.7/1/0.5	1.7/1/1
H2 TREAT, WT% ON COAL	6	6	6	6
VGO DISPOSITION	HYT	HYT	HYT	HYT
YIELD PERIODS	398, 399	401, 402	412, 413	414-416

82B-11-156

FIGURE 2-10

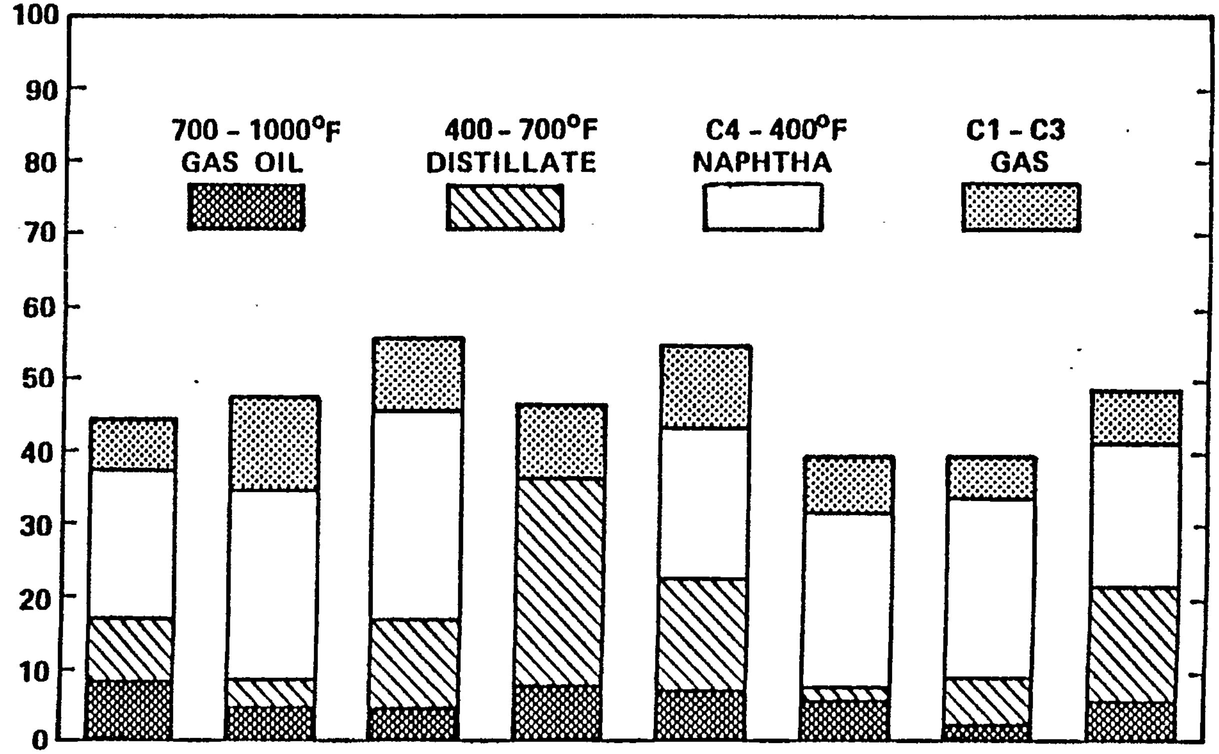
CLPP BOTTOMS RECYCLE II SYSTEM



82B-11-157

FIGURE 2-11

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	69	55	62	58	59	67
LIQUEFACTION CONDITIONS								
TEMPERATURE, F	840	840	840	840	840	840	800	840
H2 PRESSURE, PSIG	1500	2000	2000	1500	2000	1500	2000	2000
NRT, MINUTES	40	60	60	60	60	60	100	60
S/C/B, BY WT.	1.2/1/0	1.2/1/0	1.6/1/0.5	1.6/1/0	1.6/1/0.5	1.6/1/0	1.6/1/0	1.6/1/0.5
H2 TREAT, WT% ON COAL	4	4	6	4	6	4	4	6
VGO DISPOSITION	PROD.	PROD.	HYT.	PROD.	LIQ.	PROD.	HYT.	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

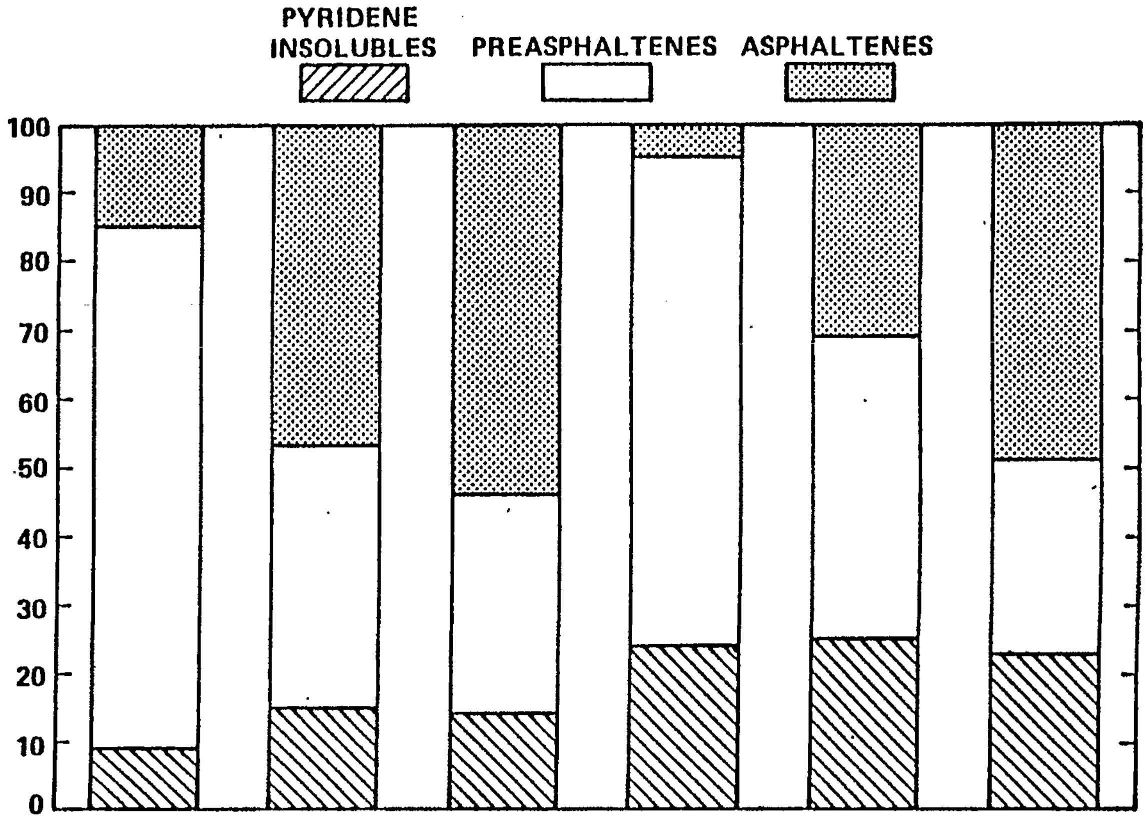
The CLPP was also used to study the effects of recycling vacuum gas oil (VGO), a nominally 800-1000°F boiling hydrocarbon liquid. Two methods of VGO recycle were devised. In the first, VGO was mixed with unhydrotreated solvent, hydrotreated, and recycled to liquefaction. In the second method, VGO was 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

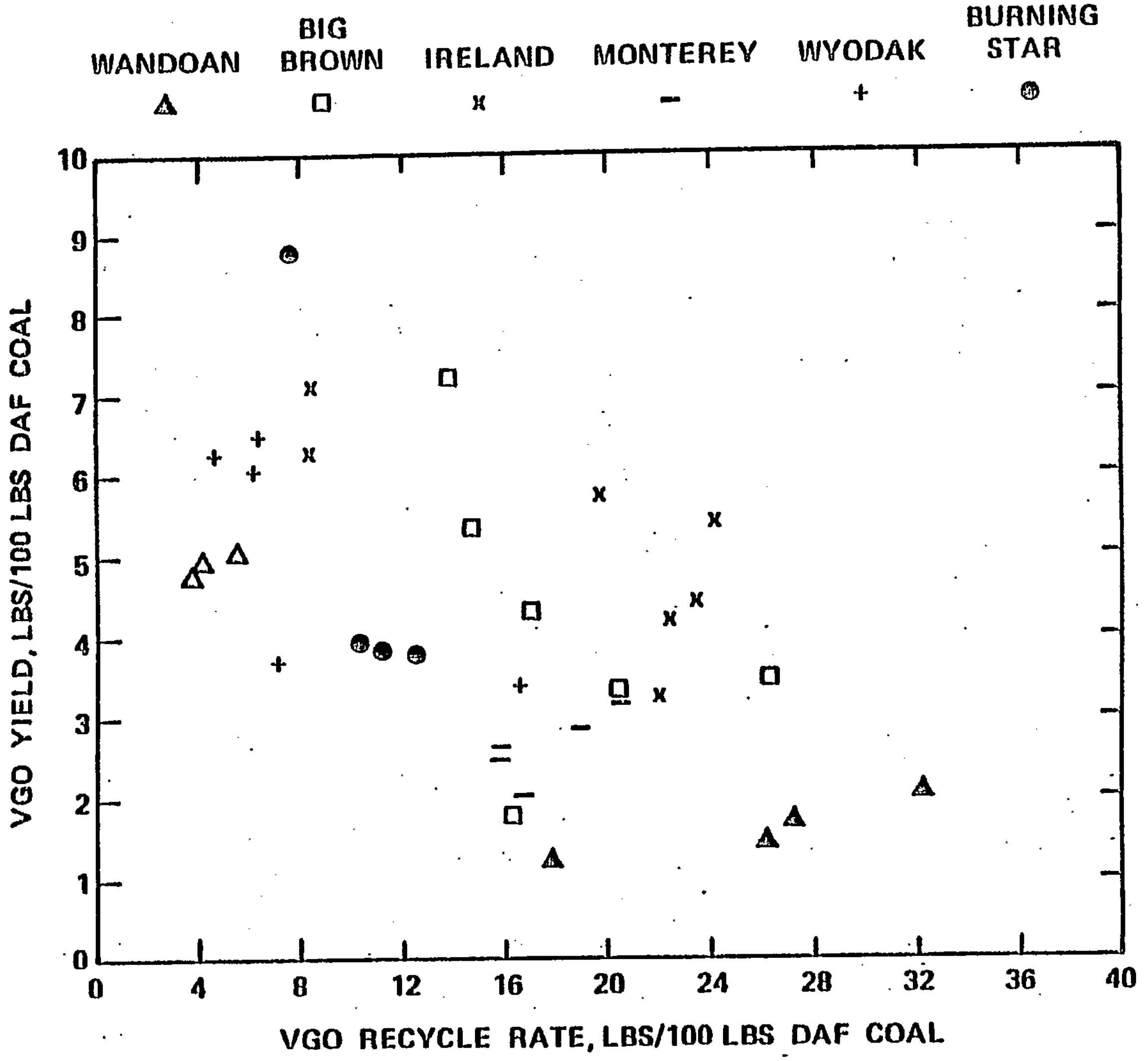
CLPP VACUUM BOTTOMS COMPARISONS FROM ONCE-THROUGH AND BOTTOMS RECYCLE OPERATIONS



COAL	MONTEREY			WYODAK		
LIQUEFACTION MODE	ONCE-THROUGH	BOTTOMS RECYCLE		ONCE-THROUGH	BOTTOMS RECYCLE	
LIQUEFACTION CONDITIONS						
TEMPERATURE, F	840	840	840	800	840	800
H2 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
H2 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 residene 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

Date	Coal	Nominal Residence Time, Minutes	Actual Residence Time, Minutes	Actual Time / Nominal Time
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

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

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(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 338-340 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

Coal	Monterey		Ireland		Wyodak		Big Brown	Martin Lake
Liquefaction Mode	Once-Through	Bottoms Recycle	Once-Through	Bottoms Recycle	Once-Through	Bottoms Recycle	Bottoms Recycle	Bottoms Recycle
Reactor Solids(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

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(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 (RCLU'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 ($\geq$ 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

Type of Study	Run Numbers	Period	References
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

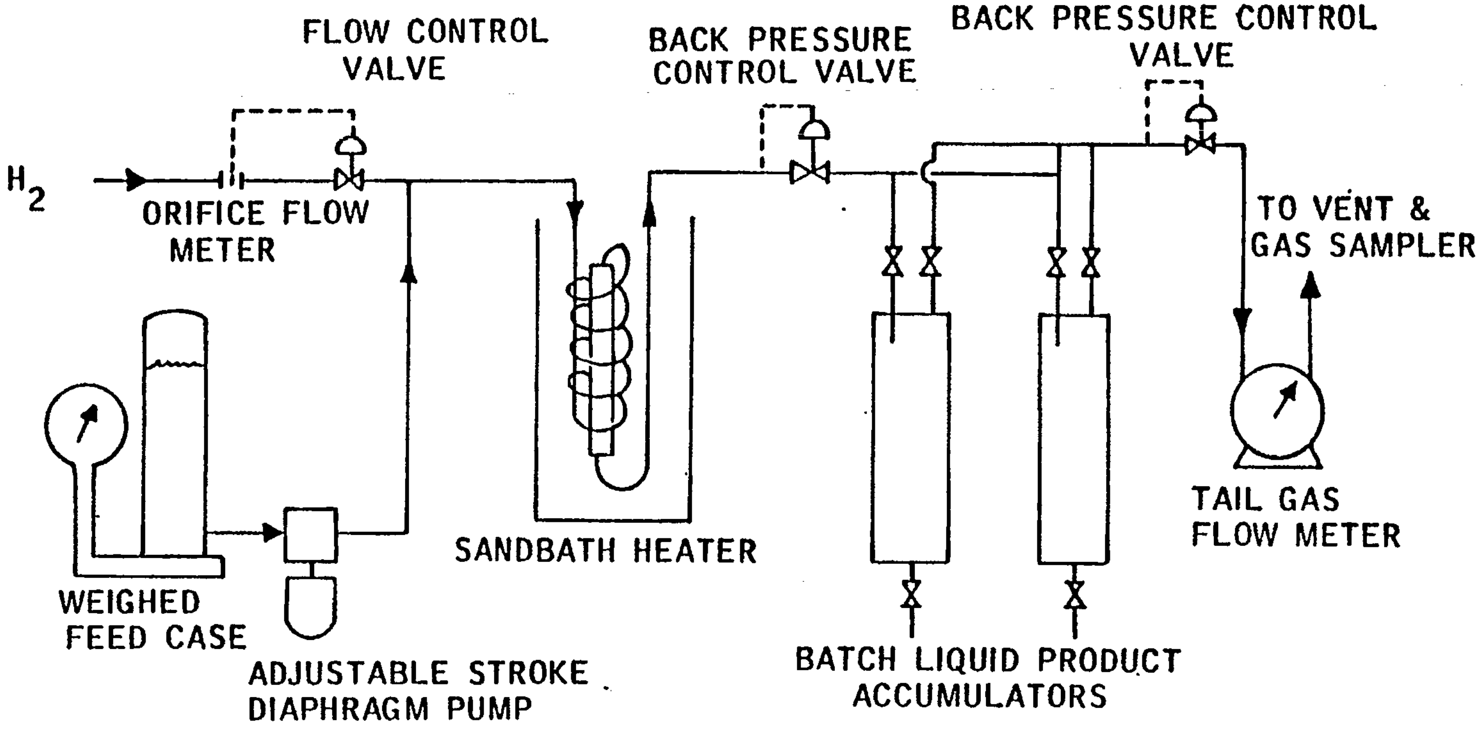
Table 3-1 (Cont'd)

SUMMARY OF KEY SOLVENT HYDROGENATION STUDIES PERFORMED DURING EDS PROGRAM

Type of Study	Run Numbers	Period	Reference
+ 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 ~1°F/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 ($\leq$ 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°F/wk to maintain constant product donor hydrogen, indicating more rapid catalyst deactivation at lower hydrogen partial pressures than reflected by the 1.0°F/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 Laboratoy 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 H_2, 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

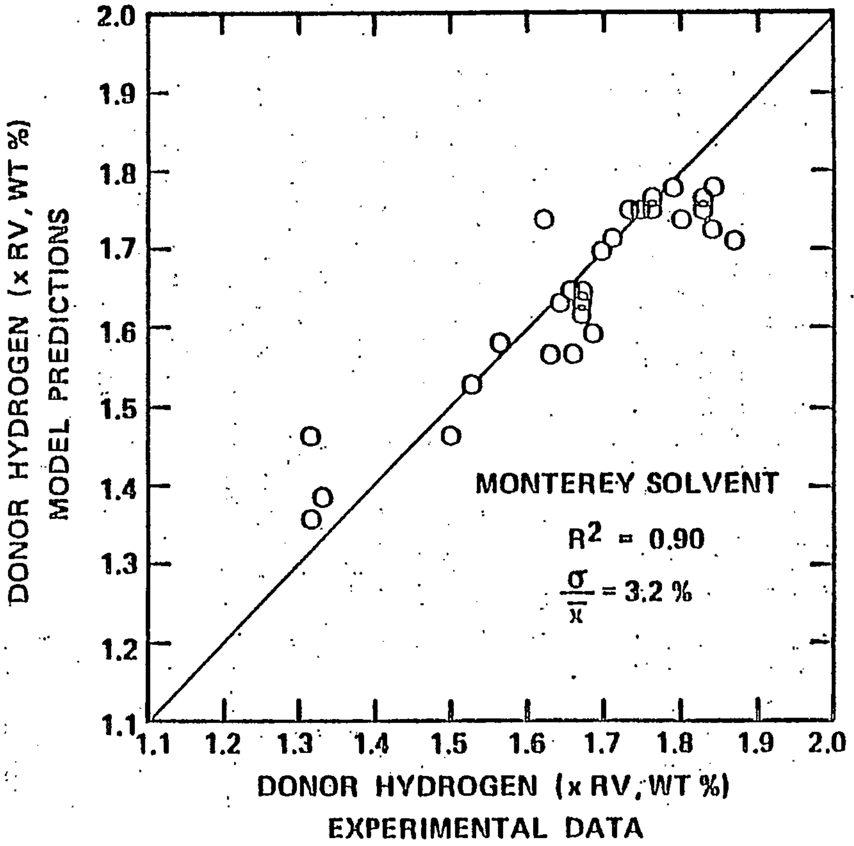


FIGURE 3-3

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

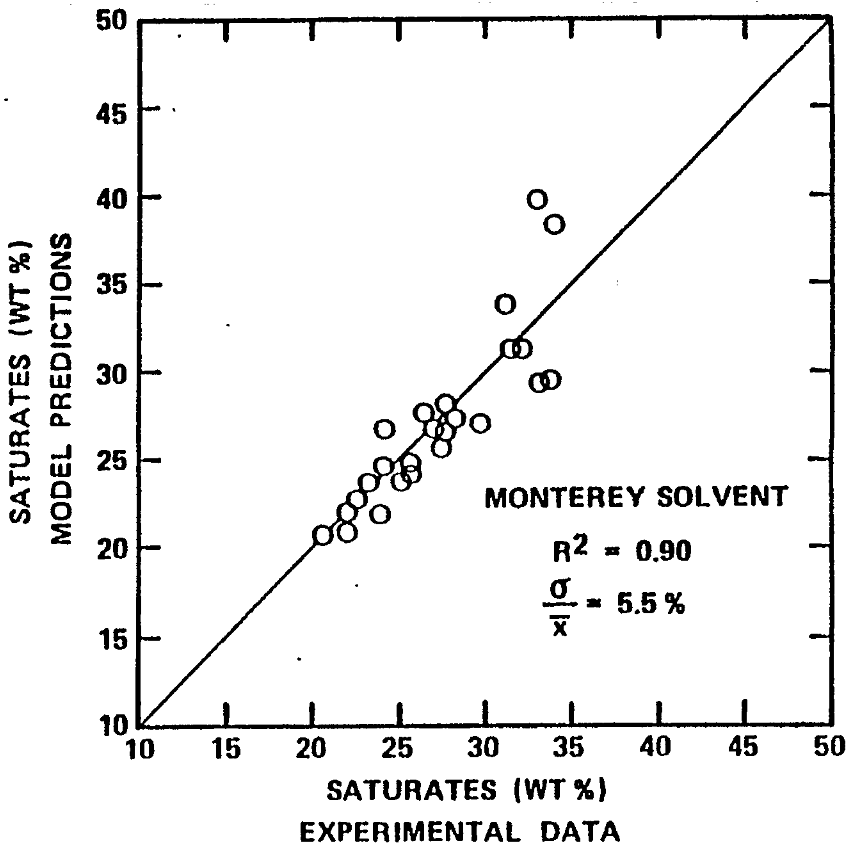


FIGURE 3-4

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

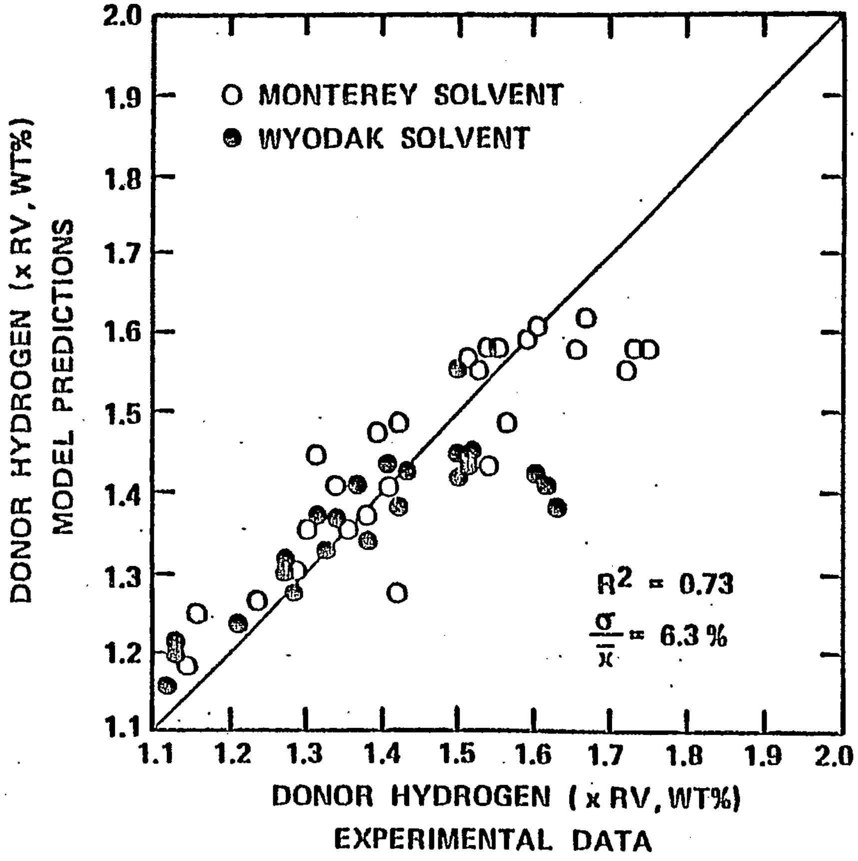
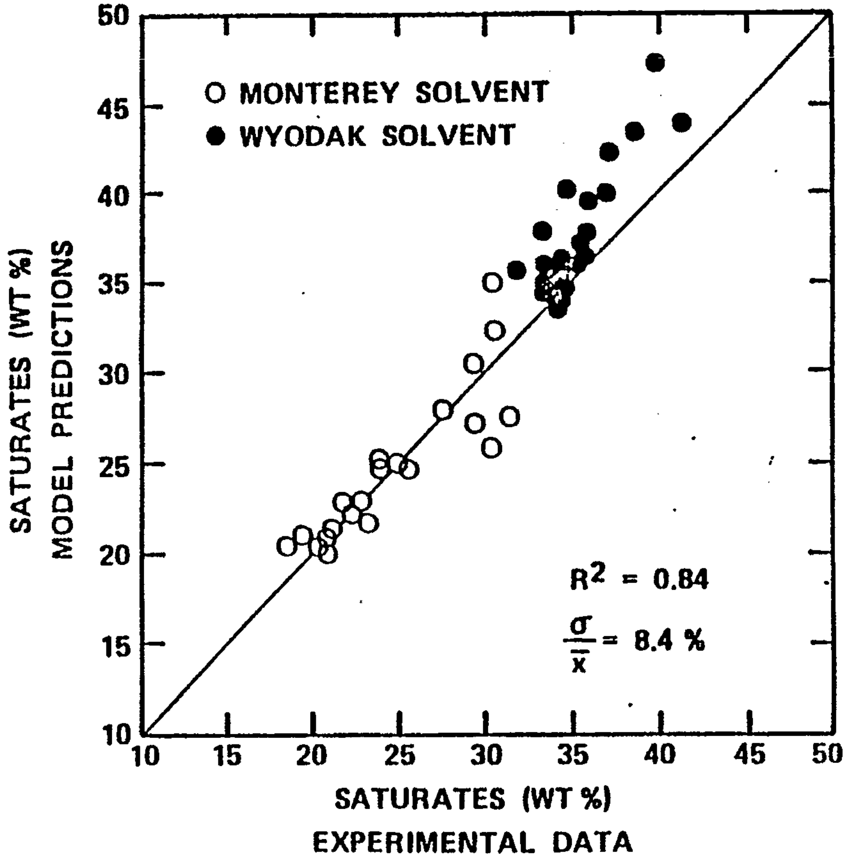


FIGURE 3-5

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)

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

H_2 Pressure (Psig)	Temperature (-RV, °F)	Space Velocity (xRV, wt%)	Donor Hydrogen (xRV, wt%)
1500	65	0.89	1.73 ± 0.06*
1200	65	0.89	1.59 ± 0.00
790	90	0.88	1.73 ± 0.01

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* 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^oF^-) and heavy (600^oF^+) 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^oF^- fraction of an Illinois solvent to typical hydrogenation conditions. The results of this study showed that the 550^oF^- 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 overhydrogeneration of a light solvent fraction, Run 27M21 was conducted during 1Q/1982 using the 600^oF^- 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 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 empiricial 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

Catalyst		Average Catalyst Activity Relative To Fresh Ni/Mo-10	
		Donor Hydrogen Basis	Saturates Basis
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

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* One Standard Deviation 0.05 for all of these determinations