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TWO-STEP COAL LIQUEFACTION IS A HYDROGEN EFFICIENT ROUTE TO DISTILLATE FUELS

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INTRODUCTION

Dwindling U.S. crude reserves and the resulting dependence on OPEC supplies of crude and refined petroleum products threaten U.S. freedom of action in the choice of alternate energy options. U.S. expenditures for imported oil have risen from $3 billion to $60 billion in less than a decade. Transportation fuel shortages have disrupted the movement of goods and people, and potential heating fuel shortages are a concern to residents of the northeastern United States. It is in this context that a number of processes to convert abundant supplies of coal to liquid fuels have been proposed and are in various stages of development. The recently proposed capping of foreign supplies to the U.S. at 8.5MM Bbl/D has added a sense of urgency to synfuels process development programs.

Several processes are at or near the point of commercial demonstration. One of these processes is Two-Step Coal Liquefaction.

TWO-STEP COAL LIQUEFACTION

Cities Service's efforts in catalytic hydrogenation and in the upgrading of solvent refined coal have led to development of a new coal liquefaction technology called "Two-Step Coal Liquefaction", TSL. The basic components of TSL are shown in Figure 1. The process is composed of a solvent refined coal unit operating in tandem with an LC-Fining* unit. LC-Fining (Lummus/ Cities Fining) is a proprietary catalytic hydrogenation process for upgrading heavy oil feedstocks.

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*LC-Fining is a service mark of C-E Lummus for engineering, marketing and technical services relating to hydrocracking and hydrodesulfurization processes for reduced crude and heavy oils.

Research on this technology began at Cities Service more than 20 years ago. The process was originally developed for upgrading bitumen from tar sands. The earliest commercial applications of the process were in the hydrocracking of heavy petroleum stocks.

In Two-Step Liquefaction, coal is dissolved in a process derived solvent, partially hydrogenated, and catalytically hydrocracked. A number of solvent recycle options are available. TSL produces light hydrocarbon gases (C_1-C_4), naphtha (C_5-350°F), middle and heavy distillates (350-850°F), and solid boiler fuel (850°F+). Salient features of this process are as follows:

- Coal dissolution and catalytic upgrading are conducted in separate reactors, allowing each step to be performed at optimum conditions.

- Unreacted coal and ash are removed in the solvent refined coal unit. Removal of this material upstream of the catalytic hydroprocessing step minimizes exposure of the catalyst to metals, reduces its exposure to coke precursors, and permits the production of low ash (∿.2 wt.%), low sulfur (∿.3 wt.%) solid boiler fuel of uniform heating value.

- Considerable flexibility in plant operation and product quality results from the decoupling of the coal dissolution and catalytic upgrading steps.

The success of LC-Fining in upgrading solvent refined coal has generated a great deal of support for the development of the Two-Step Liquefaction process.(12,13,14,15)

Under the current Lummus/Cities/DOE contract, work will proceed in two pilot plants: an LC-Fining unit, and an integrated TSL pilot unit.

Both the Air Products/Wheelabrator-Frye Joint Venture and Gulf Mineral Resources Company are seeking DOE support for 6000 TPD coal liquefaction plants. The Joint Venture's liquefaction plant, will be capable of producing solid boiler fuel, liquids, coke, and hydrocarbon gases. Such a liquefaction plant might be more appropriately called a coal refinery. The Gulf process (SRC-II), as presently conceived, will produce liquids and hydrocarbon gases.

The Joint Venture has recently completed a $8MM engineering and cost study of a commercial scale coal refinery for the United States Department of Energy. An engineering and cost analysis of LC-Fining was included in this study.

LC-Fining is an important element of the coal refinery concept. The diversity of products produced by such a refinery, and processing scheme flexibility permits wide latitude in the relative rates of production of solid and liquid fuels. This flexibility could be used to match production to seasonal variations in fuels demand to minimize tankage requirements as is done in an oil refinery.

SOLVENT REFINED COAL

Two large solvent refined coal pilot plants are currently in operation in the U.S. A 50 TPD (SRC-I mode) pilot plant is located in Fort Lewis, Washington, and a 6 TPD plant is located in Wilsonville, Alabama. The SRC-I (solid boiler fuel) process has been tested at both the Fort Lewis and Wilsonville locations. The Fort Lewis facility has been modified to produce primarily liquid fuels; the modified processing scheme is called SRC-II.

A simplified flow diagram of the SRC-I process is shown in Figure 2. The process operates as follows:

A slurry consisting of pulverized coal and a process derived solvent is mixed with hydrogen rich recycle gas and heated to reaction temperature. The resulting mixture, at the appropriate hydrogen partial pressure, reacts to form H_2S, NH_3, H_2O, gaseous and liquid hydrocarbons, a mineral residue, and large quantities (∿60 wt. % on MAF coal) of vacuum residue. The mineral residue, consisting of unconverted coal and ash, is fed to the hydrogen plant gasifier. Vacuum residue (solvent refined coal) is solidified and sold as boiler fuel.

A simplified flow diagram of the SRC-II process is shown in Figure 3. Note that the SRC-I and SRC-II processing schemes are quite similar. Significant differences between the two processes are as follows:

- The recycle solvent stream of SRC-I is replaced with a recycle slurry stream in SRC-II. Recycle slurry consists of liquid hydrocarbons, solvent refined coal, unconverted coal, and ash. Developers of SRC-II indicate that minerals in the ash catalyze some of the reactions which occur in the dissolver. No catalyst other than ash is employed in this process.

- Solids separation is not practiced in this process. The ash content of the vacuum tower bottoms is considerably higher than that of the parent coal; sale of this material as fuel is unlikely. Hydrogen plant gasifier feed is the probable disposition of vacuum bottoms.

- Coal conversion is constrained by vacuum bottoms disposal requirements as follows:

  Pumpability of this slurry sets a maximum on net liquids production.

  Hydrogen plant capacity sets a minimum on 850°F+ conversion.

LC-FINING

A simplified flow diagram of the LC-Fining process is shown in Figure 4. The process operates as follows:

A hot mixture of SRC, process derived solvent, and hydrogen at the appropriate hydrogen partial pressure react in an expanded bed of catalyst (e.g., Co/Mo or Ni/Mo extrudates). Sulfur, oxygen, and nitrogen removal occur, and a portion of the SRC (850°F+) is hydrocracked to hydrocarbon gases and liquids.

The expanded catalyst bed reactor is the heart of the LC-Fining process. A schematic of an LC-Fining reactor is shown in Figure 5.

Hydrogen rich recycle gas and fresh oil charge are introduced below the distributor plate where they join with internally circulated liquid. Internal circulation is achieved by means of a pump and motor mounted in the bottom head of the reactor. Vapor and liquid pass through the distributor plate and upward through the catalyst bed. The upward flow of liquid is sufficient to expand the bed (increase void volume) and keep the catalyst particles in random motion. Extent of bed expansion is controlled by regulating motor speed, and is monitored by nuclear detectors. The internal circulation pump takes suction above the top of the expanded bed.

The relatively large void volume and high total liquid flow permit solids, which may have entered with the feed or formed in the reactor, to pass through the bed. Thus, the plugging and consequent pressure drop problems that plague fixed bed units in dirty service are avoided. DOE/EPRI sponsored pilot plant runs at Chevron and Mobil have shown competing technology (fixed bed catalytic reactors) to be impractical for upgrading solvent refined coal. This leaves expanded bed catalytic reactor technology as the only currently available technology for upgrading solvent refined coal.

Flow patterns and turbulence in the LC-Fining reactor are such that temperature gradients are quite small (∿5°F) and reactants are well mixed. Spent catalyst may be withdrawn from, and fresh catalyst may be added to the expanded bed while onstream, permitting maintenance of equilibrium catalyst activity.

The LC-Fining process has been demonstrated on a commercial scale producing distillates from heavy petroleum fractions at: Cities Service, Lake Charles Refinery, capacity 6000 BPD; PEMEX, Salamanca Refinery, capacity 18,500 BPD. The Petroleos Mexicanos (PEMEX) unit is shown in Figure 6. The reactors shown in this figure are larger than those which would be used in a 6000 TPD commercial coal plant.

YIELDS & HYDROGEN CONSUMPTION

Table I shows an estimated yield structure and hydrogen consumption for TSL. Similar information for an SRC-II operation are also shown for purposes of comparison. Yields for both plants are based on charging Kentucky No. 9 coal; a typical analysis of this coal is shown in Table II.

TSL liquids are a composite of SRC-I unit and LC-Fining unit yields. The SRC-I contribution to the composite TSL yield is the result of a comprehensive review and correlation of solid SRC (SRC-I) pilot plant data by Air Products and Chemicals, Inc. Pilot plant data from both the Wilsonville(1,11) and Fort Lewis(2,11) facilities were used in this study.

The SRC-II yields result from similar studies by Air Products of published SRC-II process data.(3,4,5,11)

The LC-Fining contribution to the composite TSL yield is based on extensive SRC hydrocracking data from LC-Fining pilot plant operations at the CE-Lummus Engineering Development Center Annex in New Brunswick, NJ. These studies were conducted jointly by Cities Service and CE-Lummus under contract to the United States Department of Energy.

Liquid distillate production (defined here as C_5-850°F) is nearly the same for both processes (~40 wt.%). Distillate yields on a ton of MAF coal charged to liquefaction are approximately 2.4 Bbl/Ton. C_1 through C_4 light hydrocarbon yields per pound of distillate produced are significantly higher for SRC-II. As a consequence, chemical hydrogen consumption for TSL is approximately 25% lower than for SRC-II.

In the SRC-II process, the high reactor temperature (860°F outlet) and high nominal dissolver residence time (~1hr.) required to produce the yield structure shown in Table I are not optimum for either the endothermic depolymerization reactions (coal dissolution) or the exothermic hydrogenation reactions. TSL allows for the separate optimization of the coal dissolution and hydrocracking steps.

Investigators(6) at Mobil Research and Development Corporation suggest that at high temperatures (in the 850°F range) the fragments which are formed in the thermal depolymerization of coal are highly reactive. These fragments must be rapidly stabilized by hydrogen atoms derived principally from donor molecules in the solvent, or they will recombine to form coke precursors which are more likely to decompose into gas and char rather than into liquid. These investigators indicate that both hydrogen donor reactivity and concentration are important in retarding coke formation. Thermodynamics at high temperatures favor the production of aromatics over hydroaromatics (donor species).

The lower reaction temperatures used in both stages of TSL (825°F and 820°F in the SRC-I and LC-Fining units, respectively) result in higher donor species concentrations. Furthermore, the presence of an active hydrogenation catalyst in the LC-Fining stage, where roughly 50% of the 850°F+ conversion takes place, undoubtedly helps to retard gas formation by facilitating direct hydrogenation of SRC fragments and/or rehydrogenation of spent donors.

Table III shows the sulfur and nitrogen content of MAF Kentucky No. 9 coal, SRC-I liquid and solid products, TSL liquid and solid products, and the sulfur and nitrogen content of SRC-II fractions. A comparison of SRC-I product quality with that of TSL shows that the addition of the LC-Fining step results in a dramatic improvement in the sulfur content of liquid and solid products and a modest improvement in the nitrogen content of these materials. TSL liquids are also superior to those produced by SRC-II.

It should be noted that the SRC-I solid product sulfur content (0.85 wt.%) corresponds to 1.08 Lb SO_2 per MMBtu input, and, thus, complies with the current 1.2 Lb SO_2 per MMBtu input emission standard. The addition of the LC-Fining step, however, provides insurance against the advent of future, more stringent sulfur emissions legislation.

ARE TSL LIQUID PRODUCTS FUELS?

Certainly in the 1980's and probably through the 1990's coal derived liquids are likely to comprise a small fraction of the total annual U.S. fuels supply. Changes in current fuels specifications to accommodate coal liquids are improbable. Therefore, these liquids must meet, or with subsequent processing be capable of meeting, established ASTM and other applicable specifications. A preliminary review of anticipated TSL liquid product properties and literature dealing with the upgrading of coal liquids indicate a number of potential markets for synfuel liquids.(7,8,9,10) These are given in Table IV with brief comments.

Obviously synfuels stocks should penetrate those markets which produce the maximum netback to the producer; marketing studies must take into account syncrude production costs, downstream processing costs, transportation costs, competing petroleum product prices, etc. A study identifying areas of optimum market penetration is underway. Details of these studies will be released as they are developed.

THE IMPORTANCE OF EFFICIENT HYDROGEN CONSUMPTION

The following factors will necessitate onsite hydrogen generation at coal liquefaction facilities:

- Location of these facilities near sources of feed coal and (at least at present) quite distant from sources of hydrogen for sale.
- Large hydrogen demand.
- The need to dispose of liquefaction residues.

Typically, the onsites for the hydrogen generation facilities will include: coal/residue gasification, oxygen production, shift conversion, acid gas removal, compression, and sulfur production.

Hydrogen generation inefficiencies represent the major energy loss from the liquefaction facility. An estimate of the magnitude of these losses is shown in Table V. Case I shows energy losses in the hydrogen generation facilities for Two-Step Coal Liquefaction. Case II shows hydrogen generation energy losses for an SRC-II liquefaction plant. In both cases hydrogen generation is sufficient to satisfy chemical hydrogen demand, regardless of liquefaction residue production rate. The value of these energy losses is shown in the last column of Table V. The unit price of lost energy, \$1.25/MMBtu, is equivalent to \$30/Ton for Kentucky No. 9 (or similar heating value) coal. It should be noted that the hydrogen consumption and vacuum residue yield shown for SRC-II (in Table I) are not in balance. An excess of residue is produced. Gasification of this excess residue to medium Btu gas results in even greater energy losses than those shown in Table V.

CONCLUSION

The TSL process achieves a significant reduction in hydrogen consumption relative to SRC-II. The impact of this reduction on hydrogen plant operating expenses is substantial. Table V shows that a pretax saving of approximately \$20,000/D in hydrogen generation accrues to Two Step Coal Liquefaction. The magnitude of this saving is directly linked to the cost of energy and is, thus, likely to increase in the future.

Studies, currently underway, are directed at further reductions in hydrogen consumption by operating the SRC-I process at lower severities, and by optimizing solvent recycle configuration. This work will more fully demonstrate the advantages of the TSL process as a hydrogen efficient route to distillate fuels.

Acknowledgement

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BIBLIOGRAPHY

1. Catalytic, Inc., "Solvent Refined Coal (SRC) Process," Quarterly Technical Progress Report for: 1 April to 30 June, 1976, Report: FE-2270-3, Pages 13-17 and 96-104, August, 1976.

2. The Pittsburgh and Midway Coal Mining Company, "Solvent Refined Coal (SRC) Process," Research and Development Report NO. 53, for: 1 June, 1974 to 30 April, 1977, FE-496-T13, Pages 189-202 and 227-270, May, 1977.

3. The Pittsburgh and Midway Coal Mining Company, "Solvent Refined Coal (SRC) Process," Quarterly Technical Progress Report for: 1 April to 30 June, 1977, Report: FE-496-141, Pages 53-57, and 76-77, December, 1977.

4. The Pittsburgh and Midway Coal Mining Company, "Solvent Refined Coal (SRC) Process," Quarterly Technical Progress Report for: 1 July to 30 September, 1977, Report: FE-496-143, Pages 30-56 and 93-109, January, 1978.

5. The Pittsburgh and Midway Coal Mining Company, "Solvent Refined Coal (SRC) Process," Annual Technical Progress Report for: 1 January to 31 December, 1977, Report: FE-496-149, Pages 33-38 and 100-104, June, 1978.

6. Mitchell, T. O., Whitehurst, D. D., and Heck, R. H.; "New Liquefaction Technology by Short Contact Time Processes," 71st Annual AIChE Meeting, Miami Beach, Florida, November 5-9, 1978.

7. de Rosset, A. J.; "Presentation to DOE of Work by UOP, Inc. Under Contract EF-C-91-2566," DOE Coal Liquefaction Refining Review, Crystal City, Virginia, May 16, 1978.

8. Callen, R. B., Bendoraitis, J. G., Simpson, C. A., and Voltz, S. E.; "Upgrading Coal Liquids to Gas Turbine Fuels. 1. Analytical Characteristzation of Coal Liquids," Ind. Eng. Chem., Prod. Res. Dev., Vol. 15, No. 4, 1976, Pages 222-233.

9. Cabal, A. V., Voltz, S. E., Stein, T. R., "Upgrading Coal Liquids to Gas Turbine Fuels. 2. Compatibility of Coal Liquids with Petroleum Fuels," Ind. Eng. Chem., Prod. Res. Dev., Vol. 16, No. 1, 1977, Pages 58-68.

10. Phillips, E. M., Unpublished Air Products Interoffice Memo to A. S. Gupta, Subject: DOE Commercial Report -Chapter on TSL Liquids, 3 July, 1979.

11. Phillips, E. M., Unpublished Air Products Interoffice Memo to S. M. Morris, Subject: TSL - Two-Stage Liquefaction of Coal, 11 May, 1979.

12. The Cities Service Company, "Commercial Scale Expanded Bed Hydroprocessing of Solvent Refined Coal (SRC) Extract", Interim Technical Progress Report, Report FE-2038-17, November , 1977.

13. The Cities Service Company, "Commercial Scale Expanded Bed Hydroprocessing of Solvent Refined Coal (SRC) Extract", Interim Technical Progress Report, Report FE-2038-25, August, 1978.

14. The Cities Service Company, "Expanded Bed Hydroprocessing of Solvent Refined Coal (SRC) Extract", Interim Technical Progress Report, Report FE-2038-34, May, 1979.

15. Chillingworth, R.S., Hastings, K.E., Potts, J.D., and Unger, H., "LC-Fining of SRC - A Logical Second Stage in Two-Step Coal Liquefaction", 87th National AICHE Meeting, Boston, Massachusetts, August 20, 1979.

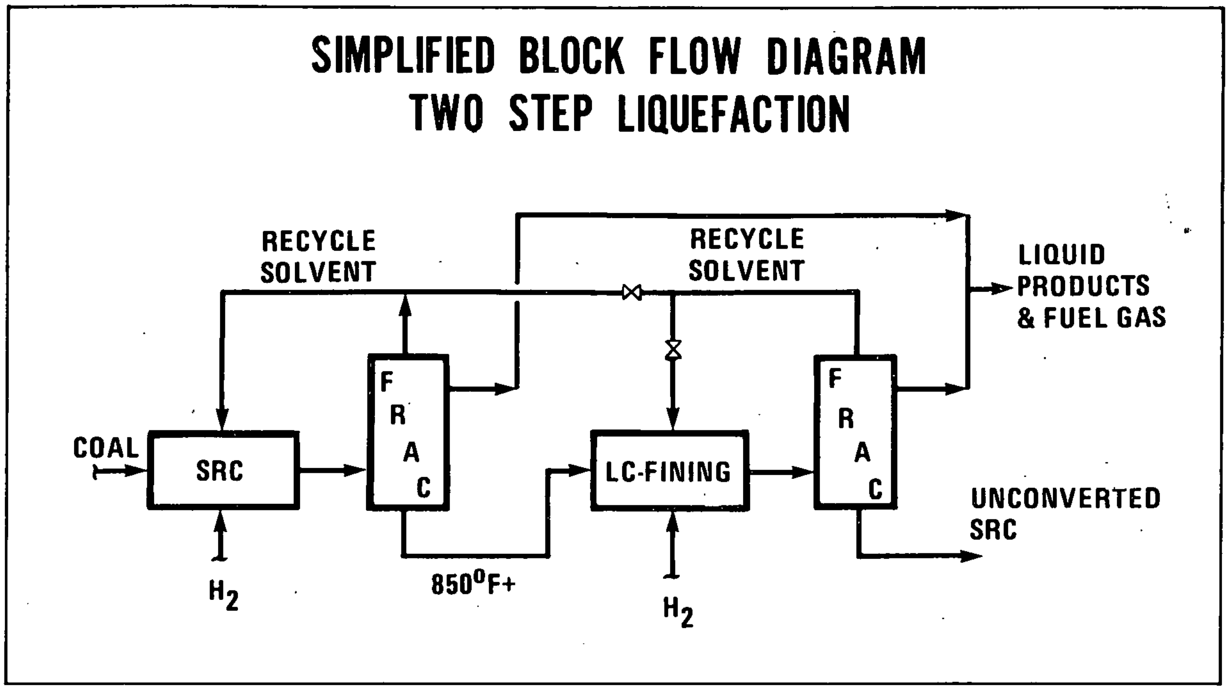
SIMPLIFIED BLOCK FLOW DIAGRAM
TWO STEP LIQUEFACTION
RECYCLE SOLVENT
RECYCLE SOLVENT
LIQUID PRODUCTS & FUEL GAS
COAL
SRC
H2
F R A C
850°F+
LC-FINING
H2
F R A C
UNCONVERTED SRC

FIGURE 1

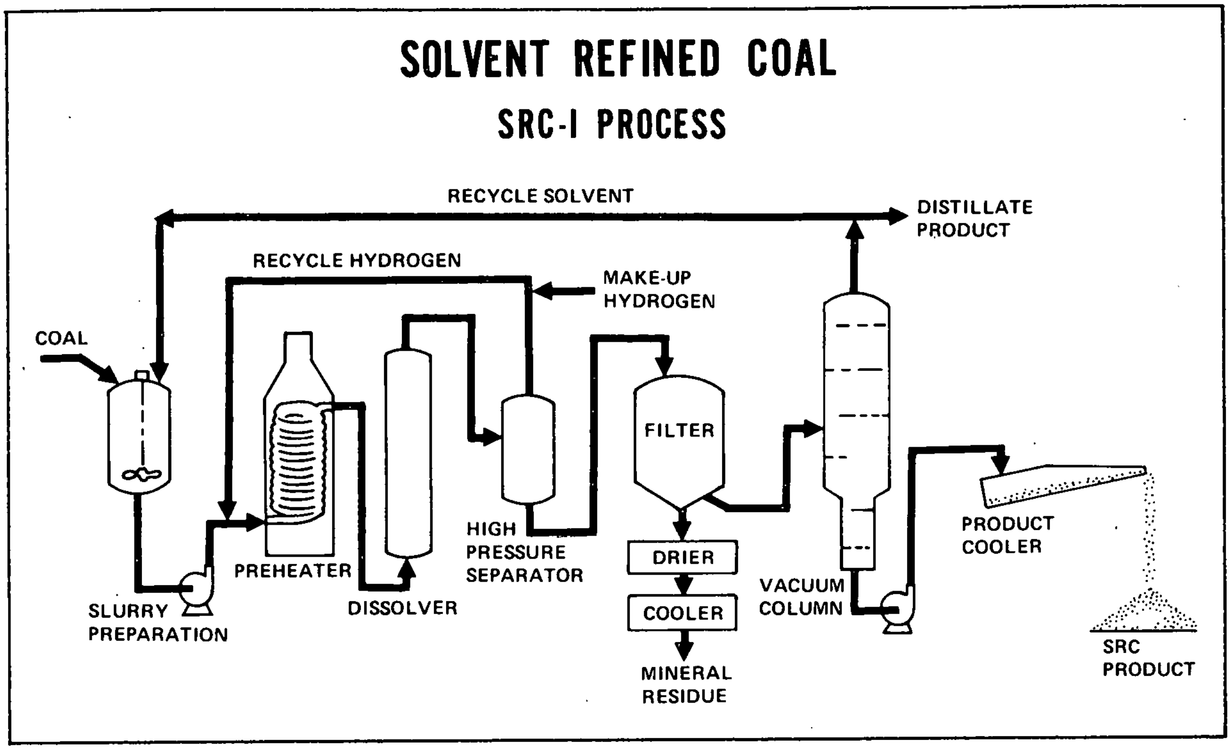
SOLVENT REFINED COAL
SRC-I PROCESS
RECYCLE SOLVENT
DISTILLATE PRODUCT
RECYCLE HYDROGEN
MAKE-UP HYDROGEN
COAL
FILTER
HIGH PRESSURE SEPARATOR
DRIER
COOLER
MINERAL RESIDUE
VACUUM COLUMN
PRODUCT COOLER
SRC PRODUCT
PREHEATER
SLURRY PREPARATION
DISSOLVER

FIGURE 2

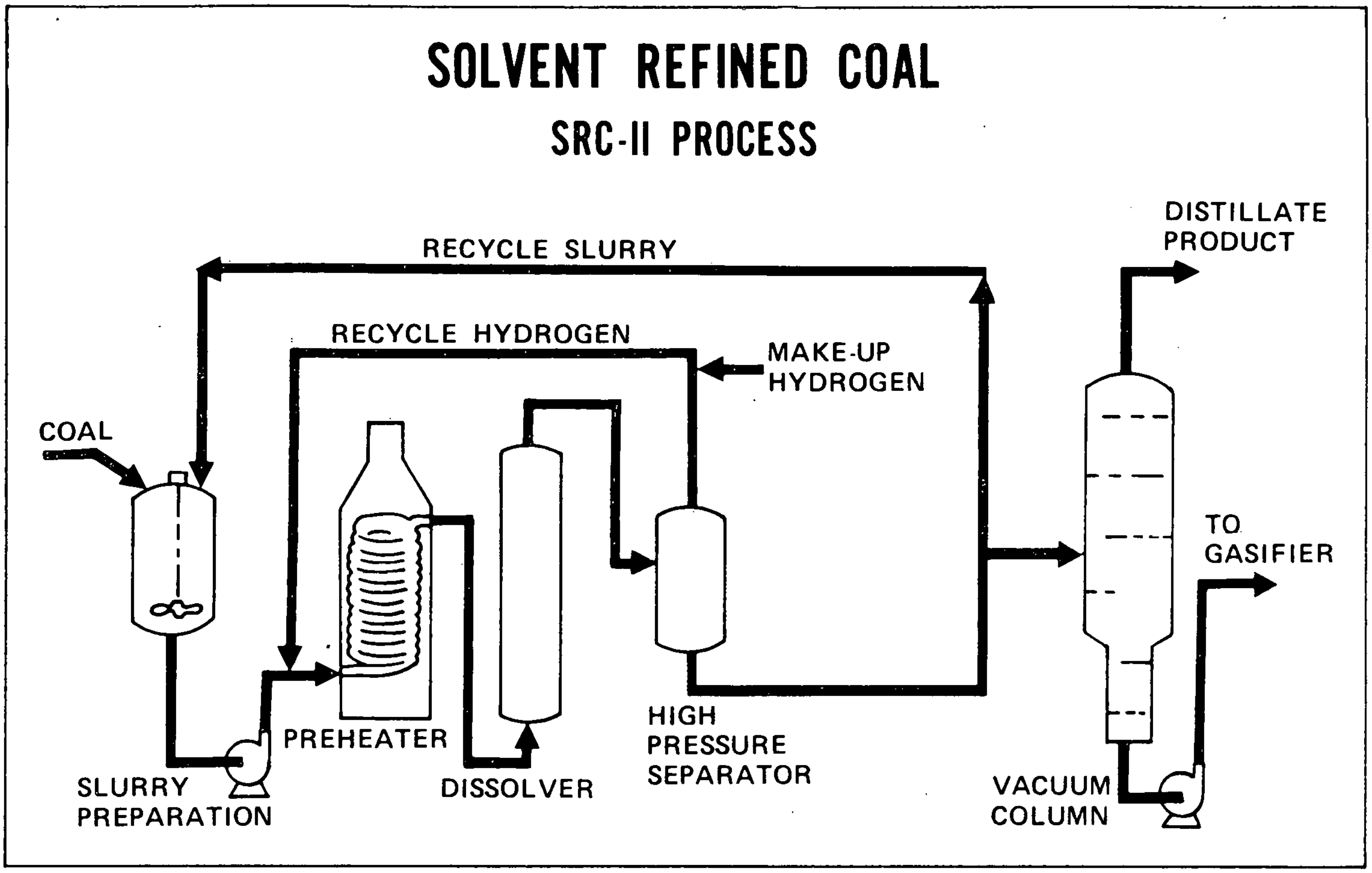
SOLVENT REFINED COAL
SRC-II PROCESS
RECYCLE SLURRY
RECYCLE HYDROGEN
MAKE-UP HYDROGEN
DISTILLATE PRODUCT
COAL
TO GASIFIER
PREHEATER
SLURRY PREPARATION
DISSOLVER
HIGH PRESSURE SEPARATOR
VACUUM COLUMN

FIGURE 3

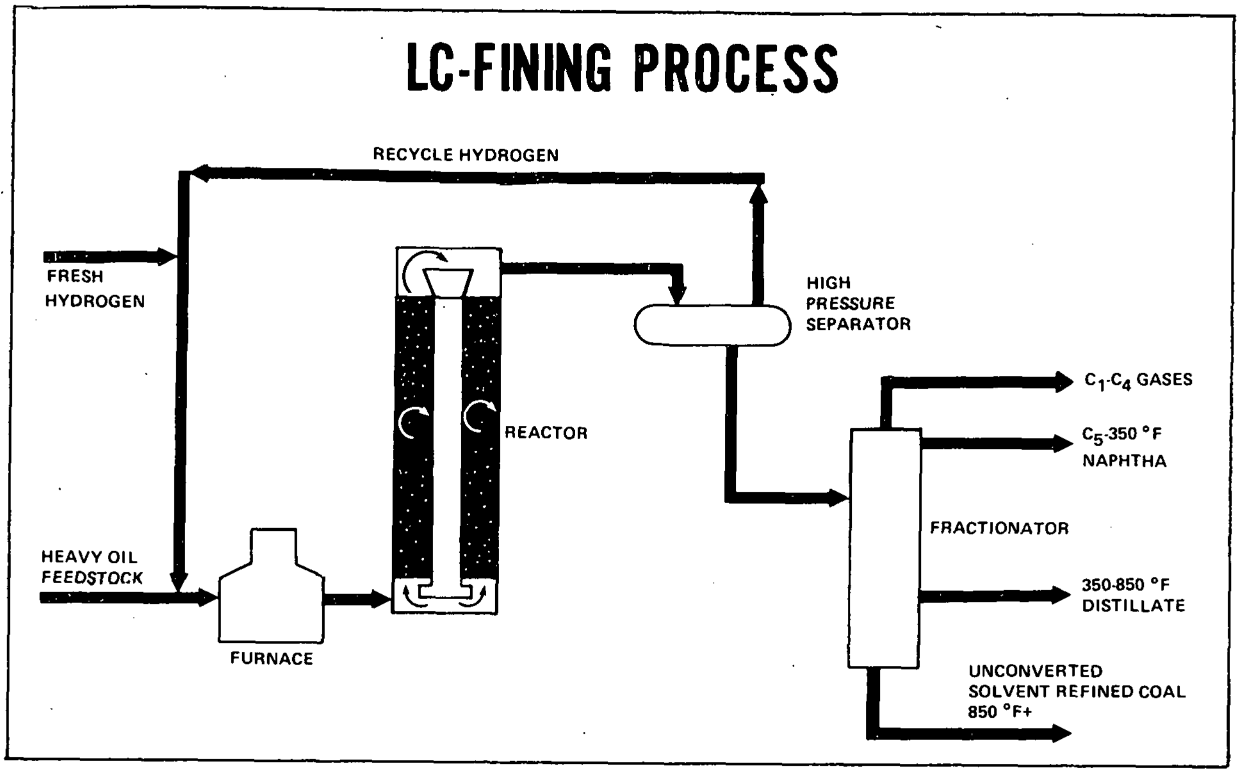
LC-FINING PROCESS
RECYCLE HYDROGEN
FRESH HYDROGEN
HIGH PRESSURE SEPARATOR
REACTOR
C1-C4 GASES
C5-350 °F NAPHTHA
FRACTIONATOR
HEAVY OIL FEEDSTOCK
350-850 °F DISTILLATE
FURNACE
UNCONVERTED SOLVENT REFINED COAL 850 °F+

FIGURE 4

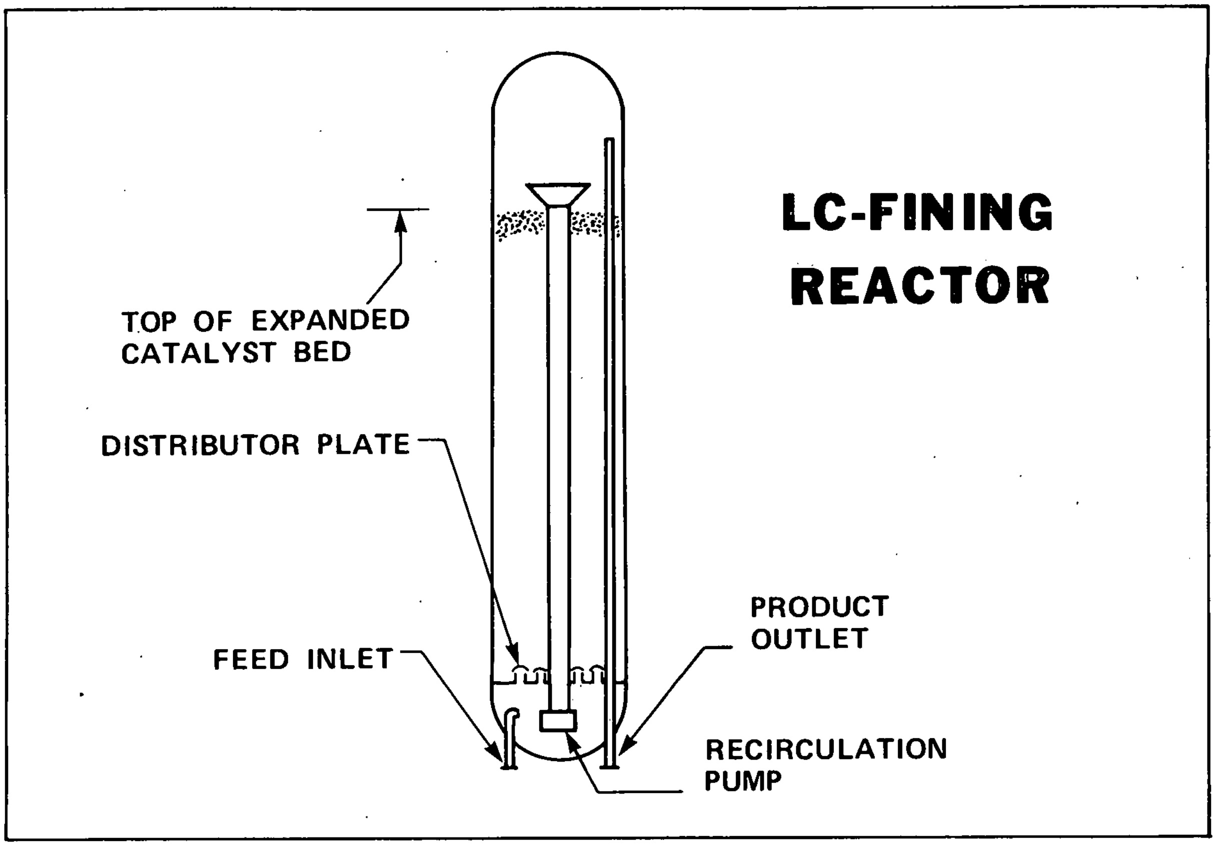
LC-FINING
REACTOR
TOP OF EXPANDED
CATALYST BED
DISTRIBUTOR PLATE
FEED INLET
PRODUCT
OUTLET
RECIRCULATION
PUMP

FIGURE 5

LC-FINING UNIT
PEMEX SALAMANCA REFINERY

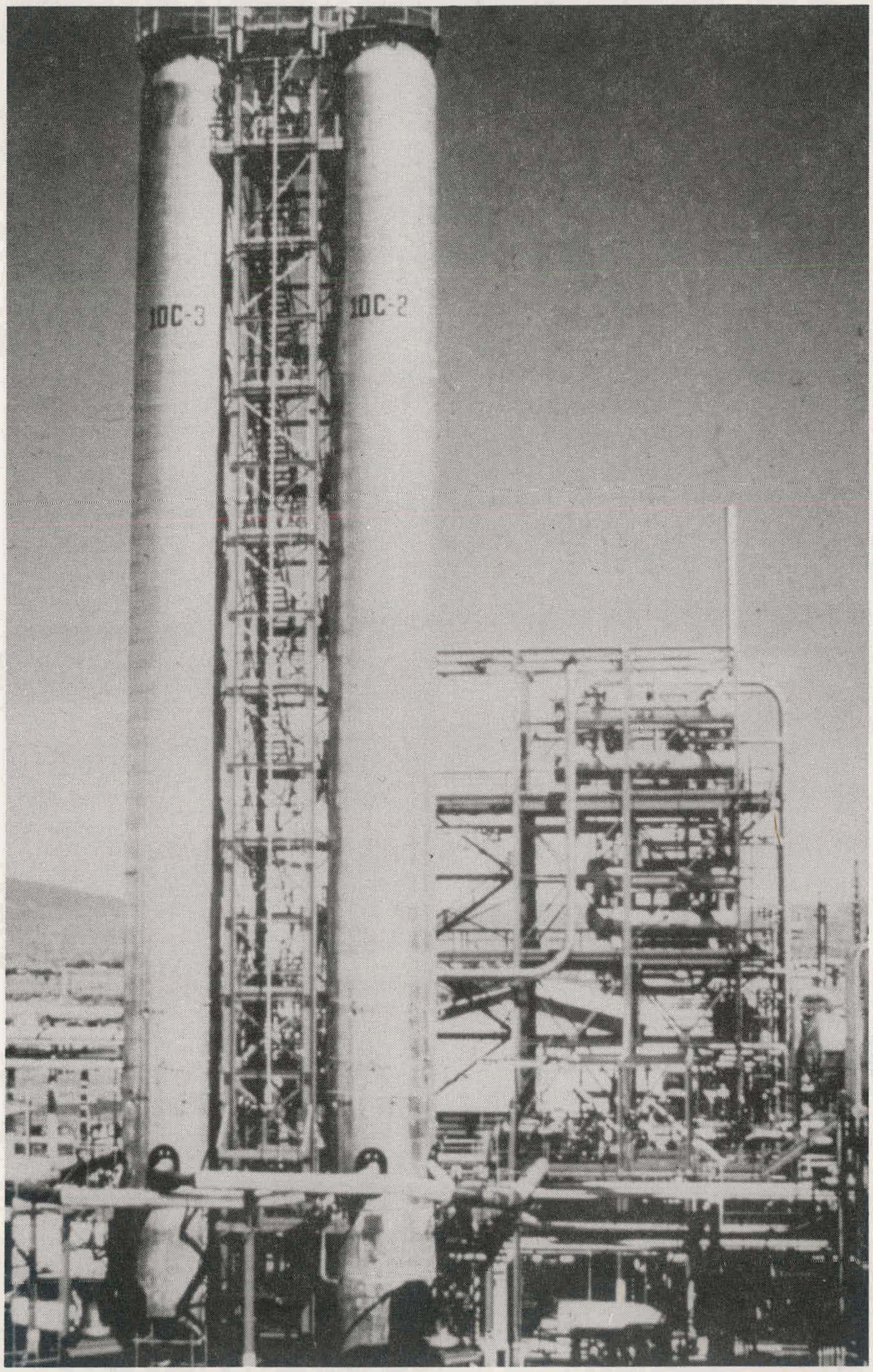

FIGURE 6

YIELDS ON MAF COAL CHARGED TO LIQUEFACTION

PROCESS COMPONENT	TSL WT.%	SRC-II WT.%
H_2	(3.8)	(4.8)
CO, CO_2	1.1	2.1
H_2S	2.5	2.6
NH_3	0.8	0.6
H_2O	8.4	6.0
C_1-C_4	12.4	18.4
C_5-350°F	9.3	11.3
350-850°F	30.5	29.4
850°F+	31.5	27.8
UNCONVERTED COAL	7.3	6.6
TOTAL	100.0	100.0
LB C_5-850 PRODUCED/100LB MAF COAL	39.8	40.7
LB C_1-C_4 PRODUCED/100 LB C_5-850 PRODUCED	31.2	45.2
LB H_2 CONSUMED/100 LB C_5-850 PRODUCED	9.5	11.8

TABLE I

TYPICAL ANALYSIS OF MF KENTUCKY NO. 9 COAL

ULTIMATE ANALYSIS

COMPONENT	WT.%
CARBON	70.6
HYDROGEN	5.0
OXYGEN	9.2
NITROGEN	1.4
SULFUR	3.4
ASH	10.4
TOTAL	100.0

TABLE II

SULFUR AND NITROGEN CONTENT WT.%

MAF COAL			SRC-I		TSL		SRC-II	
W% S	W% N	CUT	W% S	W% N	W% S	W% N	W% S	W% N
3.80	1.56	C_5-350°F	.45	.41	.20	.38	.27	.78
		350-850°F	.41	.64	.16	.53	.29	1.22
		850°F+	.85	2.05	.26	1.94	(1)	(1)

NOTES: (1) THIS MATERIAL IS NOT AN SRC-II PRODUCT

TABLE III

POTENTIAL DISPOSITION OF SYNFUELS

FRACTION	DISPOSITION	REMARKS
C_5-160°F	GASOLINE – LEADED REGULAR	• REQUIRES CAUSTIC WASH FOR PHENOL REMOVAL • REQUIRES CONVENTIONAL HYDROTREATMENT
160-400°F	REFORMER FEED	• THIS STOCK IS HIGH IN NAPHTHENES AND AROMATICS • REQUIRES CAUSTIC WASH • REQUIRES SEVERE HYDROTREATMENT
400-650°F	GAS TURBINE FUEL	• MEETS NO. 3-GT SPECIFICATIONS • A COMPATIBILITY PROBLEM WITH PETROLEUM STOCKS MAY EXIST.
650°F+	NO. 6 FUEL OIL	• MEETS SPECIFICATIONS • COMPATIBILITY PROBLEMS WITH PETROLEUM STOCKS LIKELY.

TABLE IV

ENERGY LOST IN HYDROGEN GENERATION

				BASIS 30,000 T/D MF COAL TO LIQUEFACTION	
CASE	PROCESS	CHEMICAL H_2 CONSUMPTION	H_2 PLANT OVERALL THERMAL EFF'Y	ENERGY LOSS IN H_2 GENERATION	VALUE OF ENERGY LOSS
		LB H_2/TON MF COAL		MMBTU/D	\$/D
I	TSL	68.6	67%	63,800	\$79,800
II	SRC-II	86.0	67%	80,000	\$100,000

TABLE V