OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

RESTRICTED 17205 JUNE 1988

COAL LIQUEFACTION (PHASE 2)

DP/CPR/83/002/11-54

CHINA

Prepared for the Government of China
by the United Nations Industrial Development Organization
acting as executing agency for the United Nations Development Programme

Based on the work of Mr. Thomas A. Torkos,
Expert in Two-Stage Liquefaction Processes
and Coal Liquefaction Process Technology

Backstopping Officer: R.O. Williams, Chemical Industries Branch

United Nations Industrial Development Organization
Vienna

---

* This document has been reproduced without formal editing

1L

RESTRICTED

April 22, 1988
English

TWO-STAGE LIQUEFACTION OF COAL
DP/CPR/83/002/11-54
CHINA

Technical Report: Coal Liquefaction Consultant (Two-Stage Liquefaction Processes)

Prepared for the Government of China by the United Nations Industrial Development Organization (UNIDO), acting as executing agency for the United Nations Development Program (UNDP).

Based on the work of Thomas M. Torkos, expert in Two-Stage Liquefaction Processes and Coal Liquefaction Process Technology.

United Nations Industrial Development Organization
Vienna, Austria

This report has not been cleared with the United Nations Industrial Development Organization (UNIDO), which does not necessarily share the views presented.

RESTRICTED

April 22, 1988
English

TRIP REPORT - CHINA

RESTRICTED

April 22, 1988
English

ABSTRACT

Project DP/CPR/83/002/11-54
April 8-18, 1988

This report covers a trip that included seven days in Beijing, China, for the purpose of strengthening and supporting the Chinese government's on-going research and development program in the area of direct coal liquefaction. This work is being carried out at the Central Coal Mining Research Institute (CCMRI) in Beijing. The author of this report served as a consultant in two-stage liquefaction techniques whose duties were:

1. To review their work program.

2. To review the U.S. Coal Liquefaction Program.

3. To give lectures and consultations on the following specific subjects:

    a. Short contact time reactions (Lummus ITSL)
    b. Refining of liquid product (Upgrading)
    c. Solid separation techniques

In addition to the above, the author was called on to discuss the on-going work in the U.S. on coal-oil coprocessing, in particular, the Clean Coal Technology project in coprocessing.

This report summarizes the events of my lecturing and consulting and is organized in a daily journal format for the period covered by this trip.

RESTRICTED

April 22, 1988
English

SUMMARY

This trip covered the period of April 8-18, 1988. My time in Beijing, China, was spent at the Central Coal Mining Research Institute, in particular, the Beijing Research Institute of Coal Chemistry. My duties were covered by DP/CPR/83/002/11-54 and involved my serving as a consultant in two-stage coal liquefaction techniques. This particular assignment is supported by the United Nations Industrial Development Organization (UNIDO), acting as executing agency for the United Nations Development Program (UNDP), reviewing the Chinese government's present research and development program on coal liquefaction being carried out at the CCMRI.

The purpose of this assignment was to provide CCMRI with the technical background and results on the two-stage liquefaction developed in the U.S. This information could then be used by the Chinese to develop their long range R&D program.

On the first day, I was given a tour of the CCMRI's Beijing Research Institute of Coal Chemistry (BRICC) research facilities, with discussions following the tour on the Chinese direct coal liquefaction projects. The main facilities include three bench-scale facilities described in detail by Mr. James Lacey, Coal Liquefaction Technical Advisor, in his trip report to BRICC. The Japanese and German units have both operated successfully on coal. The products generated in these facilities have been analyzed in their instrumentation laboratory at BRICC. The U.S. unit is used for coal-liquids upgrading studies. None of the facilities were in operation during my facility tour. I spent the next four days lecturing on coal liquefaction in the morning and discussing the lectures in the afternoon.

RESTRICTED

April 22, 1988
English

TABLE OF CONTENTS

Page

Introduction.. 1

Discussion.. 2

April 8, 1988.. 2
April 9, 1988.. 2
April 10, 1988... 2
April 11, 1988... 2
April 12, 1988... 2
April 13, 1988... 3
April 14, 1988... 3
April 15, 1988... 3
April 16, 1988... 6
April 17, 1988... 6
April 18, 1988... 7

Conclusions... 8

Recommendations... 9

APPENDIX A

APPENDIX B

RESTRICTED

April 22, 1988
English

INTRODUCTION

The period covered in this report is April 8-18, 1988. I served as a consultant in two-stage coal liquefaction to strengthen and support the direct coal liquefaction research and development program at the Central Coal Mining Research Institute (CCMRI), Beijing. In this capacity, I gave lectures at the Beijing Research Institute of Coal Chemistry (BRICC) which is one of the separate institutes that makes up CCMRI. Subjects of the lectures included: (1) a brief overview of the U.S. Department of Energy's Pittsburgh Energy Technology Center's (PETC) coal program; (2) the U.S. National Coal Liquefaction Program; and (3) the development of two-stage liquefaction technology in the U.S. In addition to the lectures, I held discussion sessions with key scientists and engineers at BRICC on specific aspects of two-stage liquefaction, including short contact time reactions, refining of liquid products, solid separation techniques, and various two-stage liquefaction processes. Considerable interest was expressed during the discussion sessions on the coal-oil coprocessing activities in the U.S., in particular, the clean coal technology project of Ohio Ontario Clean Fuels, Inc.

DISCUSSION

This section is organized on a daily journal basis.

Day 1 - Friday, April 8, 1988

I left Pittsburgh, Pa. (U.S.A.) and flew to Tokyo, Japan.

Day 2 - Saturday, April 9, 1988

I arrived in Tokyo for a scheduled overnight stay.

Day 3 - Sunday, April 10, 1988

I left Tokyo and flew to Beijing and was met at the airport by Madame Lei Xiangqin, Scientist and Interpreter for CCMRI, working at the Beijing Research Institute for Coal Chemistry (BRICC). She was the key link to the CCMRI during my stay in Beijing and a gracious host. I was taken to the Kunlun Hotel where I stayed while in Beijing.

Day 4 - Monday, April 11, 1988

This day was spent touring the facilities at the BRICC. Upon arriving at the BRICC, I met with several key people at the Institute. They were:

1. Mr. Wu Chun Lai, Deputy Director of BRICC
2. Mr. Li Shilun, Chief Engineer of BRICC
3. Mr. Shi Shidong, Supervisor of Liquefaction Research at BRICC
4. Mr. Jin Jialu, Vice-Supervisor of Liquefaction Research at BRICC
5. Mr. Tian Xi Gui - Senior Engineer at BRICC
6. Mr. Song Zhao - Engineer on the Coal Liquefaction Units at BRICC

(Messrs. Wu and Tian along with Madame Lei visited PETC on March 10-11, 1988)

There was no need to describe the facilities at the BRICC because this was included in Mr. Lacey's report submitted to Mr. Robert Williams on December 10, 1987.

After the tour we discussed the plans for the remainder of the week.

Day 5, Tuesday, April 12, 1988

This day was spent briefing the staff of BRICC on the Pittsburgh Energy Technology Center (PETC), in particular, the U.S. DOE/PETC Coal Liquefaction Program. During these lectures many questions were raised with respect to coal-oil coprocessing and the U.S. DOE Clean Coal Technology Project sponsored by Ohio Ontario Clean Fuels, Inc. I was asked why DOE was conducting research on coprocessing when this commercial plant would be ready for operation by 1990. I explained that this project required additional process development testing and was specific to a particular set of coals and oils (petroleum residua). The DOE objective in continuing to do research on coprocessing is to develop an extensive technology data base on many coals and residua. I also explained that coprocessing is a transition technology where coal processing can be introduced into the existing petroleum refining infrastructure on a near term basis and thus provide a link to future coal liquefaction commercialization. Mr. Wu expressed a great deal of interest in this technology.

Day 6, Wednesday, April 13, 1988 and Day 7, Thursday, April 14, 1988

These two days I lectured specifically on two-stage liquefaction technology including the following:

1. Background
2. Various process concepts and configurations
3. Solids separation techniques employed
4. Catalyst develop supporting two-stage liquefaction
5. Upgrading/refining of coal liquids from two-stage coal liquefaction
6. Biological testing of liquids
7. Solvent quality
8. Economic assessment studies
9. Wilsonville Programs

Included as Appendix A is the paper I used for the lectures on Wednesday and Thursday. I also brought along additional papers supporting the technical areas listed above. I provided these papers for homework to the staff for Friday's discussion session. These documents covered two-stage liquefaction from 1980 till 1988 as presented at the PETC Contractors' Review Meetings. Appendix B lists those documents.

Day 8, Friday, April 15, 1988

This entire day was spent addressing questions generated from the lectures and from the supporting documents. Highlights, in the form of questions and answers, are presented below.

1. Solids Separation Techniques

   What is the best approach to solids separation for two-stage liquefaction?

   Currently the Kerr-McGee Critical Solvent Deashing (CSD) process, which has been operating successfully at the Wilsonville Facility, is a likely candidate. However, with further improvements in liquid product quality expected in two-stage liquefaction, other approaches may prove to be equal or better than the CSD process. For example, filtration which proved to be unsatisfactory on earlier single-stage processes may now work. HRI currently uses pressure filtration successfully for their bench-scale unit in a batch mode. Coking of bottoms product may also prove to be satisfactory for improved two-stage processes. Future research is required to answer this question fully. Vacuum distillation by current thinking is a means to the end and not the final step in solids separation. In addition, liquefaction bottoms material is thought to be too valuable (i.e., the hydrogenated organic material) to be used to generate hydrogen required for the liquefaction process and gasification of coal is the envisioned route.

2. Catalysts

Does the recycled ash in the ashy recycle mode hurt the catalyst? Both Lummus ITSL work and Wilsonville work showed no detrimental effects of the recycled ash.

NiMo catalysts may be too costly for use in China. Are there any suitable replacements? Currently the NiMo catalysts are the best for the catalytic two-stage liquefaction (CTSL) process; however, catalyst research will continue to search for alternatives. (This may be an area for joint cooperation between the U.S. and China.) Economic studies in the U.S., based on normal catalyst consumption, do not indicate the catalyst costs have a major impact on coal liquefaction economics. The high liquid yields overcompensate for all increased costs associated with CTSL (i.e., capital and operating costs associated with two catalytic reactors).

What is the difference between Shell 324 and 317?

Shell 324 is unimodal and 317 is bimodal.

The Germans claim to get 60% distillate yield with their process. How does the German process, which uses a disposable iron catalyst, compare with CTSL?

We have not received much information on the German Process and therefore, it would be difficult and probably unfair to comment on their process. However, several questions could be asked:

- The impact of a high pressure operation on economics (German)?
- Quality of liquid product, particularly the boiling range?
- Complexity of operation?
- Effectiveness of disposable iron catalysts?
- Increased solids handling and separation?

Considering all the above, the disposable catalyst system may be a best compromise for specific coals and economies.

3. Coal Cleaning

Coal cleaning may be a problem with some high ash (25%) Chinese coals. Water washing does not reduce ash significantly. The highest distillate yield at both HRI and Wilsonville was obtained on cleaned coals. Could you comment on this?

Coal cleaning certainly has been shown to enhance distillate yield in two-stage liquefaction and further research is required to integrate coal cleaning with coal liquefaction. Advanced physical coal cleaning techniques at the laboratory scale (such as selective agglomeration and froth flotation) have been shown to be significant improvements over existing technology, especially over coal washing. This may be a possible area for research on Chinese coals (another possible area for joint cooperation between the U.S. and China).

4. Process Concepts

HRI operates their Catalytic Close Coupled Two-Stage Liquefaction (CCTSL) with a low temperature in the first stage and a higher temperature in the second stage, where as at Wilsonville it is just the opposite. Which way is the best?

As noted in the information presented in the lectures, comparably high liquid yields were obtained at both HRI and Wilsonville indicating that either approach may work. However, Wilsonville at the present, cannot preheat material going into the second stage; therefore, it must be at a lower temperature due to heat loss. HRI's bench-scale reactors are electrically heated, which allows for a higher second reactor temperature. Also, HRI uses batch pressure filtration and Wilsonville uses the CSD process for solid separation. This difference may have some impact on the quality of the recycle solvent at the two facilities; however, the net result appears to be the same.

5. Coal-Oil Coprocessing

What is the best petroleum residuum and coal combination for coal-oil coprocessing?

It is not the objective of the DOE coal liquefaction program to determine the best combination, but it is rather to provide an extensive data base for coprocessing. There are many combinations that will work; however, specific combinations must be tested in a bench-scale unit to insure synergistic effects. Coprocessing of residuum containing a high concentration of metals (e.g., Ni, Va) with coal has been shown to significantly reduce metals content of resulting distillate products.

6. Subbituminous Coal

Why is it more difficult to process subbituminous in two-stage liquefaction?

For close-coupled catalytic two-stage liquefaction (CCCTSL), equally successful operation (high distillate yield) was obtained from both subbituminous and bituminous coal. Earlier thermal-catalytic two-stage processes did have difficulty processing subbituminous coal (i.e., ITSL), and a disposable iron catalyst or high severity operation was required in the first stage to get good liquid yields. Most likely this was due to the higher level of contaminants in subbituminous coal (e.g., ash, moisture, oxygen, etc.). However once this was overcome, the residuum produced from subbituminous coal was very reactive recycle material.

7. Ebullated Bed Scale-Up

What risk is involved in scaling up the ebullated bed technology?

This technology has already been scaled up for petroleum feedstocks (i.e., LC Fining and H-Oil processes); however, for coal processing, it has only been scaled up to the 200-600 T/D size at the H-Coal Pilot Plant. Thus, some risk would be involved as with any process scale-up, but testing in a process development unit (PDU, 5-10 TPD) would certainly reduce the risk for specific feedstocks.

8. Engineering Design

We are interested in an engineering design for two-stage liquefaction. Does one exist?

Engineering design bases that exist in the U.S. for two-stage liquefaction are based on work done in the late 1970s and early 1980s for single-stage liquefaction processes. This area has been neglected over the last several years partly due to lack of funds and committment of the U.S. industry to develop liquefaction technology. Renewed interest now exists in the U.S. and plans have been made to develop an engineering design basis for two-stage liquefaction in the very near future.

Day 9, Saturday, April 16, 1988

A day of rest and sight-seeing was in order after the extensive technical sessions.

Day 10, Sunday, April 17, 1988

This day was spent in transit flying from Beijing to Tokyo for a scheduled overnight stay.

Day 11, Monday, April 18, 1988

This was the final day of my trip. I flew from Tokyo to Pittsburgh, Pa. (U.S.A.).

CONCLUSIONS

During my stay in Beijing (April 11-15, 1988), it became apparent to me that the scientists and engineers at BRICC were knowledgeable in coal liquefaction technology and the information I provided through lectures, discussions, and reports should provide a basis for them to develop a program in two-stage liquefaction. It was also apparent that CCMRI/BRICC lacks the resources, both in funds and equipment, to execute an aggressive program in two-stage liquefaction in the near future unless the government provides additional resources. This problem may be reduced somewhat by the recently established International Association for the Promotion of Science and Technology in Beijing. The objective of the association is to "promote the country's scientific and technological development, facilitate the integration of science with economic development, and expand international scientific and economic cooperation." According to Mr. Wu, the Chinese goal in liquefaction is the same as the U.S., that is, maximize the production of transportation fuels. Thus, it seems that future cooperation between the U.S. and China may benefit both countries.

RESTRICTED

April 22, 1988
English

RECOMMENDATIONS

Based on the discussions with the staff of BRICC, the following recommendations have been made:

1. Periodically review the progress achieved by CCMRI/BRICC in two-stage coal liquefaction through visits and consultations (probably on an annual basis). This would include the review of their long-range coal liquefaction program under development.
2. Exchange any technical information reports that may be available in English.
3. Develop a cooperative program in coal liquefaction between CCMRI/BRICC and PETC, which would benefit both countries in future developments. This should be in accordance with the U.S./China International Agreement established between the U.S. Department of Energy and the Ministry of Coal Industries (now part of the New Ministry of Energy Resources established during the Seventh National People's Congress). This could include other related technologies such as coal preparation.

APPENDIX A

DEVELOPMENT OF TWO-STAGE LIQUEFACTION OF COAL

Prepared for

U.S. Department of Energy
Pittsburgh Energy Technology Center

Prepared Under

Burns and Roe Services Corporation
Contract No. DE-AC22-87PC79338
Subtask 3.01 (FY88)

April 1988

DEVELOPMENT OF TWO-STAGE LIQUEFACTION (TSL) OF COAL

Prepared for
U.S. Department of Energy
Pittsburgh Energy Technology Center

Prepared by
S.N. Rao
Burns and Roe Services Corporation
and
H.D. Schindler
Science Application International Corporation

April 1988

DISCLAIMER

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

FOREWARD

This work was performed as an assignment by T. Torkos for his presentation in China. Participants in various activities associated with this task are given below:

PETC

Subtask Manager - G. McGurl
Technical Coordinator - T. Torkos

BRSC/SAIC

Subtask Manager/Coordinator - S.N. (Roger) Rao

TABLE OF CONTENTS

Page

I. INTRODUCTION 1

II. BACKGROUND 1

A. Early Research and Development 1

1. Pre-World War I Work 1
2. Pre-World War II Processes 2
3. Early Commercialization of Coal Liquefaction 3
4. Post World War II Development 4

B. Single Stage Processes Preceding ITSL Development 6

1. H-Coal 6
2. Solvent Refined Coal (SRC-I) 9
3. Exxon Donor Solvent (EDS) 11
4. SRC-II 13
5. Economic Comparison of the Four Liquefaction Processes 14
6. Features of Single Stage Processes - Summary 15
7. Non-Integrated Two-Stage Liquefaction (NTSL) 16

III. DEVELOPMENT OF THERMAL INTEGRATED TWO-STAGE LIQUEFACTION 18

A. Earlier Studies 18

B. Lummus ITSL (1980-1984) 18

1. Process Features 19
2. Features of SCT 19
3. Features of the Second Stage Hydrotreater (HTR) 20
4. Antisolvent Deashing (ASDA) 22
5. Overall Results of ITSL 23

C. Wilsonville ITSL (1982-1985) 24

1. Scale-Up of Lummus ITSL 25
2. Modifications to ITSL 26
3. Reconfigured Two-Stage Liquefaction (RITSL) 26
4. Close-Coupled ITSL (CCITSL) 28
5. Operations with Subbituminous Coal 28

IV. DEVELOPMENT OF CATALYTIC TWO-STAGE LIQUEFACTION (CTSL) 29

A. HRI CTSL (1982-Present) 29

1. Background 29
2. Features of CTSL Process 29
3. Overall Results of HRI CTSL 31

TABLE OF CONTENTS, (Continued)

Page

B. Wilsonville CTSL (1985-Present).......................... 31

C. Evolution of Liquefaction Technology..................... 32

V. ECONOMICS OF TSL PROCESSES................................ 32

VI. FUTURE CTSL PROGRAM AT WILSONVILLE........................ 33

A. Lignite Feed... 33

B. Deep Cleaning of Coal.................................... 34

C. Testing Alternative Deashing Procedures.................. 34

D. Gas Oil Recycle to Extinction............................ 34

E. Coprocessing of Coal and Petroleum Resid................. 35

F. Solvent Quality.. 35

G. Catalyst Development..................................... 35

VII. CONCLUSION.. 36

Tables.. 37-54

Figures... 55-71

DEVELOPMENT OF TWO STAGE LIQUEFACTION (TSL) OF COAL

I. INTRODUCTION

Two Stage Liquefaction (TSL) has been under development in the U.S. since 1980. During this time, the process has continuously evolved to the present two-stage catalytic configuration, which produces the highest liquid yield and product quality of any process worldwide. TSL has been successfully applied to bituminous and subbituminous coals, overcoming problems associated with earlier processes. New information from laboratory studies is providing fundamental understanding of coal reactivity and hydrogen transfer that will lead to significant improvements and an even superior process in the future.

II. BACKGROUND

A. Early Research and Development

1. Pre-World War I Work

The earliest reference to coal liquefaction technology refers to the work of Bertholet who in 1869 treated coal with hydroiodic acid at 518°F (270°C) for 24 hours and obtained liquid yields of about 60%. Similar results, i.e., liquefaction of solids, was also obtained with dried wood and partially carbonized wood; however coke and graphite could not be converted.

In 1911, Bergius, who was a co-worker with Haber (who developed high temperature, high pressure ammonia process), conducted the first work involving the hydrogenation of coal at 662°F (350°C) and at 1500 to 3000 psig pressure in the absence of a catalyst and applied for the first patent in 1913. Evaluating different coals, Bergius found that younger coals such as lignite, brown coal and bituminous coals gave higher oil yield than from the older coals such as anthracite. He also observed that by the addition of Luxmasse (mixture of iron, aluminum and titanium oxides) to a mixture of equal parts of coal and heavy oil, the sulfur in the coal converted to iron sulfide. Although, Bergius tried to establish a industrial scale unit, because of World War I no progress was made.

2. Pre-World War II Processes

Following World War I, a 30 tons/day pilot plant was constructed in 1921 for hydrogenating petroleum and coal tars. In 1924, the British Bergius Syndicate was formed to employ his coal hydrogenation patent and evaluated over 200 British coals for liquefaction. He used ferric oxide as an aid to remove sulfur. By 1927 Bergius had demonstrated the operability of commercial coal liquefaction in a single stage. The gasoline yield was small and quality was not good compared to gasoline from petroleum.

Till 1923, all hydrogenation catalysts were considered to be poisoned by sulfur. However, in 1924, at BASF laboratories, Pier prepared sulfur resistant catalysts from oxides of Molybdenum, Tungsten, Iron and other metals. This led to the first brown coal tar hydrogenation in vapor phase using molybdenum and zinc oxide catalysts to produce white gasoline but serious deactivation of catalyst occurred. By first separating the coal tars into middle distillates (B.P. below 617°F (325°C), and then hydrotreating this distillate in the presence of a catalyst to produce motor fuels became a suitable practice in 1926.

Hydrogenation of tars (from brown coal) with very low concentrations of coal and high concentrations of finely ground molybdenum suspensions in the feed stock was found to maintain reasonable activity at 3000 psig and temperatures less than 842°F (450°C). At more severe conditions, i.e., higher coal flow, temperature, or pressure, the slurry phase reactor performance and catalyst activity deteriorated drastically. Regeneration was not successful. As a result, search for other catalysts continued.

During this period, coal liquefaction technologies developed in Germany and the most notable process is the Pott-Broche process which began in 1927. This was a two stage process where the coal was initially liquefied at 1450 to 2200 psi, 780°F (415°C) to 806°F (430°C) and one hour residence time. The filtered products were further hydrogenated in the liquid phase using a supported metal catalyst. Difficulties in filtering and the poor quality of products did not allow development to a commercial process but, this technology served as the basis for many processes that are currently being developed.

3. Early Commercialization of Coal Liquefaction

The commercial coal liquefaction industry began in 1927 in both Germany and Britain. In Germany the Leuna plant for the hydrogenation of brown coal using molybdenum oxide catalyst was constructed and operated at 4500 psig. Eventually, in 1934, iron catalyst replaced molybdenum catalyst and operated at 10,000 psig. This plant was producing about 1000 tons/day of motor fuel from brown coal and coal tar. Due to the war effort, by 1943, there were 12 coal liquefaction plants producing over 12,000 tons/day of motor fuel.

International agreement between Standard Oil of New Jersey and I.G. Farbenindustrie, in 1927, and the establishment of Technical Oil Mission in 1941 significantly improved the flow of information on the hydrogenation of coal and coal tar. Concurrent with the development in Germany, substantial coal and coal tar hydrogenation effort was proceeding in France, Great Britain, Japan and the United States. However, the only commercial plant outside of Germany was in Billingham, Great Britain. The plant utilized bituminous coal to produce 100,000 tons of gasoline per year and operated at a pressure of 4000 psig. Tin oxalate and iodine were employed as catalysts. To limit corrosion, the catalyst concentration was kept low. This plant remained in operation until 1958.

Several smaller pilot plants or PDU's were constructed outside Germany and Great Britain. A 50 tons/day facility was constructed in France which operated at 4500 psig. Two plants designed for operation at 3000 psig and a capacity in the range of 35-70 tons/day were constructed in Asia but they never operated satisfactorily. In 1928, Standard Oil of New Jersey constructed a 100 Bbl/day plant at Baton Rouge, La. and in 1931 built two other plants, one at Bayway, N.J. and another at Baton Rouge, La.

4. Post World War II Development

In the late 1940's, the number of oil fields discovered in U.S. decreased for the first time. A major emphasis was thus placed on the conversion of coal to liquid fuels. This effort was headed by Bureau of Mines in Pittsburgh. Since 1924 the Bureau had substantial interest in coal liquefaction R&D on a small scale with batch autoclaves and continuous flow reactors. However, with the passage of Synthetic Fuel laws in 1944 and 1948 the Bureau's program expanded in scale to a semicommercial coal liquefaction plant producing 300 Bbl/day of gasoline. The plant was built at Louisiana, Mo. and was designed for operation at

10,000 psig. It started operation in 1949 and shut down in 1954.

A second liquefaction plant with a capacity of 300 tons/day of bituminous coal was constructed by Union Carbide at Institute, W.Va. This plant designed for operation at 842 to 1022°F (450 to 550°C) and 3000 to 6000 psig and a residence time of 4 to 5 minutes, operated during the period 1952-56. With no substantial improvements in catalysts, reactor design or quality of products, and increased petroleum production, commercial interest dwindled. During the rest of 1950s, both inside and outside of the U.S., only laboratory and bench-scale work was performed.

A renewal of interest in coal liquefaction started in 1962, with the establishment of Office of Coal Research and the development of Solvent-Refined Coal (SRC) process by the Spencer Chemical Co. With the development of the SRC process which is non-catalytic, several catalytic processes came under development during the 1960's. These include Lummus' Clean Fuels From Coal (CFFC) process, Bureau of Mines Synthoil Process, Consol's Synthetic Fuel (CSF) process, Hydrocarbon Research Inc's H-Coal process, Exxon's Donor Solvent Process, etc. Except for CSF, which is more like the Germany's two stage process (Pott-Broche), all the others are single stage processes.

Some of these processes had operational or process-related difficulties so that development was abandoned. The others, H-Coal, EDS, and the SRC-I and SRC-II processes continued to be developed through the 1970's.

B. Single Stage Processes Preceding TSL Development

The two stage approach is built upon the experience in direct liquefaction that had been accumulated in the U.S. for close to thirty years of development of single stage processes. To understand the evolution of the Two Stage Liquefaction (TSL) technology to its current state, the contribution of the major single stage processes will be discussed in the following sections.

1. H-Coal

This is a direct catalytic coal hydroliquefaction process invented in 1963 by Hydrocarbon Research, Inc. (HRI). Development of the H-Coal process proceeded through conceptual stages to bench-scale (25 lbs/day) and Process Development Unit (PDU) (3 tons/day) studies. The work culminated in the construction and operation of the H-Coal Pilot Plant, a 200-600 ton per day facility in Catlettsburg, Kentucky. This was a $300 million project funded by DOE, the Commonwealth of Kentucky, EPRI, Mobil, Amoco, Conoco, Ruhrkohle, Ashland Oil, Sun, Shell and Arco. The project started in 1973 with preliminary design and laboratory studies and continued through final design, construction and a 36-month operating period, which ended in January 1983. During pilot plant operation, data necessary for the design, environmental permitting, construction and operation of a pioneer commercial H-Coal facility were obtained.

The key component in the H-Coal process (Figure 1) is the ebullated-bed reactor (see Figure 2). Pulverized coal, recycle liquids, hydrogen and a catalyst are brought together in the reactor to convert the coal into hydrocarbon liquids and gaseous products. This single step converts the coal slurry feed to distillate products in the Syncrude operating mode, and to distillate products and low-sulfur deashed residuum in the Boiler Fuel mode. The Syncrude mode products are suitable for use as refinery feedstocks to produce gasoline and low sulfur distillate fuel, or the distillates can be used "as is" for a low-sulfur fuel. The Boiler Fuel mode products are suitable principally for use in low-sulfur utility boiler markets, although some lighter products such as naphtha are suitable as refinery feedstocks.

Program funding and schedule constraints prevented operation of the Catlettsburg pilot plant in the Boiler Fuel mode.

The catalyst particles in the H-Coal reactor are 0.8- to 1.5-mm diameter extrudates, which are fluidized by the upward flow of liquid and gas. This fluidization enables the hydrogenation exotherm to be distributed uniformly over the entire reactor volume and allows the ash and unconverted coal to flow through the reactor without causing interparticle plugging of the catalyst. In addition, catalyst addition and withdrawal is performed in a manner similar to fluid catalyst so that a constant catalyst activity is maintained and temperature staging is not required to compensate for deactivation.

The pasting, or recycle, solvent is obtained from hydroclone separation and vacuum distillation. The ash and unconverted coal are removed with the pumpable vacuum tower bottoms.

The H-Coal process embodies several unique features and advantages:

a. Coal dissolution and upgrading to distillate products are accomplished in one reactor;

b. Products have a high H/C ratio and low heteroatom content as the result of catalytic hydrogenation;

c. A high throughput of coal is achieved due to the rapid catalytic hydrogenation rates;

d. Ash is removed by vacuum distillation, followed by gasification of the vacuum tower bottoms to generate the hydrogen requirement of the process.

H-Coal, however, has several shortcomings:

a. The high reaction temperature 833 to 851°F (445-455°C) results in excessive thermal cracking and consequently high (12-15%) hydrocarbon gas yields.

b. The hydrogen consumption is high relative to the liquid yield. Some distillate product, in the vacuum tower bottoms, is gasified to satisfy the pumping and hydrogen production requirements of the process.

c. The product includes considerable vacuum gas oil (650-975°F b.p.). Subsequent tests by Chevron showed that this material would be difficult to upgrade by standard refinery processes. It, therefore, has utility solely as a boiler fuel.

Like all single-stage processes, H-Coal is best suited for high-volatile, bituminous coals. Although it was applied to subbituminous coal, the coal throughput had to be reduced and distillate yield was considerably lower than the bituminous coals. Typical H-Coal yields for bituminous coals are shown in Table 1. The composition of the coal feed is shown in Table 2.

Although H-Coal development has ceased, the ebullating bed reactor has become an integral part of all TSL flow configurations.

2. Solvent Refined Coal (SRC-1)

In 1962, the Spencer Chemical Company began to develop a process which was later taken up by Gulf, who in 1967, designed a 50 ton per day SRC pilot plant at Fort Lewis, Washington. The plant was operated in the SRC-I mode from 1974 until late 1976.

In 1972, Southern Company Services, Inc. (SCS) and Edison Electric Institute designed and constructed a six ton per day SRC-I pilot plant at Wilsonville, Alabama. This plant is still in operation, generating valuable design data and providing large samples of product for test purposes; but it no longer operates in the original SRC-I (solids product) mode.

The primary product in the original SRC-I process is a solid with a melting point of about 300°F and a heating value of 16,000 Btu/lb. In the interest of enhancing commercial viability, during the early stages of the Demonstration Project an expanded product slate with liquids that included the products of a Coker/Calciner, an Expanded-Bed Hydrocracker and a Naphtha Hydrotreater was also added.

SRC-1 is a thermal liquefaction process wherein solvent, coal, and hydrogen are reacted in a "dissolver" reactor to produce a non-distillable resid (or extract), which upon deashing can be used as a clean boiler fuel. Reaction conditions are only slightly less severe than in H-Coal, however, the absence of a catalyst diminishes hydrogenation rates, so that the product is a 842°F+ resid. This resid has H/C ratio about the same as the coal feed; all of the net hydrogen reacted goes into hydrocarbon and heterogases. The solvent is a heavy distillate that is recovered by vacuum distillation. In addition, some of the bottoms feed to the deasher may also be recycled (see Figure 3).

The process is most successful with bituminous coals, especially those that contain high concentrations of pyrite. The pyrite is considered to be the liquefaction "catalyst". In the absence of pyrite-laden ash, as is the case for all subbituminous coals, additional pyrite is required as a disposable catalyst in the slurry feed in order to maintain conversion and good operability.

The process had technical and economic drawbacks. The all-distillate solvent was often of poor quality, i.e., its ability to shuttle hydrogen from the gas to coal was insufficient to prevent coking or precipitation of heavy product, usually within the preheater to the dissolver. Solvent was often incorporated into the resid product, so that solvent balance could not be maintained. When reaction conditions were moderated, production of toluene-insolubles increased and precipitation ensued in equipment downstream of the reactor.

At first, SRC-1 economics appeared attractive because of the simpler reactor system. However, liquefaction plants have many process and non-process units, of which the reactor is but one and these contribute significantly to the economics. In addition, SRC-1 requires a more expensive deashing system. Ultimately, the low market value of the boiler fuel product rendered SRC-1 economics unattractive compared to other processes that made distillate products, suitable as refinery intermediate streams.

The non-distillate SRC-1 resid product cannot be recovered and deashed by vacuum distillation. Instead, extraction-type separation processes were developed specifically for this process. Typical of these is Kerr-McGee's Critical Solvent Deashing (CSD), which uses a light aromatic solvent to precipitate the heaviest (toluene insoluble) fraction of the resid and, with it, all of the ash and unconverted coal. This deashing procedure has been retained in TSL processing as the means to recover a heavy, but solids-free, recycle solvent.

Typical SRC-1 yields based on typical bituminous coal in Table 2 are shown in Table 1.

3. Exxon Donor Solvent (EDS)

This process development was a joint venture of DOE and private industry participants. The early phases of the program were carried out in the period from 1966 to 1975, and were financed entirely by the Exxon Research and Development Company.

The process development work progressed from bench-scale research to small-scale pilot units (100 lbs/day and 1 ton/day) and culminated in the construction and operation of a large-scale Exxon Coal Liquefaction Plant (ECLP), with a capacity of 250 tons/day, at Baytown, Texas. Mechanical completion of ECLP and start of operations took place in April 1980. This pilot plant continued in operation until it was shut down and dismantled in late 1982.

The EDS process utilizes a non-catalytic hydroprocessing step for the liquefaction of coal to produce liquid hydrocarbons. Its salient feature is the hydrogenation of the recycle solvent which is used as a donor of hydrogen to the slurried coal in a high-pressure reactor.

The EDS process is shown in Figure 4. It is considered single stage because coal dissolution and resid upgrading to distillate products take place in one thermal reactor. The recycle solvent, however, is catalytically hydrogenated in a separate, fixed-bed reactor. This solvent then transfers hydrogen to the coal in the liquefaction reactor.

Reaction conditions are similar to those of SRC-1 and H-Coal. The recycle solvent "donates" hydrogen to effect rapid hydrogenation of the primary liquefaction products; thermal hydrogenation and cracking follow to produce distillates. The product distribution is close to that of H-Coal, although product quality is poorer due to the absence of a hydrotreating catalyst. The hydrogenated solvent is mostly distillate and the resid separated from distillate by vacuum distillation is gasified to provide the hydrogen requirement. The distillate solvent is hydrogenated in a fixed-bed reactor.

The process performed well with bituminous coal. Subbituminous coal precipitated calcium salts in the thermal reactor and its preheater. This problem was later solved by adding resid containing ashy recycle to the solvent. It was believed that the ash particles acted as sites for deposition of the calcium salts.

EDS solvent had to be well-hydrogenated to be an effective hydrogen donor. This highly hydrogenated distillate solvent may, therefore, have been a relatively poor physical solvent, which could account for process operability problems. Bottoms recycle (non-hydrogenated resid) was used near the end of the process development, with improved operability and liquid yields. The improvement may have been due to the better physical solvent properties of the resid.

Distillate yields were not as high as for the H-Coal process, therefore, process economics were about the same despite the less expensive thermal reactor and the simple solids removal procedure.

The EDS process contains same features that have been incorporated into TSL. First, the donor solvent concept showed that hydrogenation of the coal could be effectively and quickly accomplished without a catalyst. Second, bottoms recycle dramatically improved operability, even though the bottoms (resid) were not hydrogenated. Finally, the use of ashy recycle enabled subbituminous coal to be processed effectively in a thermal reactor and without the need of a disposable catalyst.

Typical EDS yields with a typical bituminous coal (Table 2) are shown in Table 1.

4. SRC-II

The SRC-II process employs direct hydrogenation of coal in a reactor at high pressure and temperature to produce liquid hydrocarbon products instead of the solid products in SRC-I (see Figure 5). In 1975 a process development unit (P-99), with a one-half ton per stream day capacity was used, to provide accurate process data and design information data. The 50 ton per day pilot plant at Fort Lewis, Washington which operated from 1974 to late 1976 in the SRC-I mode was modified to run in the SRC-II mode, producing liquid products for testing. The pilot plant was operated from 1978 until it was shut down in 1981.

The SRC-II process is thermal; the mineral matter in the coal is the only "catalyst" used. Its concentration in the reactor is kept high by recycle of the heavy oil slurry. The use of recycled mineral matter and the more severe reaction conditions distinguish the SRC-II operation from SRC-I and account for the lighter products. The net product is -1000°F distillate, which is recovered by vacuum distillation. The vacuum bottoms, including the ash are sent to gasification to generate process hydrogen.

The SRC-II process is limited to coals that contain "catalytic" mineral matter, which excludes all lower rank coals and some bituminous coals. The high temperature, thermal liquefaction reaction results in high yields of hydrocarbon gases and poor liquid product quality, relative to those produced by the H-Coal process.

SRC-II yields with a typical bituminous coal are shown in Table 1.

5. Economic Comparison of the Four Liquefaction Processes

In 1985, DOE had an economic comparison made of these four single-stage processes. While these processes are generically similar in technology, they had been developed independently of each other, and quite naturally possess significant dissimilarities indicated below:

- They were at different stages of evolution toward commercialization; furthermore, due to ongoing R&D work, some were still in the process of evolving to higher levels of operating efficiency and economic viability. Both the EDS process and the H-Coal process have been evaluated in large-scale pilot plants (200-600 tpd) which were in operation for a period of years, whereas

SRC-I and SRC-II data stem from much smaller process development and pilot plant units.

- o Although each process has been screened on a variety of coals, different coal sources were chosen for the major development effort on the four processes; consequently the results obtained in large part are not accurately comparable. Since yield data vary significantly with the choice of coal, process developers, in their design, have tended to favor the type of coal which exhibits the best performance with their process.

- o The minimum commercial size module, as defined by the process developer, is different for the four processes.

Recognizing that the four direct coal liquefaction processes under consideration are inherently different in many important respects, a common basis for calculation of capital and operating costs and plant economics was developed, to the maximum extent possible. All processes are evaluated in the syncrude mode, i.e., a mode of operation in which synthetic liquid fuel comparable to petroleum crude is produced. The syncrude is then refined by conventional petroleum hydrotreating and reforming operations to marketable products. The hydrogen consumption and product yield structure for the four processes are shown in Table 3; the capital cost summary is shown in Table 4.

6. Features of Single Stage Processes - Summary

These and other single-stage processes have several features in common:

a. Reaction severity is high, with temperatures of 820-860°F and liquid residence times of 20-60 minutes.

These severe conditions were considered necessary to achieve coal conversions of over 90 percent (to THF or quinoline solubles).

b. Distillate yields are low, about 50 percent of MAF coal with bituminous coals and even lower from subbituminous coal.

c. Hydrogen efficiency is low due to high yields of hydrocarbon gases.

Although technically sound, process economics suffer for the reasons stated above. In 1980, about the time that H-Coal and EDS processes were ready to be tested at a scale of 200 tons per day, coal liquefaction began to take a new direction toward conditions that were more efficient and could produce more liquid, and of higher quality.

7. Non-Integrated Two-Stage Liquefaction (NTSL)

By the late 1970s it was apparent that the costs associated with the SRC-1 process could not be justified to produce a boiler fuel. Coal liquefaction process such as this is best applied to make higher value-added products, such as transportation fuels.

In order to do this, the SRC-I resid must first be hydrocracked to distillate liquids. Attempts at fixed-bed hydrocracking by Chevron and Mobil were unsuccessful because (a) the resid contained small quantities of ash that plugged the fixed bed and (b) the hydrogenation exotherm coked the large aromatic molecules in the feed and rapidly deactivated the catalyst.

The SRC-I resid was, however, successfully upgraded or hydrotreated by LC-Fining, variation of ebullated bed technology. Eventually, this operation was added to the SRC-I process to form Non-Integrated Two-Stage Liquefaction (NTSL), so called because the LC-Fining reactor did not contribute solvent to SRC-I (Figure 6). The NTSL process was, in fact, two separate processes, coal liquefaction (SRC-I) and resid upgrading (LC-Fining) combined together.

NTSL was an inefficient process even though the LC-Fining section had been added to maximize conversion of resid to distillates. The SRC-I section still contained the shortcomings discussed above. In addition, SRC-I product is an unreactive feed to hydrocracking and complete conversion to distillates requires high (over 800°F) temperature and extremely low space velocity. In order to keep the reactor at a reasonable size and temperature, and to prevent rapid catalyst deactivation, resid conversion was held below 80 percent, so that considerable unconverted resid goes with the product distillates (Table 5). As a result, in the NTSL configuration recycling resid to extinction to produce an all-distillate liquid product slate is not possible. Yields were nevertheless higher than for H-Coal, but hydrogen consumption was still high because of the extensive thermal hydrogenation in the SRC-I dissolver, which was renamed the Thermal Liquefaction Unit (TLU).

The NTSL development was short-lived. Soon, it was to be supplanted by a staged integrated approach, which has been the basis for all subsequent developments.

III. DEVELOPMENT OF THERMAL INTEGRATED TWO-STAGE LIQUEFACTION

A. Earlier Studies

Thermal coal dissolution investigations by Consol, Mobil, Wilsonville and others in the late 1970s had shown that coal conversion to THF (or quinoline) solubles is essentially complete in an extremely short time, 1-5 minutes. Longer dissolution times increase conversion slightly, but the incremental increase in yield goes principally to gases. Within this short dissolution period, hydrogenation from the gas phase is negligible and almost all hydrogen comes from the solvent in liquid phase. If hydrogen transfer from the solvent is insufficient to satisfy the liquefaction needs, the product will have a high concentration of toluene insolubles, causing precipitation within the reactor or in downstream equipment. With a proper well-hydrogenated solvent, however, the Short-Contact-Time (SCT) liquefaction is the preferred thermal dissolution procedure because it eliminates the inefficient thermal hydrogenation inherent in SRC-I.

Meanwhile, Cities Service Research and Development was successfully hydrocracking SRC-I resid via LC-Fining at relatively low temperatures, 750-780°F. Gas yield was low and hydrogen efficiency high. A combination of these two reaction stages, wherein the second stage, i.e., the low-temperature LC-Fining provides the liquefaction solvent to SCT first stage, had the potential to liquefy coal to distillate products in a more efficient process than any of the single-stage processes.

B. Lummus ITSL (1980-1984)

These features described above were combined by Lummus in the ITSL process. Operation of a 500 pound-per-day Process Development Unit (PDU), with ITSL process started in 1980. Because this operation departed significantly from earlier developments, this was also the forerunner of all subsequent TSL developments. The important features of the Lummus program will be reviewed below in detail.

1. Process Features

The Lummus ITSL process consists of an SCT coal dissolution first stage and an LC-Fining catalytic upgrading second stage (Figure 7). Coal is slurried with recycled solvent from LC-Fining and is converted to quinoline solubles in the SCT reactor; the resid is hydrogenated/hydrocracked to distillates in the LC-Fining stage, where recycle solvent is also generated. The ash is removed by the Lummus Anti-solvent Deashing (ASDA) process, which is similar to deasphalting operations with petroleum. The net liquid product is either -650°F or -850°F distillate. The recycle solvent is hydrogenated +650°F atmospheric bottoms. It is the recycle of this full-range bottoms, including resid that couples the two reaction stages and results in high yields of all-distillate product.

2. Features of SCT

The SCT reactor is actually the preheater for the dissolver in the SRC-I process. ITSL, therefore, eliminates a long-residence-time high-pressure, thermal dissolution reactor. The coal slurry and gas feeds flow through the SCT reactor in plug flow, exiting at a maximum temperature of 810-860°F. The kinetic average temperature is about 788°F, which is lower than the dissolver temperature in SRC-I. Liquid residence time is 2-3 minutes for bituminous coal and 8-12 minutes for subbituminous coal. Initial tests were made at 2400 psi pressure. But, as it became apparent that essentially no molecular hydrogen was being reacted, the pressure was lowered to 1000 psi and then to 500 psi in later tests, with no detrimental effects. Coal conversions were 92 percent of MAF coal for bituminous coals and 90 percent for subbituminous coal.

Molecular hydrogen gas consumption was essentially zero, and the hydrogen transferred from solvent was equivalent to 1.2 -2.0 percent of coal weight (see Table 6). The hydrocarbon gas yield was thereby reduced to about one percent for bituminous coal and to 5-6 percent for subbituminous coal. Heteroatom removal was about the same as by the SRC-I process.

The SCT resid was far more reactive to hydrocracking than SRC-I resid. It was also more stable, being able to withstand days, and even weeks, in heated holding tanks without loss of activity or the formation of solids (retrogressive reactions). In summary, the most noteworthy advantage of SCT over SRC-I was that it was able to achieve the same coal conversion with very little consumption of hydrogen and did so at milder conditions, which resulted in a more reactive resid.

3. Features of the Second Stage Hydrotreater (HTR)

The LC-Fining second reactor stage had two tasks: (1) to make essentially all of the distillate product and (2) to generate recycle solvent capable of supplying the hydrogen required by the SCT first stage. This is in contrast to the second stage of NITSL, which was required only to convert resid to product. In ITSL, all the unconverted resid was recycled to the first stage, resulting in recycle to extinction. Thus, an all-distillate product was achieved. Although bottoms recycle had been used in preceding processes, this was the first time that resid had been hydrotreated prior to recycle, so that it was more than a physical solvent, but also a donor of hydrogen and a product precursor, capable of cracking to lighter oils at SCT conditions.

The second task, to hydrogenate the recycle solvent, dictated the reaction conditions. Hydrogenation equilibrium becomes less favorable at higher temperatures and, in fact, above 800°F the second stage product is more aromatic than the feed, On the other hand, conversion kinetics suffer at low temperatures and solvent quality suffers because of accumulation of alkylated species that would otherwise crack to light oil at higher temperature. A second stage HTR temperature of 750°F provides sufficient hydrogenation and cracking activity to accomplish both tasks. [For subbituminous coal, this temperature could be as low as 700°F, due to the greater reactivity of resids from lower rank coals. When temperature and space velocity were raised to maintain the same resid conversion, a lighter (-650°F) product was made with only a minor increase in hydrogen consumption.] The low HTR temperatures kept hydrocarbon gas yields to only 5-6 percent for bituminous coal and under one percent for subbituminous coal.

Catalyst deactivation was much slower than at the higher temperatures used by other processes. As a result, the hydrogen transfer quality of the recycle solvent remained undiminished over the life of the catalyst. Ages of 3500-5500 pounds of resid per pound of catalyst were achieved without catalyst failure.

As stated earlier, the SCT resid was reactive, not only for conversion to distillate, but also for heteroatom removal. Product quality surpassed any achieved by the preceeding processes.

Chevron subsequently refined the ITSL products in a small-scale simulation of conventional refinery operations. As expected, ITSL products were easily upgraded, requiring relatively low temperatures and high space velocities. The low heteroatoms content contributed to the ease of refining, enabling Chevron to achieve specification transportation fuels with a hydrogen consumption that was lower than for any similar liquids made from the same coals.

4. Antisolvent Deashing (ASDA)

The ash was removed by ASDA, which used a process-derived naphtha as antisolvent to precipitate the heaviest components of the resid and the solids. Initially, the ASDA unit was placed between the two reactors, so that SCT product was deashed. Eventually, the best TSL yields and deasher operation were achieved when the second stage liquid was deashed. In addition, the conversion of subbituminous coal was increased to 90 percent and operability of both stages was improved when part of the deasher feed was recycled to the first stage as solvent.

The ash-reject stream from ASDA had to be pumpable in order to make use of high efficiency gasification technology. This stream, therefore, could contain no more than 55 percent solids, leading to relatively high rejection of organics with the ash. Since the process was kept in hydrogen balance and hydrogen consumption was low, the ASDA method of ash removal was acceptable. It had the advantages of low pressure (100-1000 psi), low temperature (500-540°F), and it required no external antisolvent. If, however, the liquid yield was to be increased, it could be done only by converting more resid in the second stage. This would have made the ash-reject stream from ASDA high in solids concentration (>55%) and too heavy to pump. It was this limitation on ASDA that limited the distillate yield to 60 percent of MAF coal.

5. Overall Results of ITSL

ITSL incorporated two features that are significant improvements over those developed in the past and tested them with new processing concepts that combined to produce the highest liquid yield yet attained, and at the highest hydrogen efficiency (see Table 7).

The unconverted resid was hydrotreated and recycled as part of the liquefaction solvent. Thus, resid was recycled to extinction and an all-distillate product (-650°F or -850°F) was made. This recycle also allayed the fears that resid contained coke precursors and that they would foul reactors if recycled. Instead, the hydrotreated resid is now well recognized as an excellent physical and hydrogen-donor solvent, whose full contribution to coal dissolution is now fully appreciated.

The SCT coal dissolution reactor accomplished all that SRC-I did, but more efficiently in a smaller volume reactor. Hydrocarbon gas yields were reduced to about one percent (very much smaller than 10-20% experienced with other processes) and heteroatom removal was comparable. Of even greater importance, the SCT resid was a more reactive second stage feed and caused slower catalyst deactivation.

Additionally, ITSL showed that ashy recycle (including toluene-insolubles) is not detrimental to catalyst activity; the subbituminous coal is an attractive feed for direct liquefaction, with some advantages over bituminous coal; and that a lighter product (-650°F) can be made with little loss in hydrogen efficiency. The last point is of special importance for commercialization because the -650°F liquid poses no environmental problems. The product quality, including heteroatoms content, is excellent (see Table 8) and is easily refined to marketable products by standard refinery operations.

The maximum distillate yield from ITSL was 60 percent of MAF bituminous coal and 53 percent of MAF subbituminous coal (see Table 7). These were obtained in "hydrogen balanced" operation and constituted significant improvement over H-Coal and other single stage processes. Hydrocarbon gas yields were held to about 7 percent, so that the hydrogen consumption efficiency was the highest of any process, with 10-12 pounds of distillate produced per pound of hydrogen reacted.

The distillate yield was limited by the philosophy of a "hydrogen balanced" process; one that gasified the ash-reject stream to produce all of its hydrogen requirements. If distillate yield were to be increased, less resid would have to be rejected with the ash. The next step in the evolution of TSL, therefore, was to operate in a "non-hydrogen balanced" mode, in order to maximize distillate yield. This was accomplished in subsequent developments at HRI and Wilsonville.

C. Wilsonville ITSL (1982-1985)

The Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama is sponsored by the U.S. Department of Energy, the Electric Power Research Institute and Amoco Corporation. The facility is operated by Catalytic, Inc., under the management of Southern Company Services, Inc. Kerr-McGee has participated by supplying deashing technology at Wilsonville. The technology for the design of the hydrotreater was provided by Hydrocarbon Research, Inc.

The Wilsonville facility began operation as a 6 T/D single-stage plant for the production of solvent-refined coal (SRC-I) in early 1974 and has continued over the intervening fourteen years. Over this period, the plant has evolved into the current advanced coal liquefaction facility by developments made possible by three major additions to the facility. In 1978, a Kerr-McGee Critical Solvent Deashing (CSD) unit replaced the filtration equipment that had been used for solids removal from the SRC product. In 1981, a H-Oil® ebullated-bed hydrotreater was installed for upgrading of the recycle solvent and product. The hydrotreater increased the flexibility of the facility and allowed the investigation of two-stage liquefaction configurations. In 1985, a second ebullated-bed reactor was added in the hydrotreater area to allow operation with close-coupled reactors.

1. Scale-Up of Lummus ITSL

The Lummus ITSL results had demonstrated significant advantages over single stage processes and that scale-up was warranted. This was done at Wilsonville. In late 1982, modifications were made to Wilsonville that included piping changes needed for integrated operation and to bypass the TLU. Run 242 was the first ITSL scale-up run; it was operated at 3 tons of coal per day. The Integrated Two-Stage Liquefaction (ITSL) configuration that was used at Wilsonville for the bituminous runs is shown schematically in Figure 9. In the ITSL configuration, the deashed thermal resid is fed to the hydrotreater, along with the heavier cuts of the thermal distillate. The process solvent that is recycled to the thermal stage is obtained from the hydrotreater product.

A distillate yield of 54 percent of MAF coal was confirmed (see Table 9). This yield was less than anticipated because of (a) retrogressive reactions in the CSD unit that lowered coal conversion from 92 to 88 percent (Table 9), and (b) high organic rejection with the ash-concentrate stream because of high concentration of toluene-solubles in the SCT product. Nevertheless, the distillate yields were higher than had been achieved by NITSL and the advantages of the integrated process were proven.

2. Modifications to ITSL

During most of Run 242 the second stage HTR was operated at a low temperature, with most of the liquid product being made by thermal cracking in the first stage. Thereupon, Wilsonville decided that it was preferable to shift more of the conversion to the first reactor in subsequent runs and use the second stage primarily as a solvent hydrogenation unit. An advantage of such an arrangement is that the concentration of toluene-insolubles in the first stage liquid is reduced, leading to lower organic rejection by CSD. Consequently, the TLU was reinstalled starting with Run 243 and first stage reactors of relatively long residence time were used in all subsequent ITSL runs.

3. Reconfigured Two-Stage Liquefaction (RITSL)

Lummus in further development of the ITSL process had increased distillate yield by placing the deasher after the second stage, with no detrimental effect of ashy feed on catalyst activity. This was confirmed at Wilsonville in RITSL Run 247. The RITSL configuration is illustrated in Figure 10. The slurry preparation, thermal liquefaction, and fractionation steps are the same as in the ITSL mode (Figure 9). However, the vacuum bottoms containing the thermal resid, unconverted coal, and ash are fed directly to the ebullated bed hydrotreater. The vacuum flashed bottoms from the hydrotreater is the feed to the CSD unit. The recycle solvent is composed of the deashed resid from the CSD unit and hydrotreated distillate.

A primary objective of Run 247 was to demonstrate unit operability in the RITSL mode. Because the hydrotreater feed was not deashed, it contained all the coal ash along with unconverted coal and heavy organics that would normally be removed in the deashing step in the ITSL mode (Figure 9). Thus, there was concern that catalyst deactivation would increase. Another operability question was what effect the mode would have on deashing. Since the feed to the CSD unit would be the vacuum flashed bottoms from the hydrotreater, the CSD feed properties were expected to be considerably different than had previously been experienced.

Good operability with the RITSL configuration in Run 247 was demonstrated. On-stream times of each unit were 95% or better. The hydrotreater catalyst performed well in the RITSL mode. The catalyst used was presulfided Shell 324-M and throughout the run, activity was higher than in previous runs in the ITSL configuration.

Retrogressive reactions were essentially eliminated, increasing the potential distillate yield to 70 percent. Wilsonville then successfully tested ashy recycle. The main benefit of this ashy recycle with bituminous coal was to reduce the feed to CSD by over 50 percent, and thereby reduce organic rejection in the ash-concentrate stream (See Run 250G in Table 9).

4. Close-Coupled ITSL (CCITSL)

With the deasher placed after the second stage reactor and the two stages operating at about the same pressure, the two reactors were close-coupled to minimize holding time between the reactors and eliminate pressure letdown and repressuring between stages (Figure 11). All the first stage gases and light oil entering the second stage feed did not effect the activity of the catalyst (Table 9). This close-coupling of the reactors removed several additional product letdown and separation operations in between the two stages.

5. Operations with Subbituminous Coal

All single stage processes had found subbituminous coal more difficult to convert to soluble liquids than bituminous coal. At first, ITSL had experienced the same difficulty. Two changes in the ITSL process resulted in conversions of over 95 percent with Wyodak subbituminous coal (see Table 10). First, iron oxide and a sulfiding liquid, dimethyl disulfide, were added to the coal slurry to provide the beneficial effects for which iron sulfide is well known. This raised coal conversion to about 90 percent. Then, secondly ashy recycle, Run 249, raised conversion to above 95 percent (see Table 10). The energy rejection, which had been high (30% or higher) in low conversion runs, was reduced to 13 percent in Run 251 (Table 10), lower than 16% realized for bituminous coal (Run 250 in Table 9). Additionally, the TSL approach in Runs 246-251 showed subbituminous coal had a significant advantage over bituminous coal due to the high reactivity of its resid which is apparent in the second stage. Wilsonville PDU was therefore able to produce an all-distillate product and make a high quality solvent with a second stage temperature below 698°F which is lower than the temperature utilized for bituminous coal. Subbituminous coal also produced a -650°F product with greater ease (lower temperature) than does bituminous coal. These runs verified the earlier conclusion by Lummus ITSL Runs with ashy recycle that subbituminous coal is an attractive feed for direct liquefaction.

IV. DEVELOPMENT OF CATALYTIC TWO-STAGE LIQUEFACTION (CTSL)

A. HRI CTSL (1982-Present)

1. Background

HRI fully recognized the limitations of single stage processes such as H-Coal and decided to improve them. H-Coal is inherently a high temperature (830-845°F) catalytic process, in which extensive thermal cracking produces excessive hydrocarbon gases at the expense of additional hydrogen consumption. The higher temperature is good for liquefaction and upgrading reaction rates but is unfavorable for making a hydrogen-donor solvent. To control the reaction rates and to improve the solvent quality, a two stage process was developed.

2. Features of CTSL Process

In 1982, HRI initiated the development of a catalytic two-stage concept, in which the first stage temperature was lowered to 750°F to more closely balance hydrogenation and cracking rates, and to allow the recycle solvent to be hydrogenated in situ to facilitate hydrogen transfer to coal dissolution. The second stage was operated at higher temperature (820-830°F) to promote resid hydrocracking and generate an aromatic solvent, which is then hydrogenated in the first stage (see Figure 12). The lower first stage temperature provides better overall management of hydrogen consumption, with hydrocarbon gas yields reduced by about 50 percent, compared to H-Coal.

CTSL development also incorporated new thinking regarding deashing. The product from the second stage has undergone catalytic hydrogenation twice and is a much lighter deasher feed than the SRC-I resid for which deashers were designed. Its flow characteristics are more amenable to standard liquid-solid separation techniques, such as filtration. HRI realized that higher distillate yields could be attained only by the reduction of resid that is rejected in the ash-concentrated stream and the subsequent conversion of that recovered resid to distillate. Their CTSL process, therefore, successfully incorporates a pressure filter to reduce resid concentration in the reject stream (filter cake) below the 45-50 percent in vacuum tower bottoms of H-Coal process and even lower than had been achieved at that time by CSD. This change in deashing philosophy was in response to economic studies, which showed that overall liquefaction economics improve if the process maximizes distillate yield and produces hydrogen by natural gas reforming or by coal gasification. These studies signalled the end of the "hydrogen balanced" processes.

A third change by HRI was in the catalyst. H-Coal process had used a cobalt-molybdenum (CoMo)-on-alumina catalyst (American Cyanide 1442B) that had been successful in hydrocracking petroleum resids. In petroleum applications, however, thermal cracking occurs first, followed by catalytic hydrogenation of the cracked products. In coal liquefaction, hydrogenation of solvent must occur first, before the aromatic molecules can thermally crack. The catalyst must hydrogenate large molecules and this hydrogenation capability determines the rate at which resid is converted. The H-Coal catalyst was not well-suited for this task because its porosity distribution was designed for smaller molecules. For CTSL, it was replaced by a nickel-molybdenum (NiMo) catalyst of a bimodal pore distribution with larger micropores, 115-125°A as opposed to 60-70°A for H-Coal catalyst. The nickel promoter is also more active for hydrogenation than cobalt.

These three changes constitute the major advances of CTSL over H-Coal. Their combined effect on liquid yields has been dramatic.

3. Overall Results of HRI CTSL

The latest reported results with Illinois No. 6 coal show a 78 percent distillate yield. Gas oil recycle to extinction has produced only slightly lower yield of -650°F distillate (see Table 11 CTSL and H-Coal yields). Hydrogen efficiency is over 10 pounds of distillate per pound of hydrogen reacted. In addition, the two catalytic reaction stages produce a liquid with low heteroatom concentrations and a high H/C ratio, making this liquid closer in properties to petroleum than any coal liquids made by earlier processes.

B. Wilsonville CTSL (1985-Present)

At the Wilsonville Advanced Coal Liquefaction Facility a second ebullated bed reactor was installed in 1985 and the plant has since operated in the CTSL mode. However, Wilsonville has made substantial modifications to the process operating conditions. The most significant being the reactor temperatures. As in ITSL, Wilsonville prefers to have most of the thermal cracking take place in the first reactor and solvent hydrogenation in the second reactor. Therefore, the first reactor is at the higher temperature (800-820°F), while the second reactor is kept slightly lower at 795°F. Other reaction conditions are similar, including the catalyst type (see process flow diagram Figure 13).

Wilsonville, unlike HRI, continues to deash by CSD, and steady improvement in operation has reduced organic rejection to 8-15 percent, about the same as HRI achieves by filtration. This has enabled Wilsonville to operate CTSL at over four tons of coal per day during Run 254G and obtain the same distillate yields of up to 78 percent (Table 12). Yields with subbituminous coal are 62 percent (see Table 13 of yields from Runs 251-III). However, Wilsonville, has still to test gas oil recycle to extinction.

C. Evolution of Liquefaction Technology

Since the early 1970's, after the oil embargo, substantial improvement in liquefaction processes and catalysts associated with these processes have taken place. The yields of liquids have increased and simultaneously quality of liquids have improved substantially. History of process development improvements in the form of yields and quality of distillates are shown in Table 13. Yields of distillates have increased from 41% to 78%, resulting in equivalent liquid yields of about 5 barrels/ton of MAF bituminous coal (such as Illinois No. 6 and Ohio No. 6). Quality is comparable or better than No. 2 Fuel Oil with good hydrogen content and very low heteroatom content.

V. ECONOMICS OF TSL PROCESSES

Several economic studies have charted the progress of TSL, all of which show the same trend of reduced cost per barrel of liquid product. Recently, Wilsonville PDU operators (Stearns - Catalytic) performed an analysis of the impact of process developments in liquefaction technology. Relative economics of the TSL development is shown in Figure 14. The total plant capital and operating costs increased substantially due to an additional reactor and other equipment. However, the liquid yields and product quality improved substantially to reduce the overall cost of production of liquids by about 20%. With the CTSL process at Wilsonville, the cost of liquids was reduced further by 3-5%.

Mitre has performed a cost comparison of various two stage processes based on the 1981 UOP/SDC cost estimates of NTSL process. These results are shown in Figure 15. Their analysis also shows a sub stantial reduction of about 25% in the cost of production of liquids.

Recently, Lummus performed such a study for EPRI, in which they compared, on a consistent basis, CTSL and close-coupled ITSL with single stage process such as H-Coal. The study showed a significant reduction in product cost relative to H-Coal, with the first year product cost from CTSL of $38.00 per barrel. Bechtel has also performed a similar study for Amoco and has estimated a product cost of $35 per barrel. These figures are roughly half the cost of coal liquids in 1980. The cost reduction is attributed to greater product yield, higher product quality, improved design, improved economic factors (lower interest and inflation rates) and refined cost estimates.

VI. FUTURE CTSL PROGRAM AT WILSONVILLE

The Wilsonville PDU program is designed to effect further reductions in cost. Some of the programs to be carried out in the near future are as follows:

A. Lignite Feed

This work is now in progress. Lignite is a low cost feed in great abundance in the Western U.S. (N. Dakota) and Southern U.S. (Texas). Its resid is extremely reactive and is a good candidate to make a light distillate (-650°F) product. Past efforts have had difficulty in removing the large amount of ash. These problems have been overcome, and it is believed that with this current test the CTSL process will be extended to lignite.

B. Deep Cleaning of Coal

The quality of resid rejected with the ash is a function of the amount of ash in the coal. Deep cleaning the coal to 5 percent ash, instead of the current 10 percent, could increase liquid yield by about 5 percent for the same coal feed rate due to lower energy rejection with liquefaction bottoms. Additionally, reduction in ash concentrations will also reduce corrosion and erosion of instruments and components in the process.

C. Testing Alternative Deashing Procedures

CSD was developed for the SRC-1 process. It may not be as suitable for CTSL as other methods of liquid-solid separation, which may also be less costly to install and operate in the commercial plant.

Bench-scale fluid coking tests on CSD feeds have produced good yields of distillate, about 60 percent toluene solubles. Consol hydrogenated this coker distillate and reported it to be an excellent recycle solvent.

Other deashing procedures, such as filtration and centrifugation will also be tested to determine if energy rejection can be reduced below the current level of 8-16 percent achieved by CSD.

D. Gas Oil Recycle to Extinction

For environmental and refining reasons, a lighter product is desirable (see Sections on "Environmental Considerations" and "Chevron Refining of Coal Liquids"). The market value of a -650°F product is substantially higher than for a -850°F product.

Production of the lighter product will improve the liquefaction economics.

E. Coprocessing of Coal and Petroleum Resid

Of current interest is the simultaneous processing of coal and heavy petroleum resids to distillate products. Coprocessing uses a heavy petroleum stream as a once-through liquefaction solvent. Second stage reaction conditions need not be determined by the need to make a good recycle solvent. This gives the process greater flexibility and should reduce liquefaction costs. This concept has been tested in smaller scale units with great success. A 11,700 barrel-per-day coprocessing plant (Ohio-Ontario Clean Fuels Projet) costing $230 million has received DOE approval for funds (about 20%) under the Clean Coal Program and is in early stages of design. Wilsonville facility is scheduled to test co-processing sometime in late 1989 or 1990.

F. Solvent Quality

Figure 16 obtained from the 1987 IEA report shows the beneficial effect of resid on the solvent's ability to liquefy coal. Recently, Consolidated Coal has developed procedures to measure solvent quality by measuring coal conversion to THF solubles in the presence of the full range recycle solvent and with only the distillate. Conversions with distillate only are consistently lower than for the full-range solvent. Understanding the role that resid plays in liquefaction is a fruitful area for research that could benefit liquefaction processes.

G. Catalyst Development

For at least the last ten years, direct liquefaction processes have relied exclusively on hydrogenation catalysts. Table 15 (IEA report) shows that acidic catalysts have good activity for dissolution of coal, especially tin and zinc chlorides. This type of catalyst may provide the basis for a completely new process to make liquids directly from coal.

The early work in liquefaction used tin, molybdenum and iron. The German technology still relies on iron. Tables 16, 17, and 18 show that these metals are active and are still of interest in liquefaction; especially as the active metal in dispersed catalysts.

Figure 17 reproduced from IEA report on Catalysis in Direct Coal Liquefaction is the result of a study by Sandia National Laboratory, which is one of the laboratories that provides technical support to the Wilsonville program. The results plotted in this Figure show that catalyst activity suffers with heavier feed. This activity decline has been attributed to the following causes:

- basic amines in the resid
- phenols in the resid
- pore mouth plugging

Liquefaction processes could be improved significantly if a catalyst were developed that had high activity for converting the resid.

VII. CONCLUSION

The direct coal liquefaction program has demonstrated remarkable progress since 1980 as the result of two-stage liquefaction. Steady improvement has been made to TSL, and it is today the best direct liquefaction process in the world. Developments continue with the potential of even further advances in the technology within the next few years. The economics of TSL show that direct coal liquefaction is a viable "cap", or ceiling, for the cost of petroleum-based products.

TABLES

TABLE 1. YIELD DATA FOR FOUR (4) LIQUEFACTION PROCESSES
COAL SOURCE: ILLINOIS NO. 6 BURNING STAR MINE

	EDS	H-COAL	SRC-I	SRC-II
Yield Periods/Run/Ref.	430-432	Run 5	AF-1122 (EPRI)	ORNL/SUB-7240/2
Temperature, °F	840	851	840	852
Hydrogen Pressure, psig	2000	2700	1820	1900
Solvent/Coal/Bottom Ratio	1.6/1/0.5	1/0.5	1/0.45	1/0.33
Overall Yields, wt% on MF				
H_2	-4.89	-4.91	-1.89	-3.3
H_2O	8.86	6.67	4.80	7.4
CO_2	1.53	0.48	0.85	1.8
NH_3	0.91	1.08	0.12	0.3
H_2S	2.43	2.64	1.94	2.1
C_1-C_4	12.71	13.22	5.4	11.1
C_5-350°F	15.58	16.20	4.2	5.8
350-650°F	18.32	20.37	4.77	14.8
650-1000°F	4.7	7.96	19.75	13.4
1000°F+	39.84	36.25	60.00	46.8

TABLE 2. TYPICAL COMPOSITION OF BURNING STAR MINE COAL

	As Received	Dried
Moisture, Wt%	12.39	2.39
Proximate, Dry Basis, Wt%		
Ash	10.61	10.73
Volatile Matter	42.05	36.06
Fixed Carbon	47.54	53.21
Ultimate, Dry Basis, Wt%		
Carbon	70.83	69.20
Hydrogen	4.67	4.63
Nitrogen	1.39	1.23
Sulfur	3.30	3.53
Ash	10.62	10.73
Chlorine	0.03	0.03
Oxygen (Difference)	9.17	10.65
Btu (Dry Basis), Gross	12,724	12,621
Sulfur Forms, Wt% (Dry)		
Pyritic	1.20	1.48
Sulfate	0.00	0.03
Organic	1.89	1.85
Total	3.09	3.36
Mineral, Wt% Ignited Basis:		
Phosphorus Pentoxide, P_2O_5	0.07	0.02
Silica, STO	50.35	47.38
Ferric Oxide, Fe_2O_3	16.60	19.29
Alumina, Al_2O_3	20.66	17.65
Titania, TiO_2	0.90	0.77
Lime, CaO	4.90	6.45
Magnesia, MgO	0.90	0.75
Sulfur Trioxide, SO_3	2.61	4.60
Potassium Oxide, K_2O	20.9	1.77
Sodium Oxide, Na_2O	0.68	0.72
Undetermined	0.24	0.60
Screen Size (U.S.S)		
+5		5.55
50/70		5.35
70/100		9.79
100/140		13.66
140/200		13.73
200/325		22.40
325/Pan		29.51

TABLE 3. HYDROGEN REQUIREMENTS AND PRODUCT YIELD STRUCTURES

	EDS	H-Coal	SRC-I[1]	SRC-II
H_2 Req'd for Liquefaction TPD	294	231.5	105.9	184.8
H_2 Req'd for Naphtha HTU, TPD	17.67	13.85	22.65	28.4
H_2 Req'd for Hydrotreating, TPD	37.54	28.73	121.79	43.3
	349.24	274.07	250.34	256.5
Vac Bttm Req'd for H_2 Gen., TPD	2632	2065.5	1886.7	1933
Oxygen, TPD	1963	1541	1407	1442
Supplementary Coal	256	357	207	101
Coal for STM Gen	592	465	552	552
C_1, MMSCFD	13.27	9.1	5.22	14.0
C_2, MMSCFD	6.99	5.94	3.40	5.98
Propane, BPD	2125	1846	900	1564
Butane, BPD	1365	1221	209	458
Reformate, BPD	5328	4333	3862	4092
Fuel Oil, (MD+HD), BPD	7717	7409	9236	9592
Total BPD	16,535	14,827	14,206	15,706
BBL/Ton	2.76	3.15	2.54	2.80
Overall H_2 Consumed, Wt%	5.82	5.81	4.47	4.58
Major By-Products				
Phenols, TPD	37	29	39	34
NH_3, TPD	69	54	64	64
Sulfur, TPD	194	152	181	178

[1] Based on design of 6000 TPD Demonstration Plant in which liquids from SRC-I reaction, coker distillate and LC-Fining liquid products are fractionated, stabilized, and then upgraded by further hydrogenation.

TABLE 4. CAPITAL COST SUMMARY

	EDS	H-Coal	SRC-I[1]	SRC-II
Capacity, TPD (MF)	6000	4714	5600	5600
SNG, MMSCFD	15.6	5.0	2.3	6.0
Propane, BPD	2125	1864	900	1564
Butane, BPD	1365	1221	208	458
C_5+ Distillates	13045	11742	13098	13684
Phenolics, TPD	37	29	39	34
NH_3, TPD	69	54	64	64
Sulfur, TPD	194	152	181	178
Total Coal, TPD	7118	5533	6359	6253
H_2 Consumption, Wt%	5.82	5.81	4.47	4.58
Power Purchased, MW	110	94	84	87
Thermal Efficiency	60.6	60.5	52.1	60.5
INVESTMENT COST (FY '85) $MM				
Coal Preparation	75	62.9	70	69.5
Coal Liquefaction	327.9	267.3	273.7	222.6
Gasification	303.5	232.9	214.2	231.0
Products and Gas Cleanup	252.8	210.7	192.8	210.4
Product Upgrading	64.9	60.2	60.4	63.4
Offsites	515.4	435.4	473.9	479.7
Total	1539.5	1269.4	1285.0	1276.6
Contingency	234.0	168.6	170.7	169.6
Total Erected Costs	1774.0	1438.0	1455.7	1446.2
BBL/Ton	2.76	3.15	2.54	2.8

[1] See note in Table 3.

TABLE 5. WILSONVILLE FACILITY - NTSL
(ILLINOIS NO. 6 COAL)

OPERATING CONDITIONS	
Run No.	241CD
Configuration	NTSL
Catalyst	Armak
Thermal Stage	
Average Reactor Temperature, °F	805
Coal Space Velocity, lb/hr ft^3 > 700°F	20
Pressure, psig	2170
Catalytic Stage	
Average Reactor Temperature, °F	780
Space Velocity, lb Feed/hr lb Catalyst	1.7
Catalyst Age, lb Resid/lb Catalyst	260-387
YIELDS, WEIGHT PERCENT MAF COAL	
C_1-C_3 Gas	7
C_4+ Distillate	40
Resid	23
Hydrogen Consumption	4.2
Hydrogen Efficiency	
lb C_4+ Distillate/lb H_2 Consumed	9.5
Distillate Selectivity,	
lb C_1-C_3/lb C_4+ Distillate	0.18
Energy Content of Feed Coal Rejected to Ash Concentrate, percent	20

TABLE 6. INTEGRATED TWO-STAGE LIQUEFACTION PROCESS YIELDS (LUMMUS SCT ONLY)

	Run 2 SCT 10	Run 3 SCT 2
	Illinois #6	Wyodak
Components	Net Yields (lb/100 lb MAF Coal)	
H_2S, NH_3, H_2O, CO_x	6.4	19.6
C_1-C_4 Gases	0.6	6.0
C_5 - 500°F Distillate	1.6	6.9
500-850°F Distillate	0.5	3.4
Solids Free 850°F+	83.2	52.8
Unconverted Coal	8.0	11.2
	100.3	100.0
Hydrogen From Recycle Solvent	1.4	2.0
Hydrogen From Gas	0.3	---

TABLE 7. LUMMUS ITSL PRODUCT YIELDS

	lbs/100 lbs MAF Coal	
	Illinois No. 6	Wyodak
H_2S, H_2O, NH_3, CO_x	15.08	22.45
C_1-C_4	4.16	6.61
TOTAL GAS	19.24	29.06
C_5/390°F	6.92	1.24
390/500°F	11.46	7.86
500/650°F	17.26	18.71
650/850°F	23.87	14.95
TOTAL DISTILLATE PRODUCT	59.51	42.76
Organics Rejected with Ash	26.09	31.96
GRAND TOTAL	104.84	103.78
Chemical Hydrogen Consumption	4.84	3.78
Hydrogen Efficiency lb dist./lb H_2	12.28	11.29
Distillate Yield, Bbl/Ton MAF	3.52	2.46

TABLE 8. LUMMUS ITSL DISTILLATE PRODUCT QUALITY (ILLINOIS NO. 6)

	°API	C	H	O	N	S	HHV Btu/lb
NAPHTHA							
NTSL	36.8	86.79	11.15	1.72	0.18	0.16	19,411
ITSL	45.4	86.01	13.16	0.62	0.12	0.09	20,628
LIGHT DISTILLATE (390 - 500°F)							
NTSL	15.5	88.62	9.51	1.50	0.28	0.09	18,673
ITSL	22.9	87.75	11.31	0.73	0.13	0.08	19,724
MEDIUM DISTILLATE (500 - 650°F)							
NTSL	7.5	90.69	8.76	0.27	0.25	0.03	18,604
ITSL	12.9	89.29	10.26	0.28	0.12	0.05	19,331
HEAVY DISTILLATE (650 - 850°F)							
NTSL	-1.5	91.47	7.72	0.26	0.50	0.05	18,074
ITSL	1.8	90.77	8.47	0.45	0.23	0.08	18,424

TABLE 9. WILSONVILLE FACILITY ITSL
(ILLINOIS NO. 6 COAL)

OPERATING CONDITIONS						
Run No.	241CD	242BC	243JK/244B	247D	250D	250G(a)
Configuration	NTSL	ITSL	ITSL	RITSL	CC-ITSL	CC-ITSL
Catalyst	Armak	Shell 324M	Shell 324M	Shell 324M	Amocat 1C	Amocat 1C
Thermal Stage						
Average Reactor Temperature, °F	805	860	810	810	824	829
Coal Space Velocity, lb/hr ft^3 > 700°F	20	43	28	27	20	20
Pressure, psig	2170	2400	1500-2400	2400	2500	2500
Catalytic Stage						
Average Reactor Temperature, °F	780	720	720	711	750	750
Space Velocity, lb Feed/hr lb Catalyst	1.7	1.0	1.0	0.9	2.08	2.23
Catalyst Age, lb Resid/lb Catalyst	260-387	278-441	350-850	446-671	697-786	346-439
YIELDS, WEIGHT PERCENT MAF COAL						
C_1-C_3 Gas	7	4	6	6	7	8
C_4+ Distillate	40	54	59	62	64	63
Resid	23	8	6	3	2	5
Hydrogen Consumption	4.2	4.9	5.1	6.1	6.1	6.4
Hydrogen Efficiency, lb C_4+ Distillate/lb H_2 Consumed	9.5	11	11.5	10.2	10.5	9.8
Distillate Selectivity, lb C_1-C_3/lb CC_4+ Distillate	0.18	0.07	0.10	0.10	0.11	0.12
Energy Content of Feed Coal Reject to Ash Concentrate, percent	20	24	20-23	22	23	16

TABLE 10. WILSONVILLE FACILITY - ITSL
(WYODAK SUBBITUMINOUS COAL)

Run No.	246G	249H	251-IIB
Thermal Stage			
Average Reactor Temperature, °F	813	802	819
Inlet Hydrogen Partial Pressure, psi	2,040	2,170	2,510
Coal Space Velocity, lb/hr ft^3 > 700°F	17	17	25
Solvent-to-Coal Ratio	1.8	2.0	2.0
Solvent Resid Content, wt%	30	22	25
Catalytic Stage			
Reactor Temperature, °F	623	700	743
Space Velocity, lb Feed/hr lb Catalyst	1.0	1.6	2.8
Feed Resid Content, wt%	34	27	31
Catalyst Age (lb resid/lb catalyst)	496	1683-1703	915-968
Yield* (% MAF Coal)			
C_1-C_3 Gas	9	7	8
C_4+ Distillate	53	57	61
Resid	1	5	4
Hydrogen Consumption	5.4	6.3	6.3
Hydrogen Efficiency, lb C_4+ Distillate/H_2 Consumed	9.8	8.9	9.7
Distillate Selectivity, lb C_1-C_3/lb C_4+ Distillate	0.18	0.12	0.13
Energy Content of Feed Coal Rejected to Ash Concentrate, %	20-24	18	13

---

*Elemental balanced yield structures
246G SO_3-free ash

TABLE 11. CTSL DEMONSTRATION RUN COMPARISON WITH H-COAL (ILLINOIS NO. 6 COAL)

Process	H-Coal (PDU-5)	CTSL Run No. (227-20)	CTSL Run No. (227-47)
YIELDS, Wt% MAF			
C_1-C_3	11.3	6.6	8.6
C_4-390°F	22.3	18.2	19.7
390-650°F	20.5	32.6	36.0
650-975°F	8.2	16.4	22.2[1]
957°F+ Oil	20.8	12.6	2.7[1]
HYDROGEN CONSUMPTION	6.1	6.3	7.3
COAL CONVERSION, Wt% MAF	93.7	94.8	96.8
975°F+ CONVERSION, Wt% MAF	72.9	82.2	94.1[1]
C_4-975°F, Wt% MAF	51.0	67.2	77.9[1,2]
HYDROGEN EFFICIENCY	8.4	10.7	10.7
C_4+ DISTILLATE PRODUCT QUALITY			
EP, °F	975	975	750
°API	26.4	23.5	27.6
% Hydrogen	10.63	11.19	11.73
% Nitrogen	0.49	0.33	0.25
% Sulfur	0.02	0.05	0.01
BBL/TON	3.3	4.1	5.0

---

[1] 750°F Distillate end point.
[2] Coal contained 5.8% ash.

NOTE: All data at catalyst age representative of typical commerical replacement rates.

TABLE 12. WILSONVILLE FACILITY - CTSL

OPERATING CONDITIONS

Run No.	253A	254G	251-IIIB
Coal	Illinois #6	Ohio 6[1]	Wyodak
Catalyst	Shell 317	Shell 317	Shell 324
First Stage			
Average Reactor Temperature, ^{o}F	810	811	826
Inlet Hydrogen Partial Pressure, psi	2,040	2,170	2,510
Feed Space Velocity, lb/hr/lb Catalyst	4.8	4.3	3.5
Pressure, psig	2600	2730	2600
Catalyst Age, lb Resid/lb Catalyst	150-350	1003-1124	760-1040
Second Stage			
Average Reactor Temperature, ^{o}F	760	790	719
Space Velocity, lb Feed/hr lb Catalyst	4.3	4.2	2.3
Catalyst Age (lb resid/lb catalyst)	100-250	1166-1334	371-510
Yield, Weight Percent MAF Coal			
C_1-C_3 Gas	6	8	11
C_4+ Distillate	70	78	60
Resid	-1	-1	+2
Hydrogen Consumption	6.8	6.9	7.7
Hydrogen Efficiency, lb C_4+ Distillate/H_2 Consumed	10.3	11.3	7.8
Distillate Selectivity, lb C_1-C_3/lb C_4+ Distillate	0.08	0.11	0.18
Energy Content of Feed Coal Rejected to Ash Concentrate, %	20	10	15

---

[1] Approximately 6% Ash.

TABLE 13. HISTORY OF PROCESS DEVELOPMENT AND PERFORMANCE FOR BITUMINOUS COAL LIQUEFACTION

Process	Configuration	Distillate (wt% MAF coal)	Yield (bbl/t MAF coal)	Distillate Quality (gravity °API)	Nonhydrocarbon (wt%)		
					S	O	N
SRC II (1982)	One-stage, noncatalytic	41	2.4	12.3	0.33	2.33	1.0
H-Coal (1982)	One-stage, catalytic	52	3.3	20.2*	0.20	1.0	0.50
Wilsonville (1985), RITSL	Integrated two-stage, thermal-catalytic	62	3.8	20.2**	0.23	1.9	0.25
Wilsonville (1986), CTSL	Integrated close-coupled two-stage catalytic-catalytic	70	4.5	26.8**	0.11	<1	0.16
Wilsonville (1987), CTSL	Integrated close-coupled two-stage low-ash coal	78	5.0	+	+	+	+
HRI, CTSL (1987)	Catalytic-catalytic	78	5.0	27.6	0.01	-	0.25

---

*Light product distribution, with over 30% of product in gasoline boiling range; less than heavy turbine fuel.

**Higher boiling point distribution, with 20% of product in gasoline fraction and over 40% turbine fuel range.

+API and elemental analysis data unavailable at this time.

TABLE 14. RELATIVE COST FACTORS

	H-Coal	CCITSL
Total Plant Cost	1.00	1.10
Total Capital Required	1.00	1.11
Operating Cost	1.00	1.35
Annual Production Cost	1.00	1.37
Annual Production Rate	1.00	1.59
Required Product Selling Price[1]	1.00	0.78[2]

---

[1] First year price.

[2] CTSL product selling price is expected to be 3-5% lower.

TABLE 15. ACTIVITY OF METAL CHLORIDES FOR SRC CONVERSION (TANNER AND BELL, 1981)

Catalyst	% Solubility in Benzene	H/C Ratio in Soluble Products
None	46.7	0.85
$AlCl_3$	20.3	0.89
$FeCl_3$	13.8	0.86
$SbCl_3$	38.2	0.95
$HgCl_2$	37.8	0.93
$ZnCl_2$	46.8	1.01
$SnCl_2$	57.9	0.97

Reaction conditions: 572°F, 2030 psi H_2, 90 min., catalyst/SRC weight ratio of 1.0.

TABLE 16. EFFECT OF CATALYST DISTRIBUTION ON LIQUEFACTION OF A BITUMINOUS COAL (WELLER AND PELPETZ, 1951A)

		Yield (% MAF Coal)			
Catalyst	Mode of Addition	Conversion (benzene-solubles)	Asphaltene (hexane-insoluble	Oil*	Gas
None		33.4	2.8	21.6	9.0
$FeSO_4$ (1% Fe)	Powder	38.9	6.9	18.9	13.1
	Impregnated	84.9	38.9	31.0	15.0
$NiCl_2$ (1% Ni)	Powder	44.2	6.8	24.0	13.4
	Impregnated	88.3	15.5	54.8	18.0
$SnCl_2$ (1% Sn)	Powder	82.3	26.5	41.3	14.5
	Impregnated	88.3	19.9	52.9	15.5
Am molybdate	Powder	33.7	1.0	24.6	8.1
	Impregnated	92.7	27.2	51.9	13.6
$+H_2SO_4$	Impregnated	94.7	10.0	70.8	13.9

*by difference

Solvent-free hydrogenation; 842°F; 1h; 1015 psi (cold) H_2 pressure

TABLE 17. INTERDEPENDENCE OF CATALYST ACTIVITY AND SOLVENT COMPOSITION (GARG AND OTHERS, 1985)

Catalyst	None	250 ppm Mo	None	250 ppm Mo
SRC/Solvent ratio	0	0	0.13	0.13
<u>Product distribution (% MAF coal)</u>				
Gases	11.7	10.8	10.4	10.6
Oil	29.2	44.0	38.5	51.3
SRC	35.8	39.8	23.0	30.2
IOM	23.3	5.4	28.1	7.9
Conversion	76.7	94.6	71.9	92.1

Reaction conditions: bituminous coal; solvent:coal = 1.0; 824°F; 1204 psi H_2; 60 min reaction time.

TABLE 18. THE PROMOTIONAL EFFECT OF CHLORINE ON THE ACTIVITY OF TIN (WELLER AND OTHERS, 1950)

Catalyst	% Conversion to benzene-solubles	% gas	% Asphalt* per unit conversion
None	30.9	13.9	0.01
Sn(1%)	44.2	13.6	0.17
NH_4Cl(0.5%)	33.5	--	0.01
Sn(1%) + NH_4Cl(0.5%)	88.6	15.3	0.37

*hexane-insoluble

Solvent-free hydrogenation of hvCb bituminous coal; 842°F; 1h; 1015 psi (cold) H_2 pressure; powdered catalyst.

FIGURES

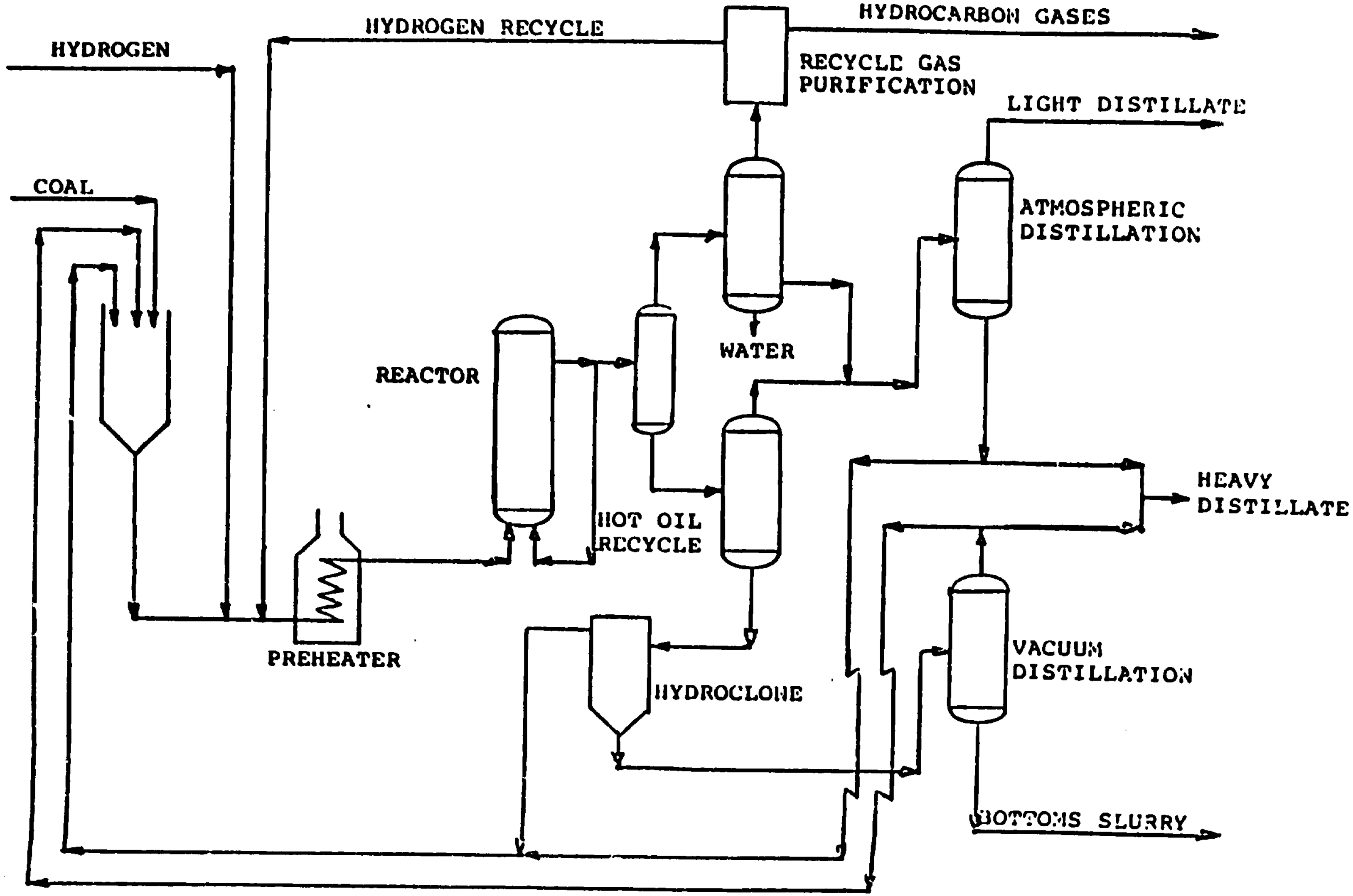

FIGURE 1. H-COAL® PROCESS DEVELOPMENT UNIT

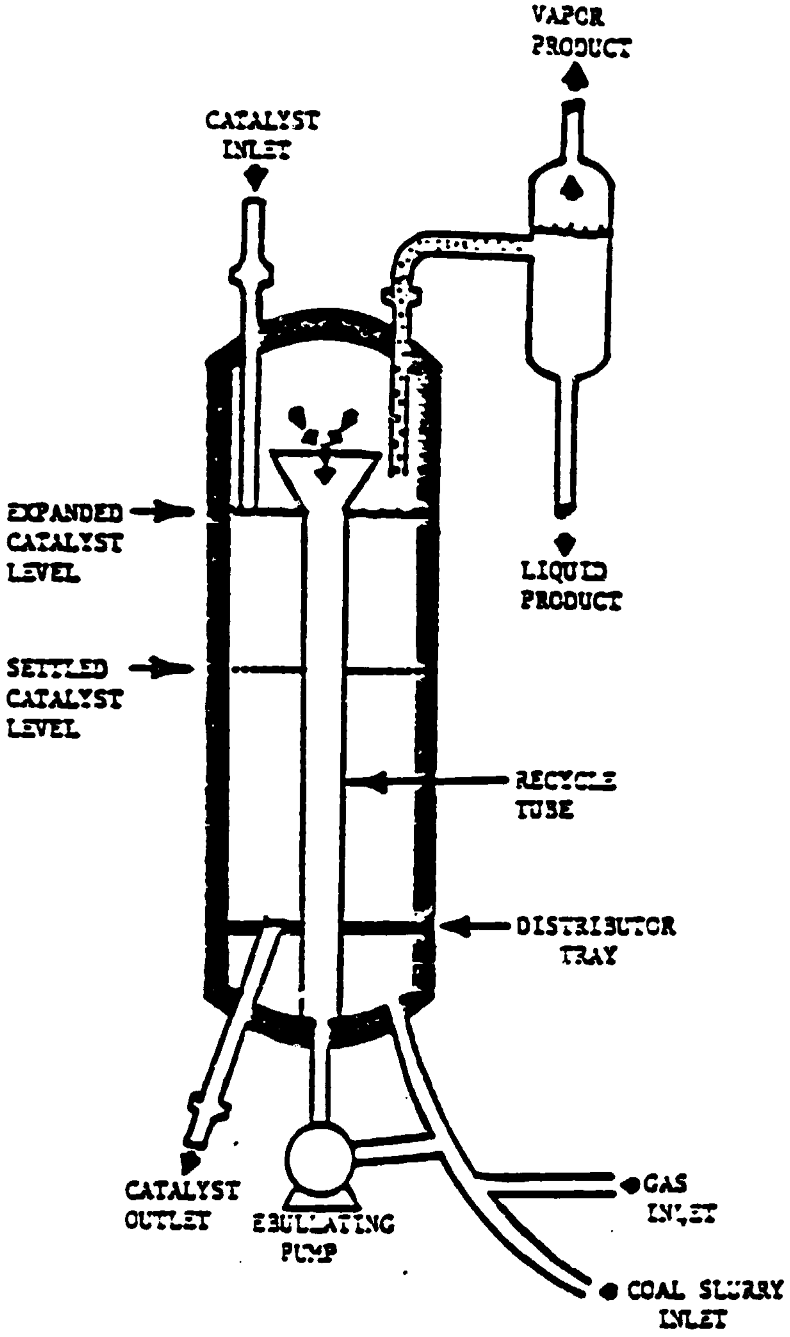

FIGURE 2. H-COAL EBULLATED BED REACTOR

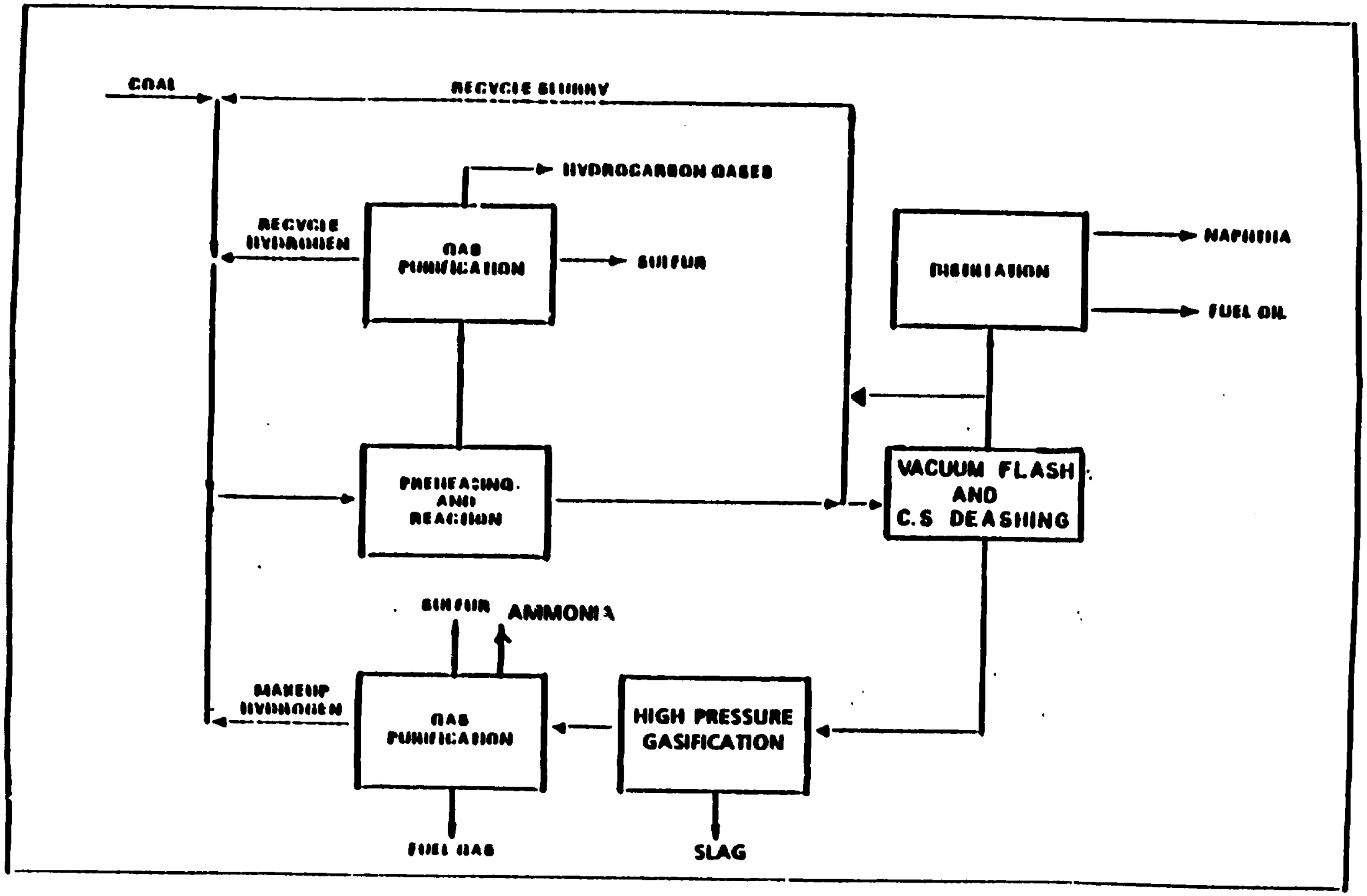

FIGURE 3. SRC-I LIQUEFACTION PROCESS BLOCK FLOW DIAGRAM

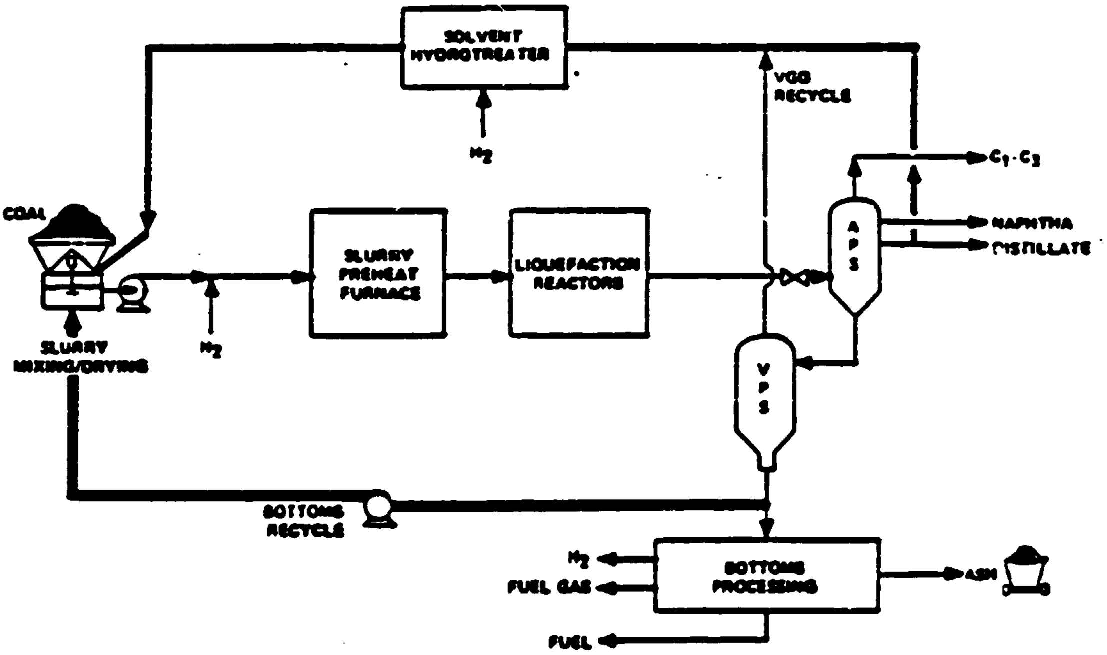

FIGURE 4. EDS COAL LIQUEFACTION PROCESS

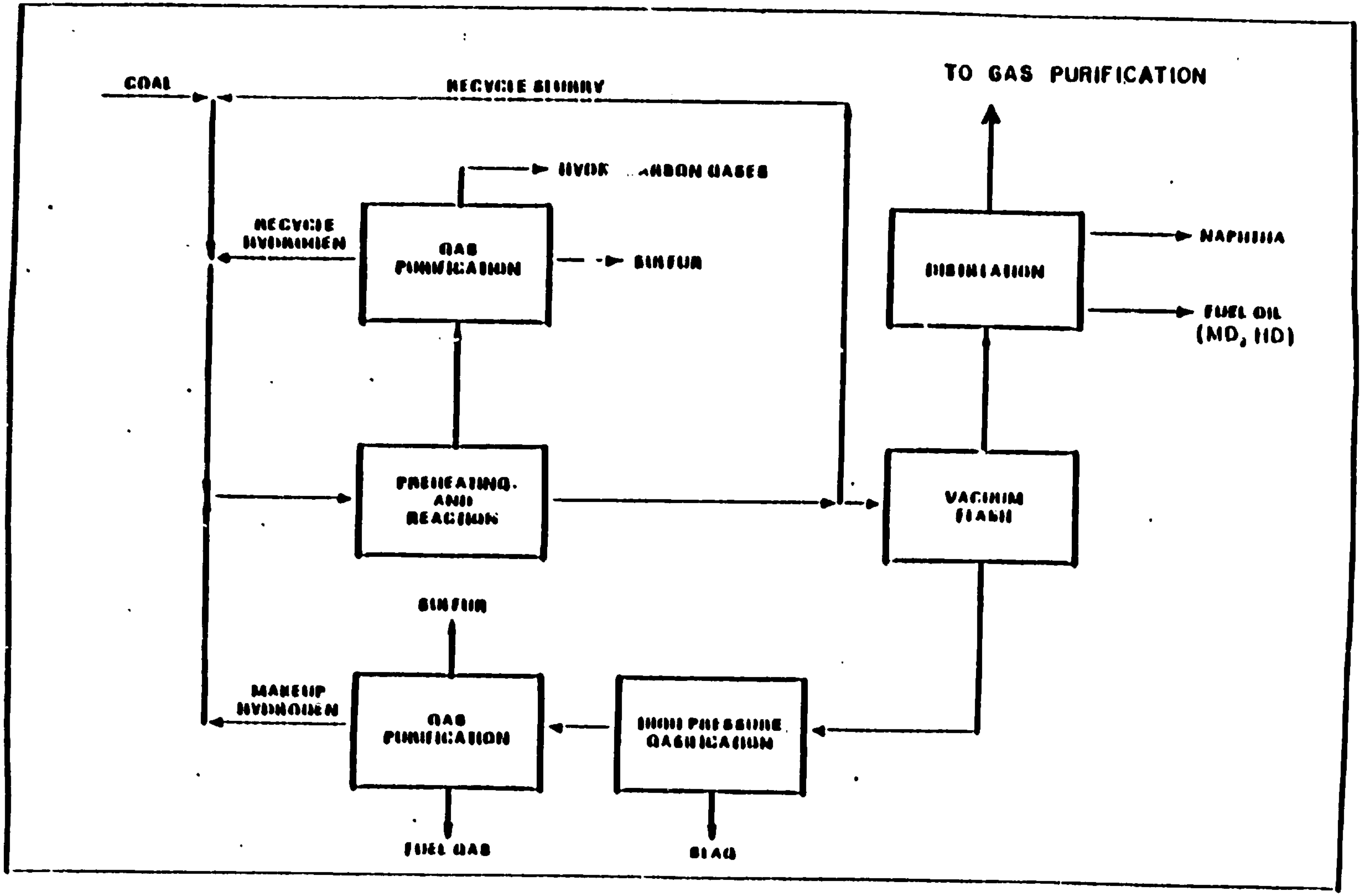

FIGURE 5. SRC-II LIQUEFACTION PROCESS

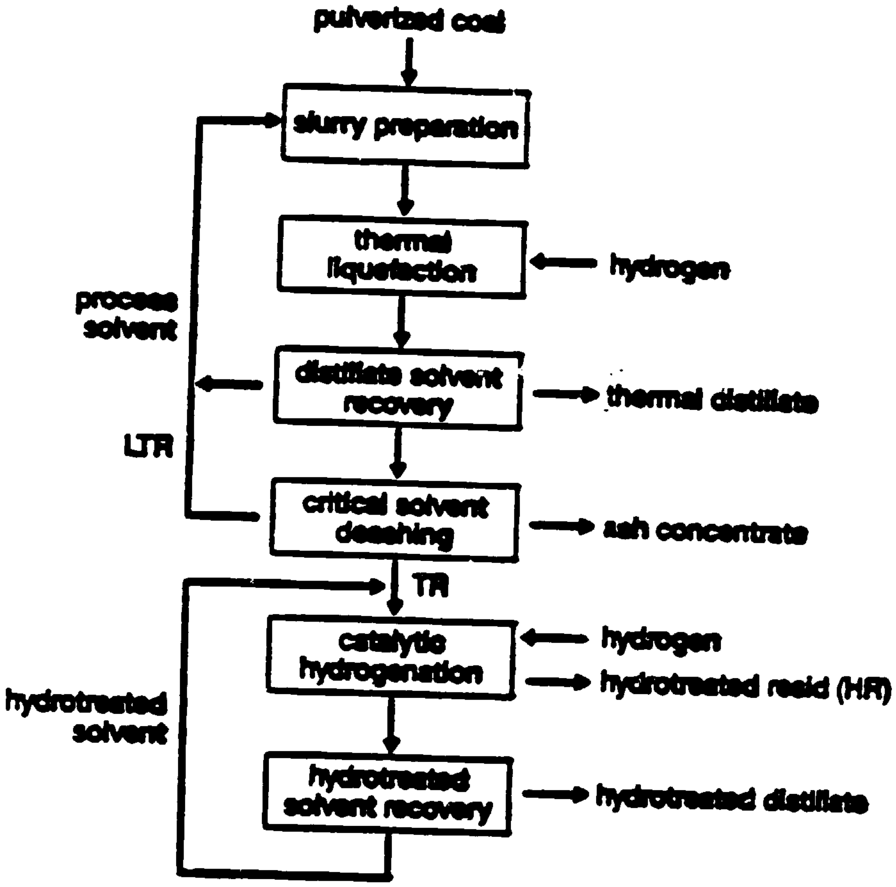

FIGURE 6. BLOCK FLOW DIAGRAM OF NTSL OPERATION

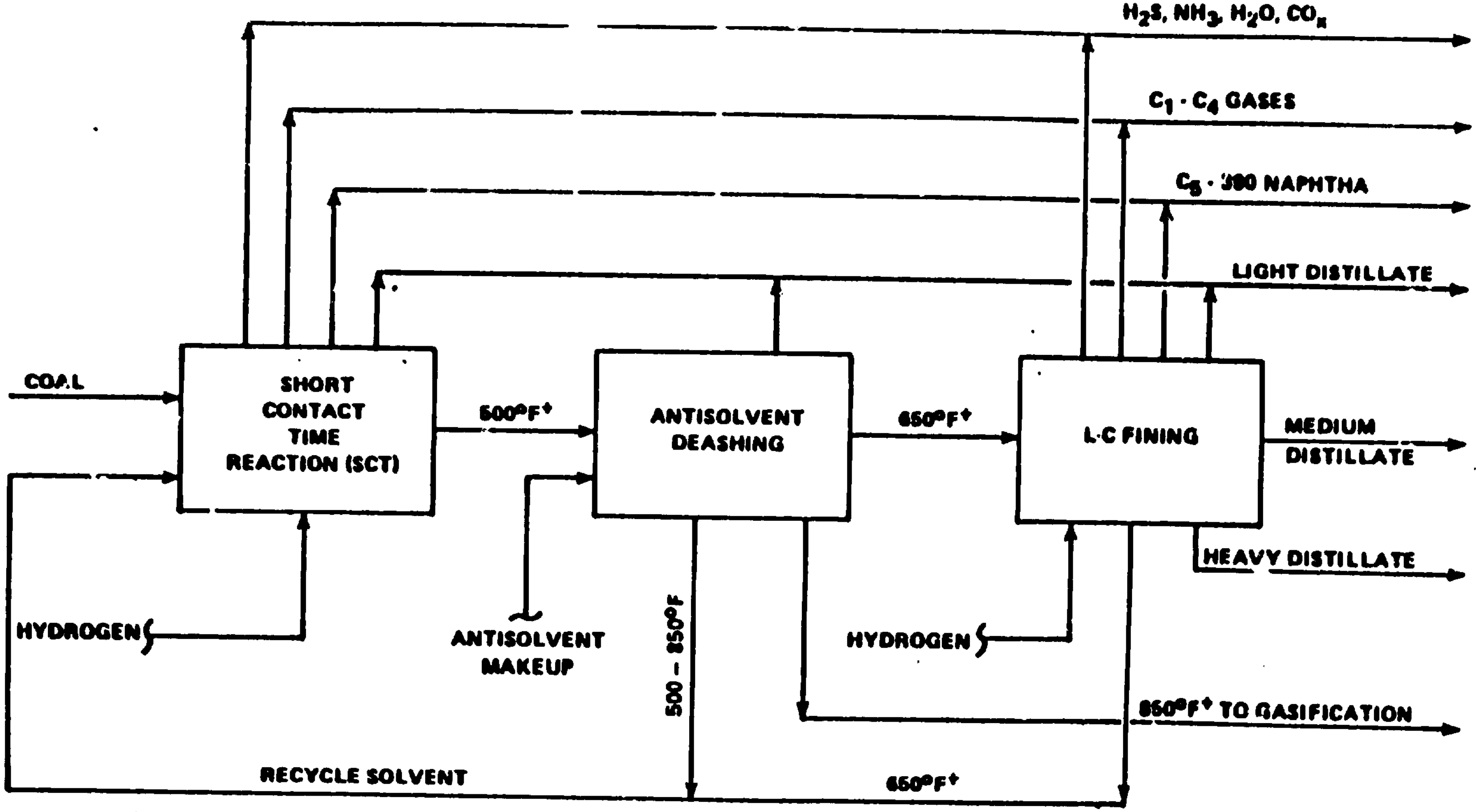

FIGURE 7. BLOCK FLOW DIAGRAM INTEGRATED TWO-STAGE LIQUEFACTION

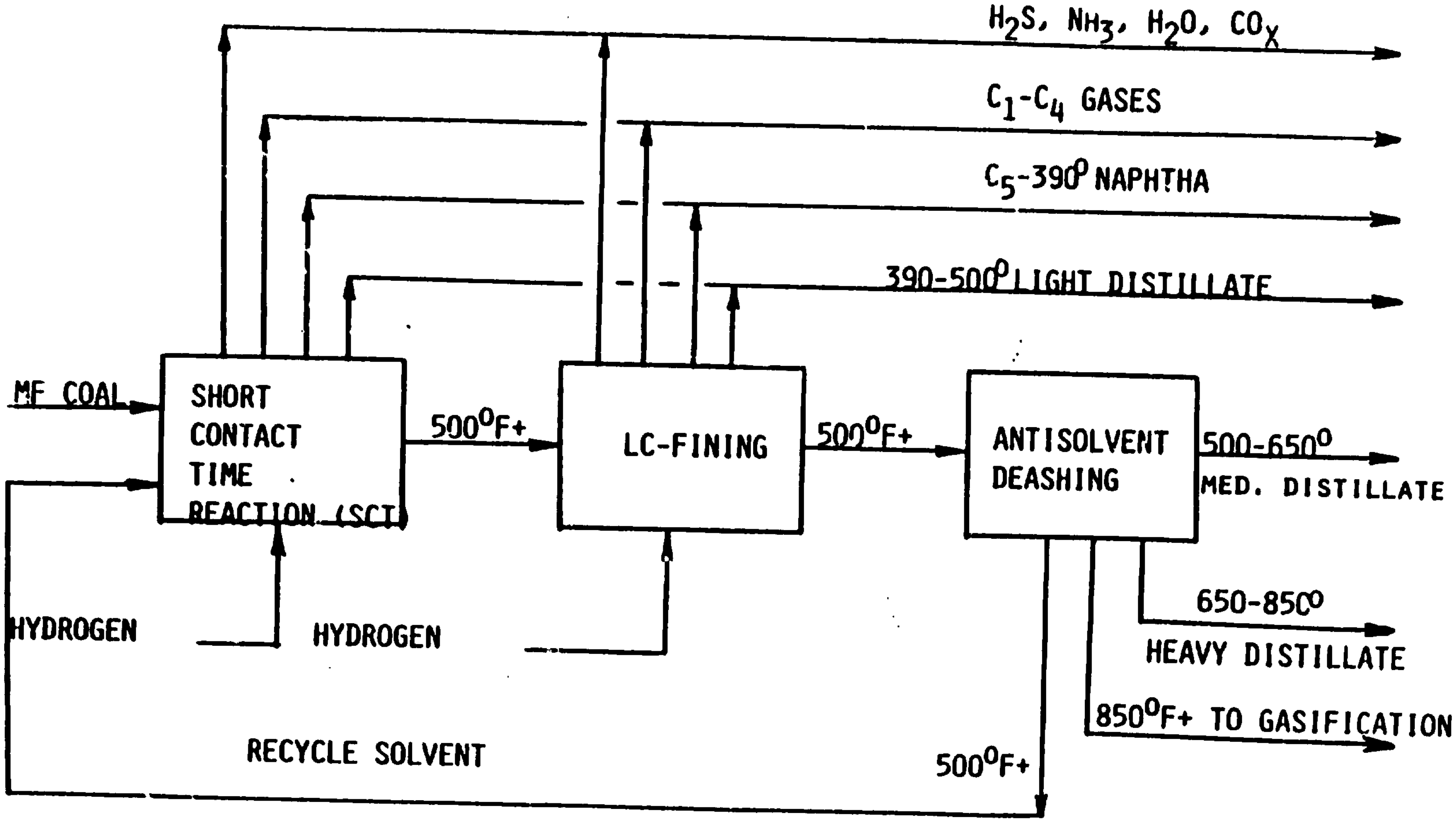

FIGURE 8. INTEGRATED TWO-STAGE LIQUEFACTION PROCESS
SCT / LC-FINING / DEASHING
ILLINOIS NO. 6 COAL

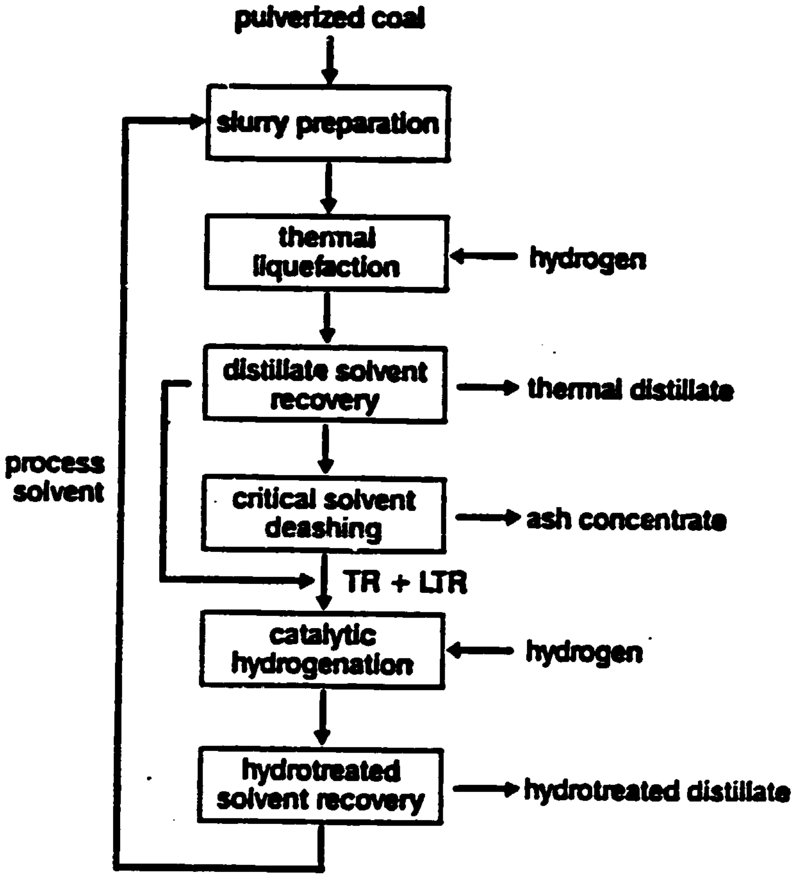

FIGURE 9. INTEGRATED TWO-STAGE LIQUEFACTION (ITSL)

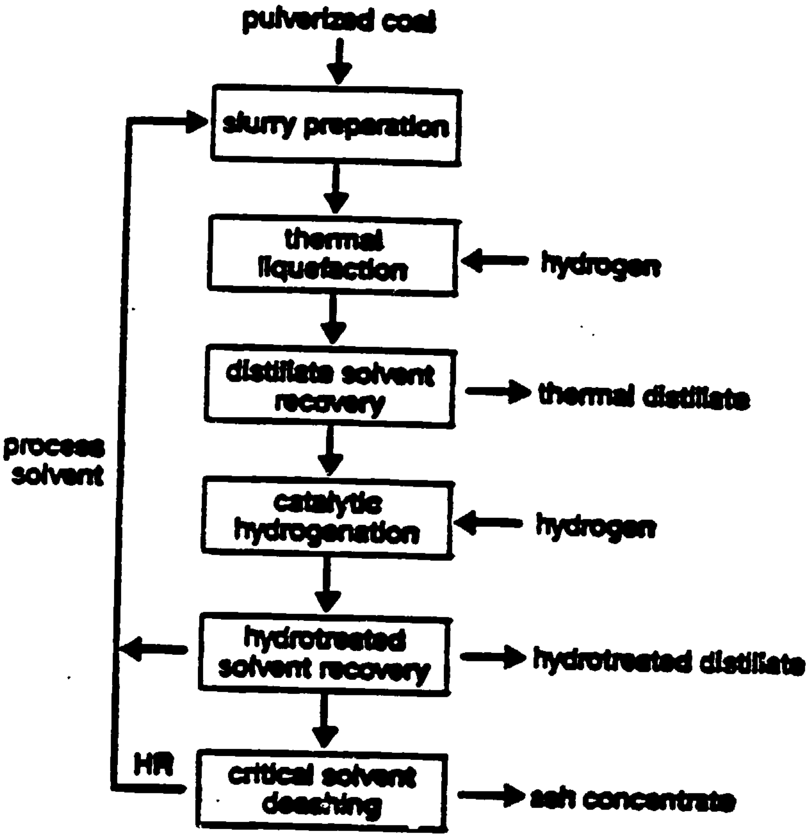

FIGURE 10. BLOCK FLOW DIAGRAM OF RITSL OPERATION

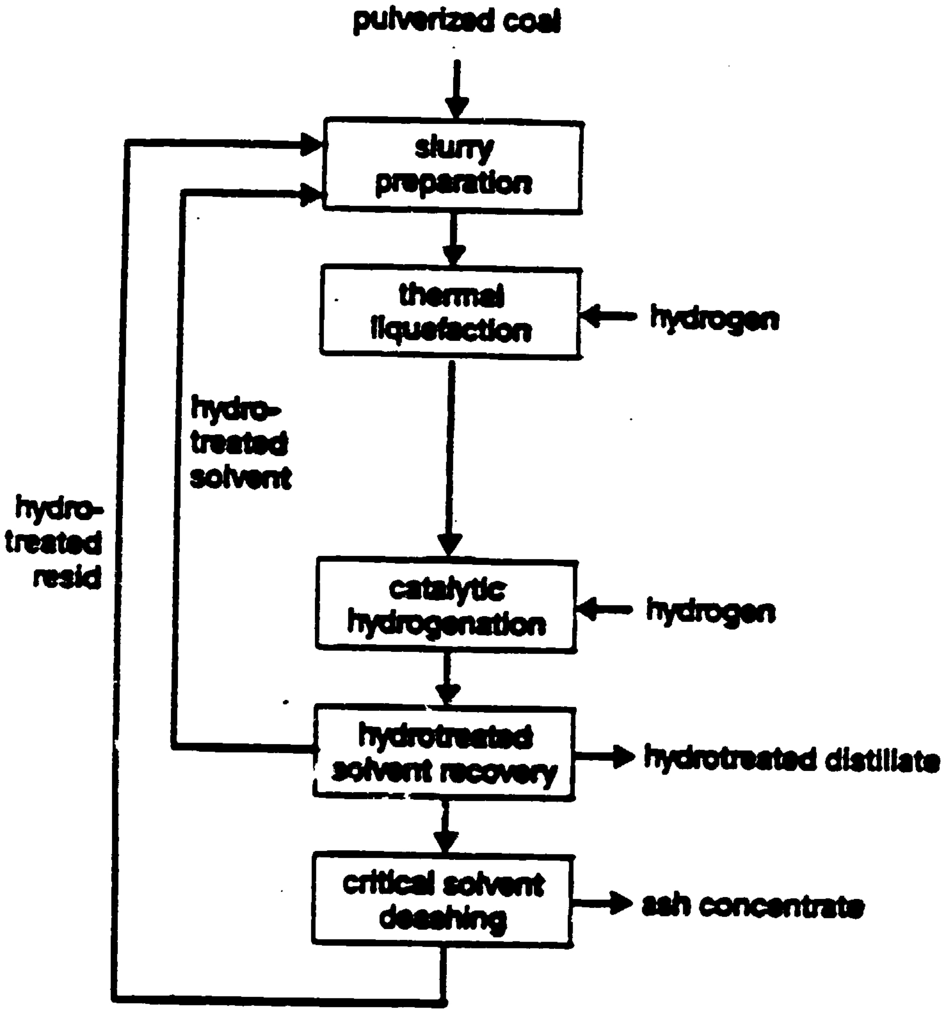

FIGURE 11. BLOCK FLOW DIAGRAM OF CC-ITSL OPERATION AT WILSONVILLE

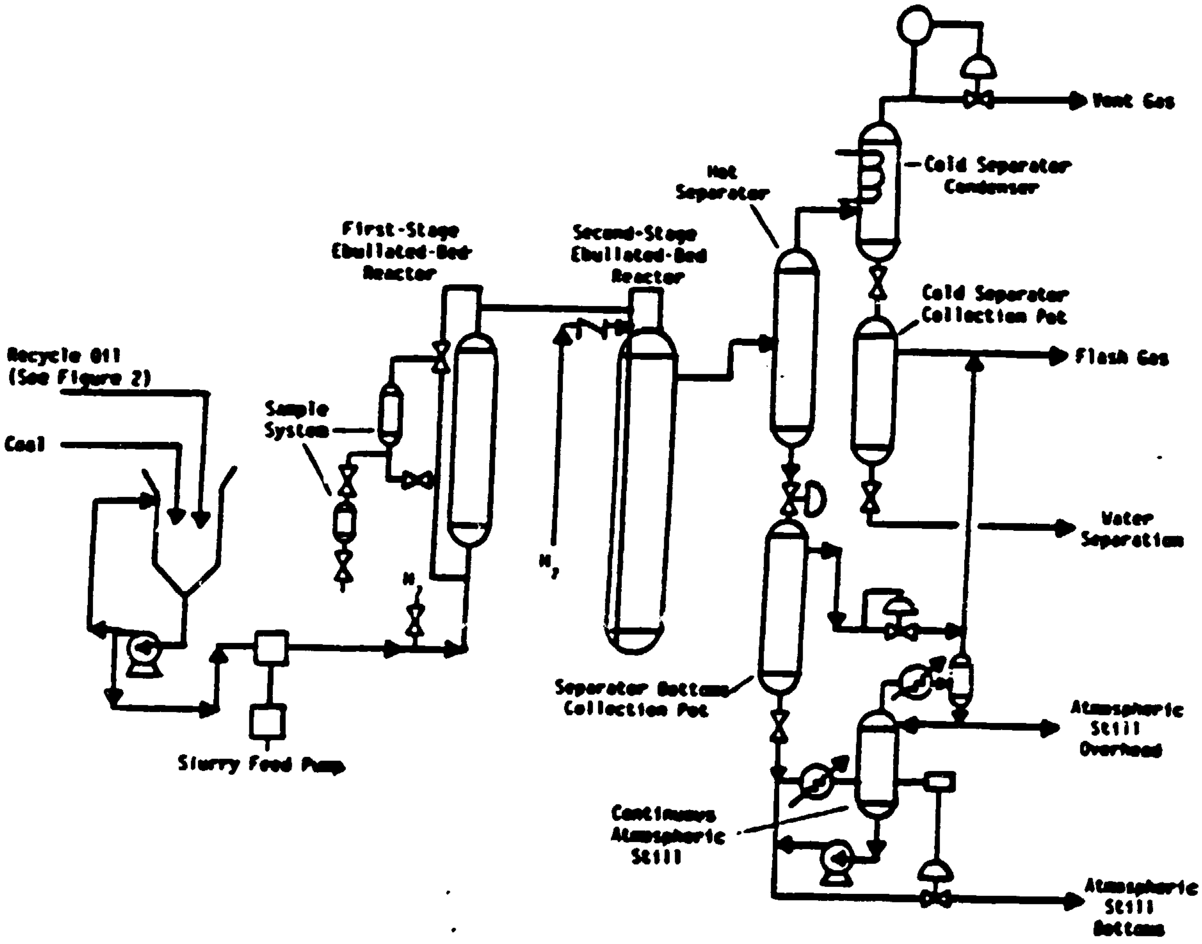

FIGURE 12. HRI CATALYTIC TWO-STAGE UNIT

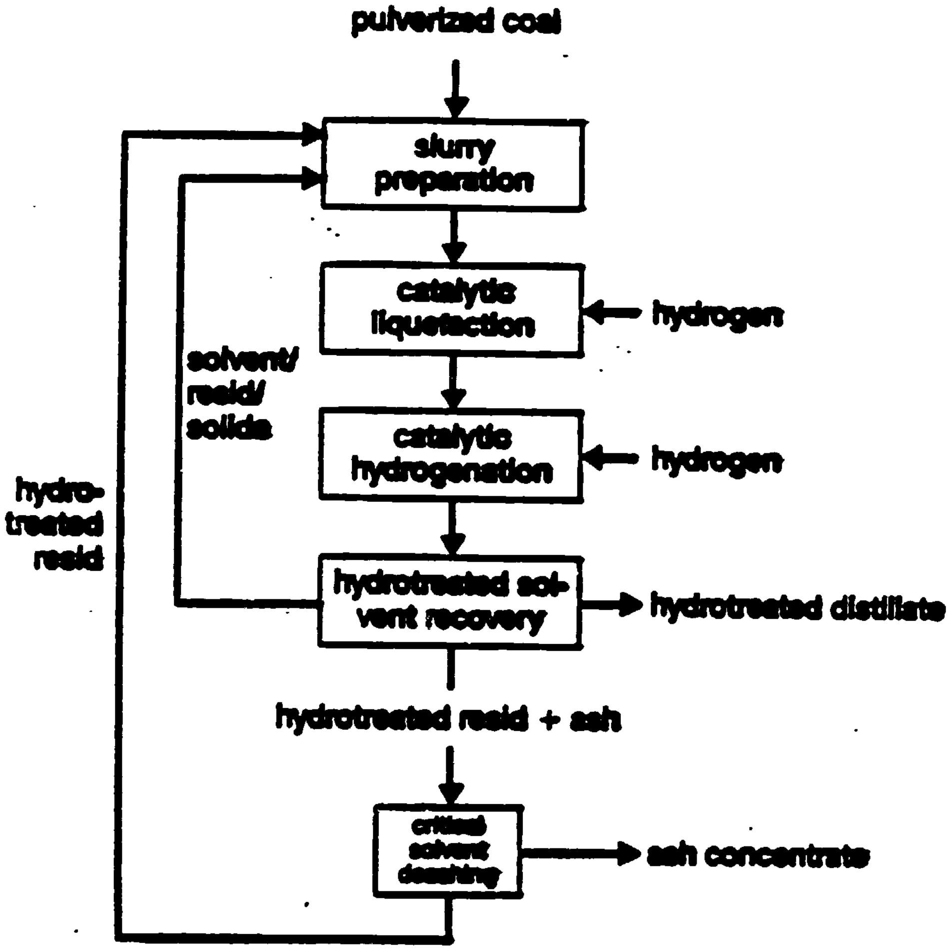

FIGURE 13. BLOCK FLOW DIAGRAM OF CTSL OPERATION WITH SOLIDS RECYCLE AT WILSONVILLE

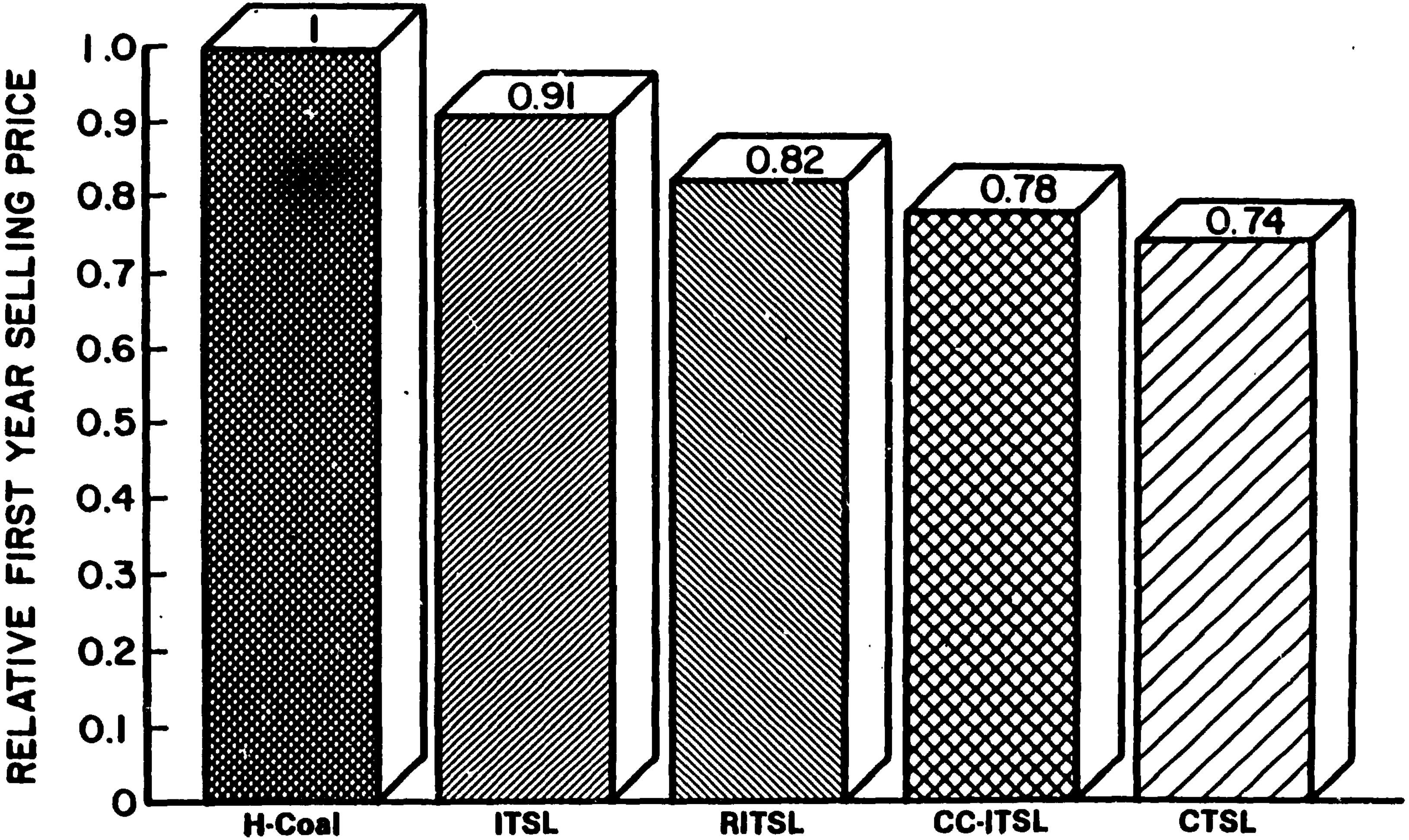

FIGURE 14. RELATIVE ECONOMICS OF TSL PROCESSES

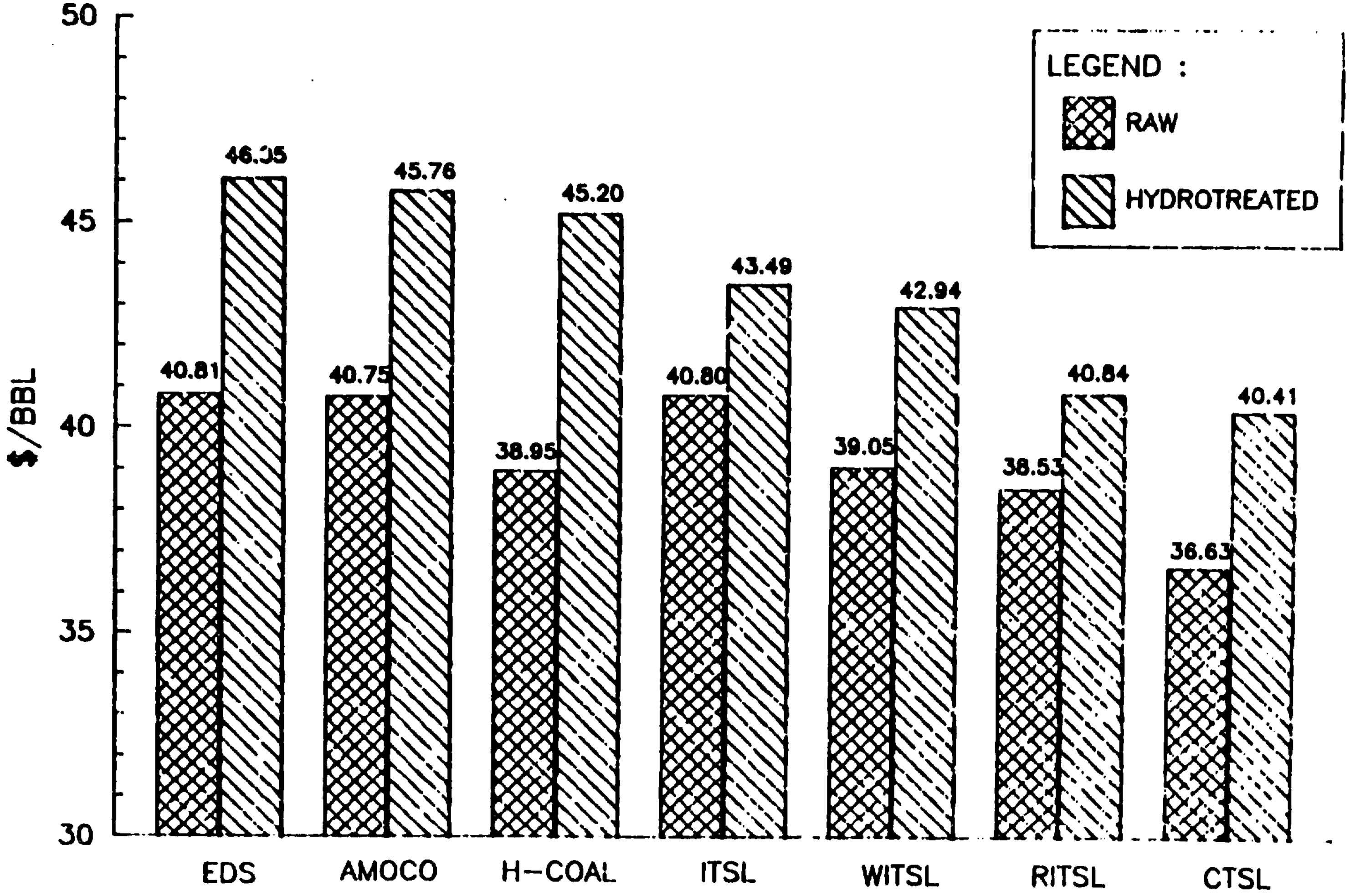

FIGURE 15

SUMMARY OF PROCESSES – ILLINOIS NO. 6 COAL

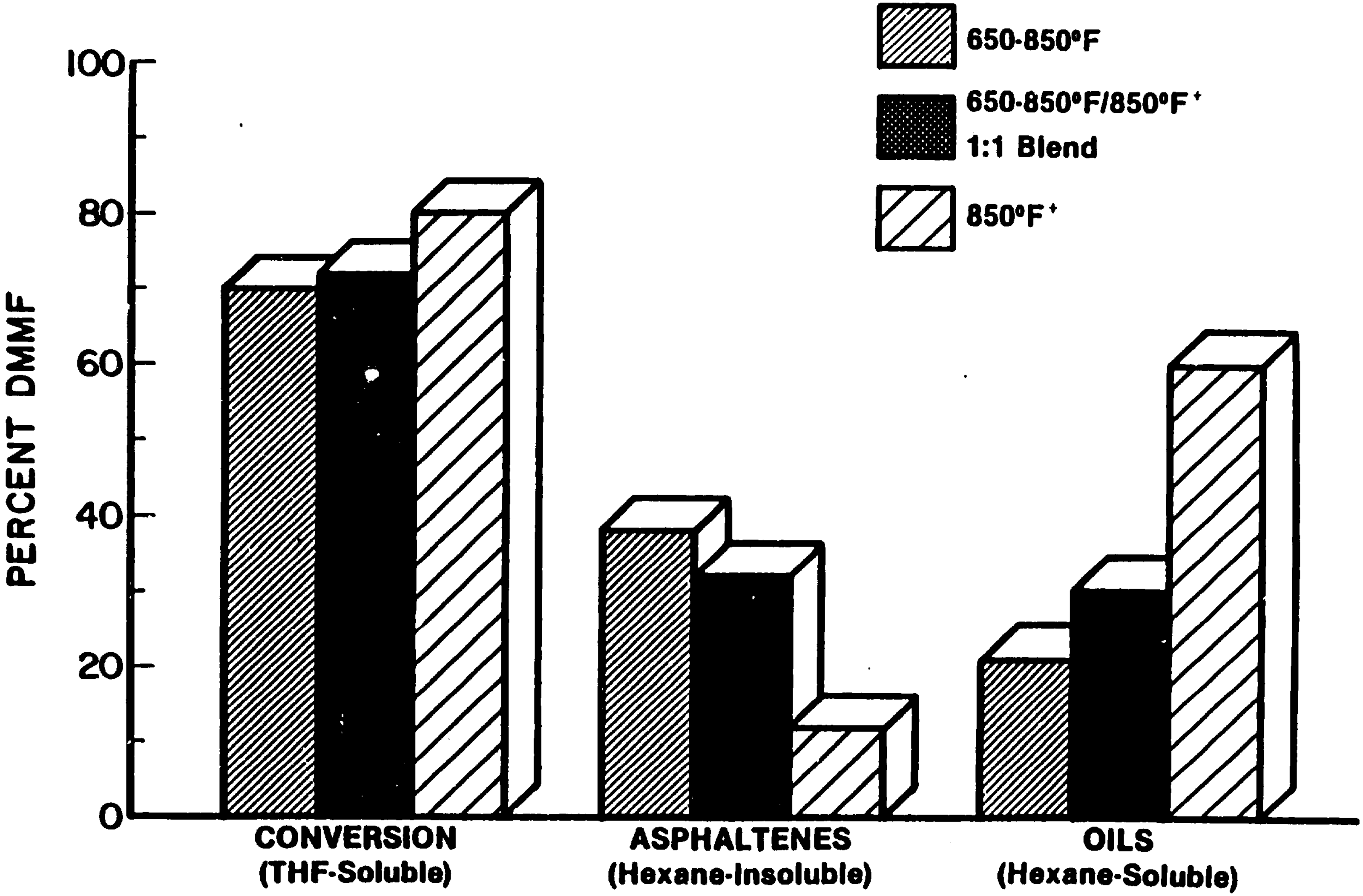

FIGURE 16. INTERDEPENDENCE OF CATALYST ACTIVITY AND SOLVENT COMPOSITION

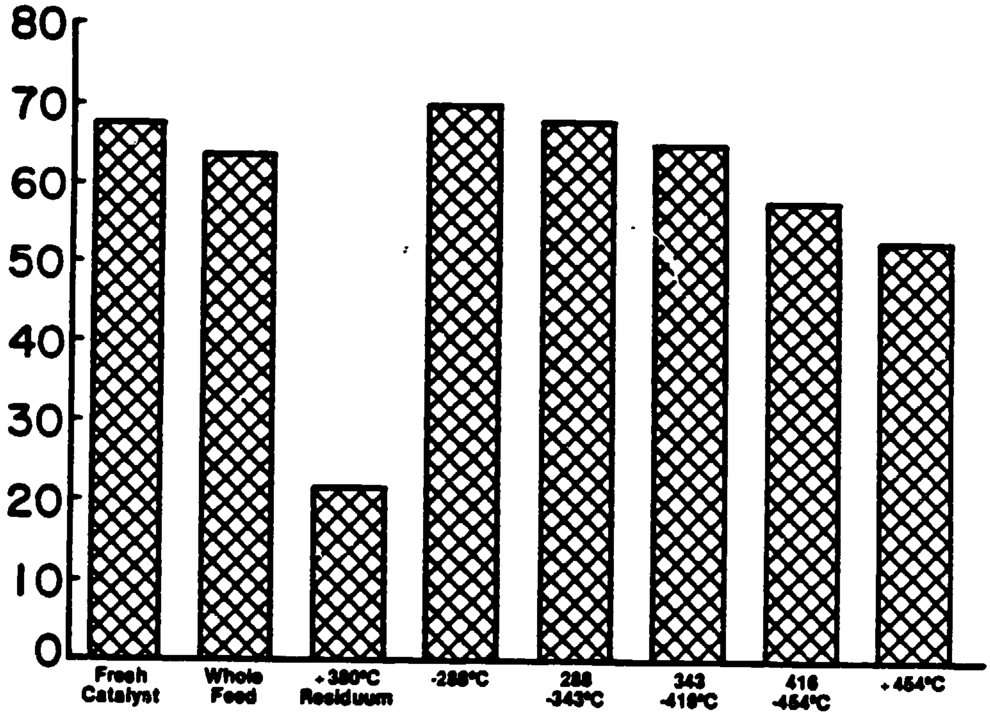

FIGURE 17. HDS ACTIVITY OF Ni-Mo/Al_2O_3 CATALYST AFTER REACTION WITH DIFFERENT BOILING RANGE FRACTIONS OF COAL LIQUIDS. (Stohl and Stephens, 1985b)

(Reaction with coal liquids: presulphided catalyst; 350°C; 120 min.; 8.4 MPa H_2 initial pressure. HDS activity test: thiophene; 350°C; atmospheric pressure)

NOJ16,584

APPENDIX B

RESTRICTED

April 22, 1988
English

APPENDIX B

ITSL

1. Integrate Two-Stage Liquefaction -- 1981.
2. Recent Developments ITSL PDU Operations -- 1982.
3. Performance of LC Fining Unit -- 1982.
4. Process Flow Modifications and Operations with Wyodak -- 1983.
5. SCT Modifications and LC Fining Kinetic Models -- 1984.
6. Catalytic Expanded Bed Hydroprocessing of Coal Extracts -- 1984.
7. Development of Lummus Crest Inc., Integrated Two-Stage Coal Liquefaction Process -- 1985.

WILSONVILLE

1. Comparison of TSL and H-Coal Reactor Yield Selectivity (Runs 233, 234, 235 - ICRC) -- 1982.
2. Advanced Coal Liquefaction Process Development at Wilsonville PDU (Run 239 vs. 236) -- 1982.
3. Recent Developments in Two-Stage Coal Liquefaction at Wilsonville (Runs 236, 240, 241 - Nonintegrated) (Runs 242, 243 JK, 243M - Integrated) -- 1983.
4. Integrated Two-Stage Liquefaction of Subbituminous Coal at Wilsonville (Run 246) -- 1984.
5. Recent Development in Two-Stage Coal Liquefaction at Wilsonville (Runs 247, 248, 249) -- 1985.

6. Status of Coal Liquefaction Development at Wilsonville (Runs 250, 251 I&II) -- 1986.
7. Catalytic-Catalytic Close-Coupled Liquefaction Process Development at Wilsonville Plant (Runs 251III, 252, 253) -- 1987.

HRI-CCCL

1. HRI's Two-Stage Catalytic Coal Liquefaction Program (bituminous) (Run 227-20) -- 1984.
2. The Catalytic Two-Stage Liquefaction Process (subbituminous) (Runs 227-21, 22, 25, 26, 27) -- 1985.
3. Process Variable Studies and Residual Oil-Extinction Recycle in Catalytic Two-Stage Liquefaction (Runs 227-22 (subbituminous), 32-34 (bituminous) -- 1986.
4. Catalytic Comparisons in Catalytic Two-Stage Liquefaction -- 1986.
5. Catalytic Two-Stage Liquefaction Process Demonstration Results for Illinois No. 6 Coal (Run 227-47) -- 1987.

KERR-MCGEE PROCESS

1. Integrated Two-Stage Bench-Scale Operation (Runs 6, 7, 9, 11) -- 1982.
2. Recent Developments in the Two-Stage Coal Liquefaction Program at Kerr-McGee, Corp. (subbituminous, iron oxide) -- 1983.
3. Use of Iron Oxide and Hydrogen Sulfide to Improve Integrated Two-Stage Coal Liquefaction.

RESTRICTED

April 22, 1988
English

AMOCO - 2-Stage

1. Thermal Reaction Process Variable Study -- 1983.
2. Amoco's Integrated Close-Coupled Coal Liquefaction Bench-Scale Test (HRI 227-24) -- 1985.
3. Aspects of Coal Liquefaction Catalyst Deactivation (Amocat catalysts) -- 1986.

UPGRADING (CHEVRON)

1. Refining of Syncrudes from Direct Coal Liquefaction Process -- 1983.
2. Two-stage Hydrocracking of ITSL Oil for Jet Fuel and Naphtha -- 1984.
3. Effects of Feed Boiling Range on Hydrotreating of Wyodak and Illinois ITSL Oils -- 1985.
4. Refining comparisons: CSTL, ITSL, and H-Coal Syncrudes -- 1986.

SANDIA (CATALYST STUDIES)

1. Deactivation of Direct Coal Liquefaction Catalysts (Runs 242, 246) -- 1984.
2. Formation of Carbonaceous Deposits on Coal Liquefaction Catalysts (Wilsonville feed - Shell 324M) -- 1985.
3. The Impact of Nitrogen Compounds on Catalyst Activity -- 1986.

RESTRICTED

April 22, 1988
English

PETC (CATALYST STUDIES)

1. Bench-Scale Upgrading of Coal Extract-Catalyst Testing -- 1982.
2. Catalyst Testing for Two-Stage Liquefaction -- 1982.

BIOLOGICAL TESTING (PNL)

1. Mutagenicity and Carcinogenicity Tests Results on ITSL Process Streams -- 1982.
2. Chemical Analysis and Biological Testing of Catalytic-Catalytic Two-Stage Direct Coal Liquefaction Process Materials -- 1985.
3. Two-Stage Coal Liquefaction Process Materials from the Wilsonville Facility Cperated in the Nonintegrated and Integrade Modes -- 1985.

SOLVENT QUALITY (CONOCO)

1. Recycle Slurry Oils in the Lummus Two-Stage Liquefaction Process -- 1981.
2. Recycle and Process Oil Characterization in ITSL -- 1982.
3. ITSL Process Oil Characterization Wilsonville and Lummus (Runs 242 and 3LCF 7, 8, 9) -- 1983.
4. Structural Properties of Integrated Two-Stage Liquefaction Solvents and Coal Dissociation Products (Comparison of Wilsonville and ITSL) -- 1984.
5. Composition of Recycle Oil from HRI's Catalytic Two-Stage Liquefaction Process -- 1985.

RESTRICTED

April 22, 1988
English

ASSESSMENT STUDIES (MITRE)

1. Fundamentals of ITSL -- 1981.
2. Effect of Coal Rank on Direct Coal Liquefaction Processes -- 1984.
3. Recent Advances in Two-Stage Liquefaction -- 1985.
4. Coking of Coal Liquid Bottoms (Batch Bench Coking Tests-CE) -- 1987.
5. The Impact of Bottoms Coking on Two-Stage Liquefaction Processes; Preliminary Assessment -- 1987.
6. Economics of Coal Liquids Revisited -- 1988.