



DE86010350

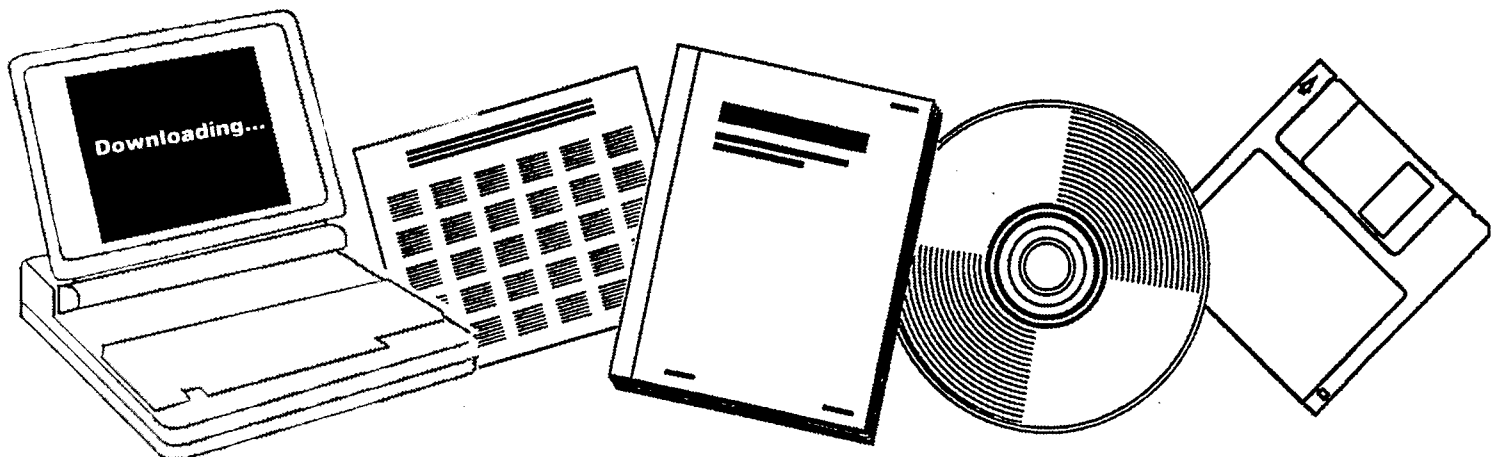
NTIS

One Source. One Search. One Solution.

**COAL LIQUEFACTION. INVESTIGATION OF
REACTOR PERFORMANCE, ROLE OF CATALYSTS AND
PCT PROPERTIES. QUARTERLY PROGRESS REPORT,
JANUARY 1-MARCH 31, 1986**

PITTSBURGH UNIV., PA

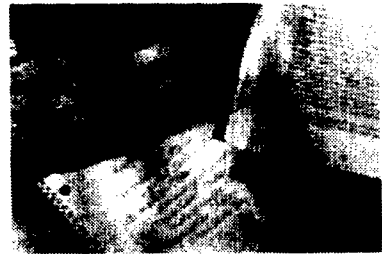
1986



U.S. Department of Commerce
National Technical Information Service

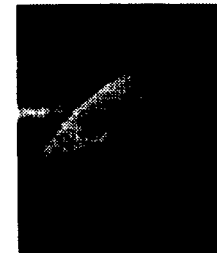
One Source. One Search. One Solution.

NTIS



Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.



Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on www.ntis.gov. You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provide the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov



U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

DE86010350



DOE/PC/60054--T10

DE86 010350

Received by OSTI

APR 28 1986

Quarterly Progress Report

COAL LIQUEFACTION - INVESTIGATION OF REACTOR PERFORMANCE,
ROLE OF CATALYSTS AND PCT PROPERTIES

Yatish T. Shah
John W. Tierney
Irving Wender

Sebastian Joseph
Chaur S. Wen

University of Pittsburgh
Pittsburgh, PA 15261

Prepared for the Department of Energy
Contract No. DE-FG22-83PC60054

January 1, 1986 to March 31, 1986

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes 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, trademark, 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.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1. Objective and Scope of Work

The objective of this work is to investigate areas of science and technology that have been defined as being of prime interest to coal processing technology development. These areas include properties of coal liquids and slurries, reactor design and performance in relation to reaction mechanisms. The work comprises investigations of the following high priority areas:

- Reaction kinetics and reactor performance in coal liquefaction;
- Role of catalysts in indirect liquefaction and direct coal liquefaction;
- Physical, chemical and thermodynamic properties of coal liquefaction products.

Work done during the first year of work on this project is summarized in Technical Progress Report DOE/PC/60054-T4 dated October 1984 and work during the second year in a Technical Progress Report submitted to the Department of Energy dated November 1985.

This report summarizes work done during the period January 1, 1986 through March 31, 1986. A detailed description of work is given below.

2. Modeling of Coal Liquefaction Processes

The objective of this work is to develop computer simulations which can be used to evaluate the performance of slurry reactors used for direct and indirect coal liquefaction processes. These programs are being written in Fortran language and are designed to be interactive in nature and easily adapted to use in the ASPEN simulator.

Scope of Work

Work during the current year is being done in two areas -- modeling of the Two Stage Liquefaction (TSL) process and enhancing models for indirect

liquefaction processes which were developed previously so that they can be used in conjunction with the ASPEN simulator at the Pittsburgh Energy Technology Center.

In the last quarter a literature search was conducted for two stage liquefaction processes, concentrating on the second stage which consists of an ebullated bed reactor. The Wilsonville Integrated Two Stage Liquefaction process is a typical candidate for modeling of Two Stage Liquefaction processes. A brief summary of the review is given below, and a kinetic model which will be used in the modeling effort is presented. Progress in the ASPEN modeling is also reported.

Two Stage Liquefaction Processes

The two principal routes for the direct hydrogenation of coal to form a liquid involve:

- (a) Addition of hydrogen directly from the gas phase
- (b) Addition of hydrogen from a donor solvent.

The first route is called catalytic liquefaction or hydroliquefaction while the second route is called solvent extraction. Though both methods involve direct hydrogenation, the difference lies in the catalytic hydrogenation stage.

Solvent Extraction: This is essentially a two-step process involving a mild hydrogenation extraction stage at temperatures up to 500°C to produce a solid/liquid extract which may be subsequently converted to liquid fuels and/or chemical feedstocks via a catalytic hydrogenation step. The solvent extraction stage can be carried out either directly under H₂ pressure or without H₂ in the dissolver, the solvent being hydrogenated in a separate step before being returned to the extraction stage. The EXXON Donor Solvent (EDS), Solvent Refined Coal

(SRC) and National Coal Board (NCB) processes are classified as solvent extraction processes. Bubble column slurry reactors are used for these processes.

Catalytic Liquefaction: This involves stronger hydrogenation over active catalysts in a fixed, ebullating or trickle bed reactor to produce hydrocarbon products directly and rehydrogenation of solvent occurs in-situ. The Synthoil and H-Coal processes are examples of this type.

Each process involves removal of ash, mineral matter and unconverted coal after the first hydrogenation stage. A general diagram to distinguish these processes is shown in Figure 1 (Pullen, 1983).

In two-stage direct liquefaction processes, extraction and hydrogenation take place in separate reactors. Conditions for each stage can thus be optimized. A summary of the various two-stage liquefaction (TSL) processes is given in Table 1.

TABLE 1: Summary of TSL Processes

Process	Extraction Pressure (atm)	Hydrogenation		
		Catalyst	Environment	Reactor-Type
Chevron	100-170	Co-Mo, Ni-Mo or Ni-W	Digest	Fixed Bed
Lummus	165	Ni-Mo	Solution	Expanded Bed
Wilsonville	140	Ni-Mo	Solution	Ebullated Bed
NCB Liquid Solvent Extraction	15	Co-Mo	Solution	Fixed Bed

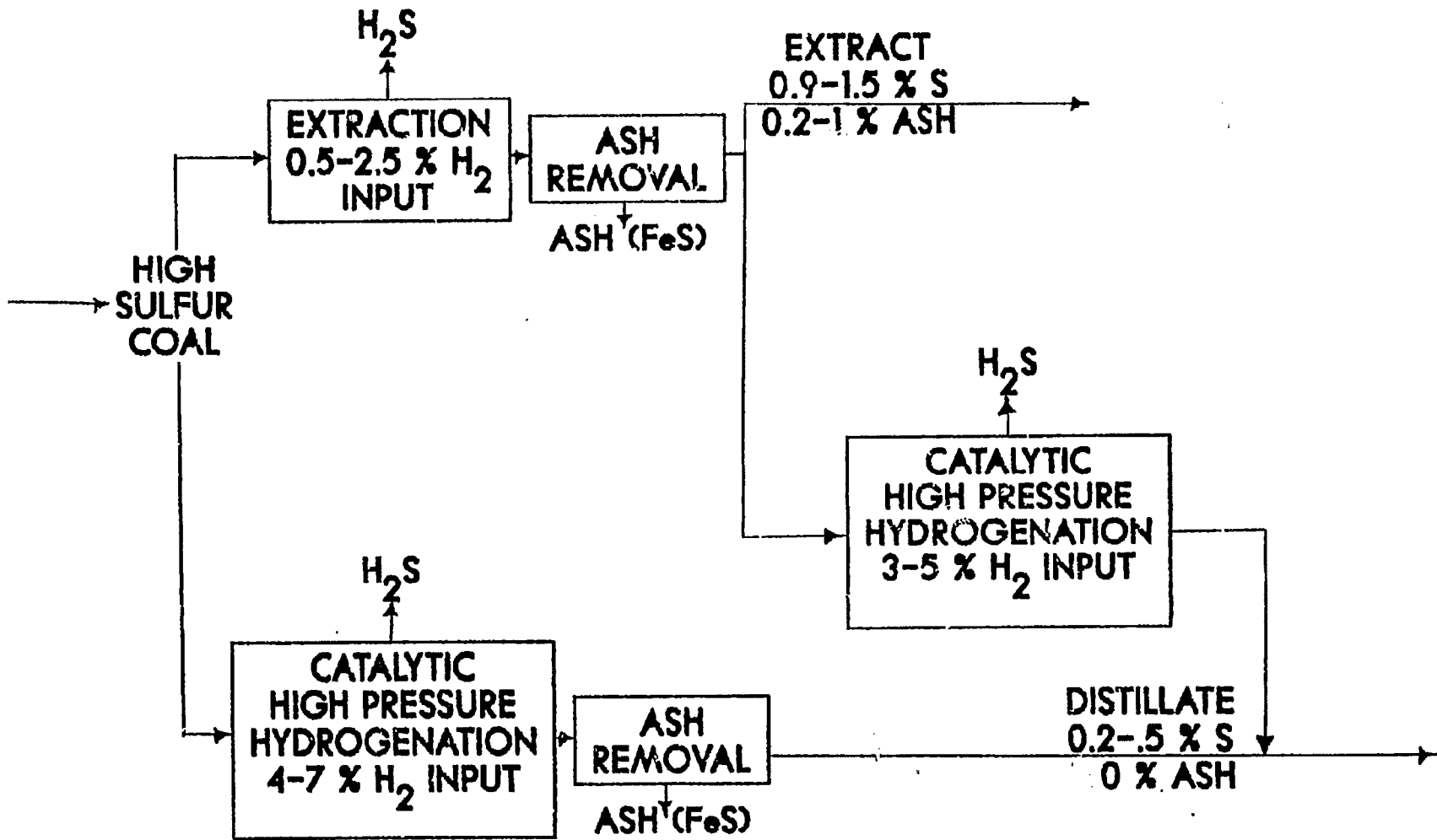


Figure 1: Alternative Routes for Direct Coal Liquefaction (Pullen, 1983)

Emphasis of this work is on modeling the second stage of the Wilsonville Integrated TSL process. The original facility at Wilsonville consisted of a single-stage thermal process (SRC-I). A Critical Solvent Deashing process was installed in 1978 and a second stage catalytic hydrogenation unit began operation in 1981. The second stage consists of an ebullated bed catalytic reactor based on the H-Coal concept. A block diagram of the ITSL process is shown in Figure 2. The salient features of the various process units are shown below.

<u>Unit</u>	<u>Salient Features</u>
<u>First Stage</u> Thermal Liquefaction Unit (TLU)	<ul style="list-style-type: none"> . dissolver or short contact time (SCT) . disposable catalyst may be utilized . 90-95% coal conversion (Cresol solubles)
Critical Solvent Deashing (CSD) Unit deashing solvent	<ul style="list-style-type: none"> . proprietary extraction process . conditions near critical point of . capable of fractionating coal extract . very efficient deashing achieved
<u>Second Stage</u> Hydrotreating (HTR)	<ul style="list-style-type: none"> . ebullated bed reactor . commercial supported-catalyst utilized . catalyst addition/withdrawal capability . wide range of stable operating conditions

The first stage is conventional SRC technology. In the second stage, the SRC is catalytically hydrocracked in the presence of hydrogen. In the hydrocracking step, the SRC is selectively cracked to gases and distillate fuels. A major portion of the sulfur and some nitrogen and oxygen are converted via hydrogenation to H₂S, NH₃, and H₂O. Table 2 gives a summary of catalytic reactions involved in coal conversion.

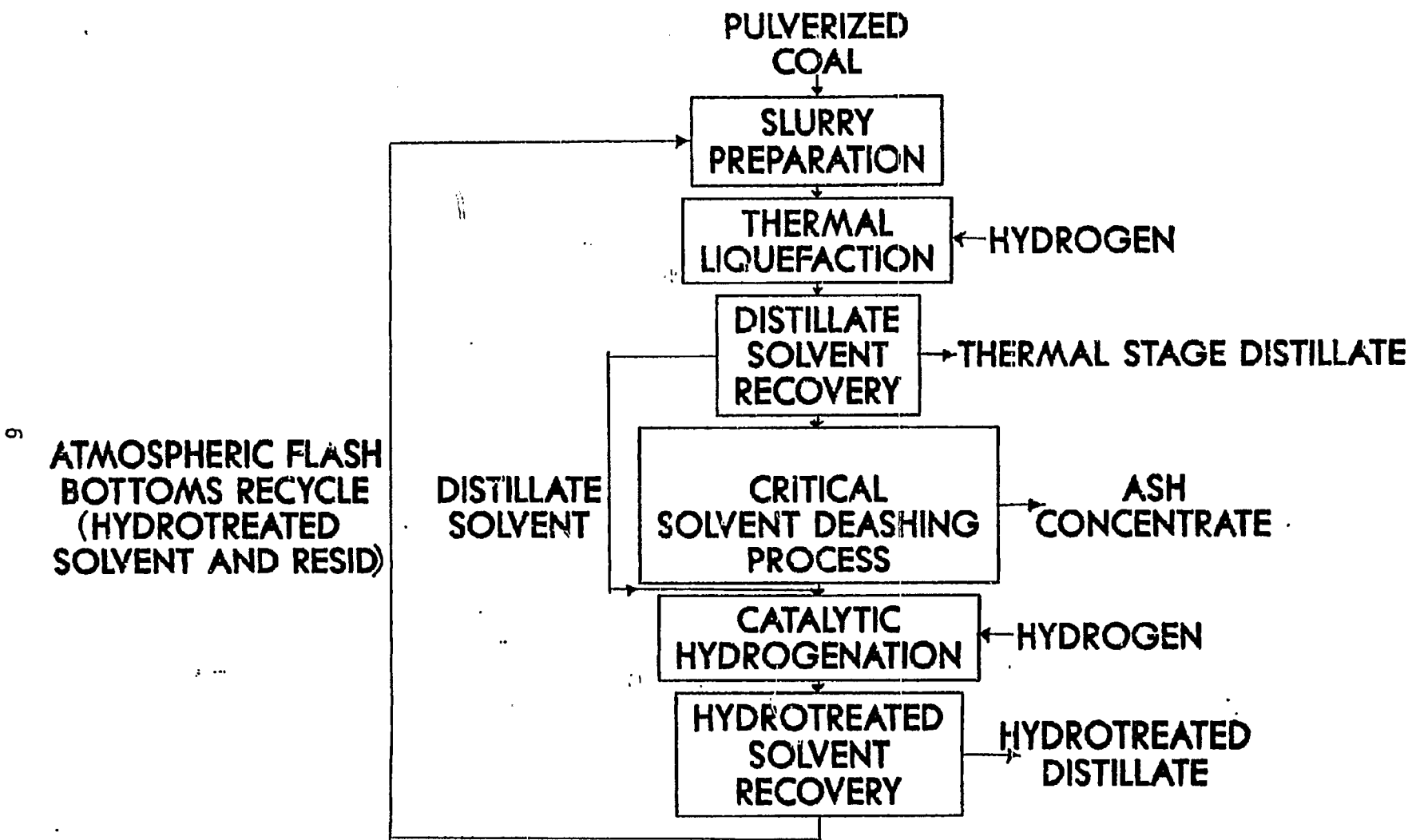


Figure 2: Schematic Representation of Wilsonville Integrated Two Stage Liquefaction (ITSL) Process

TABLE 2: Catalytic Reactions in Coal Conversion (Cusumano et al., 1972)

Process	General Reactions	Specific Reactions/Products
Direct Liquefaction	Hydrogenation Cracking Hydrofining	Aromatic Liquids Hydrodesulfurization (HDS) Hydrodenitrogenation (HDN)
Liquids Refining and Upgrading	Cracking Reforming Hydroforming	Hydrogenation Dehydrogenation Dehydrocyclization Isomerization Hydrogenolysis HDS, HDN

Three Phase Fluidized Bed Reactors

The first stage in the Wilsonville ITSL process is a thermal liquefaction unit, which consists of a bubble column slurry reactor. Though this reactor consists of three separate phases (gas, solvent, and coal) the slurry of coal and solvent is approximated for modeling purposes, as a pseudo-homogeneous liquid and the reactor is modeled as a two-phase system. However, the second stage which is the hydrotreating step consists of an ebullated bed reactor. Since a distinct solid phase (catalyst) is present in this reactor, the ebullated bed reactor is classified as a three-phase fluidized bed reactor. The mode of operation of three-phase fluidized beds is quite different from that of a slurry reactor as pointed out by Epstein (1981) and Muroyama and Fan (1985) in recent review articles. Some of these differences are given in Table 3.

TABLE 3: Characteristics and Applications of Three-Phase Processes⁽⁵⁾

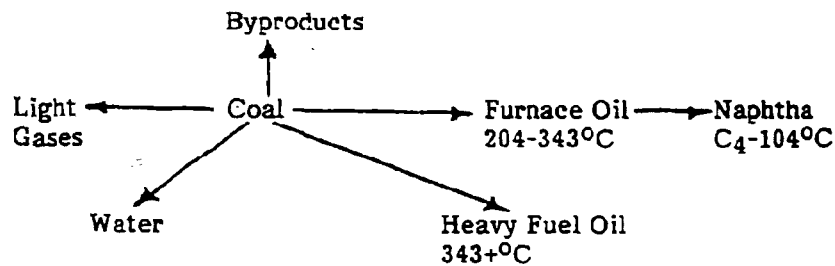
	<u>Three-Phase Fluidized Bed</u>	<u>Slurry Reactor</u>
Continuous Phase	Liquid	Liquid
Solids Suspended by flow of	Liquid	Gas
Solids Concentration Gradient	No	Yes
Typical Solids Holdup	10-50% vol.	< 10% vol.
Typical Particle Diameter	0.1-5 mm	< 0.5 mm
Applications	Heterogeneous reactions particularly hydrogenation of coal; catalytic reactions such as hydroprocessing; Fischer-Tropsch reaction. Biological processes such as fermentation and hydrogenation of fats.	

The dynamics of three phase fluidized beds are quite different from those of a slurry bed and equations developed to describe the hydrodynamic behavior of a slurry bed are not quite applicable to a three phase fluidized bed (Epstein, 1981). Ebullated bed fluid dynamics for the H-Coal process have been studied by Vasalos et al. (1982) and equations developed by them will be used in the model.

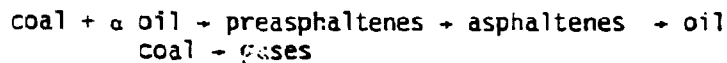
The reactor model used will be a one-dimensional axial dispersion model, and the equations of this model have been presented previously for thermal the liquefaction unit.

Kinetic Model

The kinetics of thermal liquefaction of coal have been briefly summarized by Gollakota et al. (1986) who have also investigated the thermal and catalytic kinetics in direct coal liquefaction. Shah et al. (1978) studied the kinetics of catalytic liquefaction of Big Horn coal in a segmented bed reactor. They proposed the following reaction mechanism.



Gollakota et al. (1986) have used the sequential progression of coal liquefaction in the modeling of kinetic data:



where α is a stoichiometric parameter.

These workers have investigated the relative influence of pore diffusion and the relative selectivity of thermal/catalytic reaction pathways. Effectiveness factors are evaluated for each reaction pathway and this kinetic model can be used to model the reactions occurring in the second stage ebullated bed reactor.

ASPEN Modeling

The indirect coal liquefaction processes that were modeled last year included the Methanol to Gasoline process, Methanol synthesis and Fischer-Tropsch synthesis. Of these three processes, the product spectrum is clearly defined only in the Methanol synthesis process. The reactants and products also appear in the ASPEN data base. Hence, as a first step, the Methanol synthesis models have been converted into an ASPEN compatible form and steps are being taken to transfer the program onto the PETC computer system.

3. Role of Catalysts in Indirect Liquefaction and Direct Coal Liquefaction

The objective of this work is to review and discuss key advances in direct coal liquefaction catalysis, especially for the innovative use of certain catalysts in direct coal liquefaction. This study will provide an overview of streams of knowledge which have contributed to the development of coal liquefaction catalysis and which have high potential for contributing in the future. Newer types of catalysts, discovered after World War II, will constitute the main subjects of this report.

Scope of Work

The use of catalysts in direct coal liquefaction provides several advantages including activating molecular hydrogen, minimizing hydrogen consumption, permitting milder operating conditions, and increasing distillate production. Included among the catalyst systems to be reviewed and whose potentials are to be evaluated are: the use of liquid clathrate systems, homogeneous catalysts such as metal carbonyls and transition metal complexes, germanium and tin salts, iodine and hydrogen iodide, Lewis acids such as $ZnCl_2$ and $AlCl_3$, hydrogen fluoride, and

superacids such as fluorosulfonic acid (FSO_2OH) and the less corrosive solid acids such as $\text{Fe}_2\text{O}_3\text{-SO}_4^{2-}$ and $\text{TiO}_2\text{-SO}_4^{2-}$.

Role of Catalysts in Coal Liquefaction

Over the last decade a large number of catalysts for coal liquefaction have been investigated with the aim of improving coal conversion to light oils. Several researchers have reported the use of transition metal carbonyls for the preparation of dispersed metallic catalysts during coal liquefaction. Since a good dispersion state of the catalyst can generally be achieved with the use of metal carbonyls as catalyst precursors, it is anticipated that the soluble transition metal complex can penetrate into the pores of the coal which facilitates strong interaction between the coal and catalyst.

Recent work reported that iron pentacarbonyl, $\text{Fe}(\text{CO})_5$, soluble in organic solvents, serves as an excellent catalyst for coal hydroliquefaction. The finely dispersed metallic iron derived from $\text{Fe}(\text{CO})_5$ seems to be able to permeate into coal and to give high catalytic activity. The catalytic ability of metal carbonyls to promote hydrogen transfer from molecular hydrogen to coal fragment radicals at temperatures of coal mesophase formation (e.g., 375°C) is also important during coal liquefaction. This could partly explain the failure of early experiments, carried out by Holly et al. and Cox et al., to obtain significant amounts of coal dissolution or conversion. They both employed a lower reaction temperature (below 200°C) for liquefaction.

Metal carbonyl catalysts offer the advantage of high selectivity at relatively mild operating conditions. Unlike heterogeneous catalysts, every metal atom in a metal carbonyl catalyst is available to participate in the reaction, and furthermore, the chemical reactivity of the catalyst can be easily modified by the

addition of different ligands and solvents. However, metal carbonyl catalysts have their own limitations in that recovery is usually difficult. The catalytic species are difficult to separate from reaction products. In addition, thermal stability may also present problems in practical applications, although most organometallic carbonyl catalysts can be operated at substantially high CO partial pressure to maintain stability.

A review of work on the effect of superacids on coal liquefaction will start next month.

References

Cusumano, J.A., R.A. Dalla Betta, R.B. Levy, Catalysis in Coal Conversion, Academic Press, NY (1978).

Darton, R.C., "The Physical Behavior of Three-Phase Fluidized Beds," Fluidization, J.F. Davidson, R. Clift, and F. Harrison, eds., 2nd edn., Academic Press, London (1985), pp. 495-528.

Epstein, N., "Three-Phase Fluidization: Some Knowledge Gaps," Can. J.Chem. Eng. 59, 649 (1981).

Gollakota, S.V., J.A. Guin, and C.W. Curtis, "Parallel Thermal and Catalytic Kinetics in Direct Coal Liquefaction," Ind. Eng. Chem. Process Des. Dev., 24, 1148 (1985).

Muroyama, K. and L.S. Fan, "Fundamentals of Gas-Liquid-Solid Fluidization," AIChE J., 31, 1 (1985).

Pullen, J.R., "Solvent Extraction of Coal," Coal Science, Vol. 2, M.L. Gorbaty, J.W. Larsen and I. Wender, eds., Academic Press, NY (1983), pp. 173-288.

Shah, Y.T., D.C. Cronauer, H.G. McIlvried, and J.A. Paraskos, "Kinetics of Catalytic Liquefaction of Big Horn Coal in a Segmented Bed Reactor," Ind. Eng. Chem. Process Des. Dev., 17, 288 (1978).

Vasalos, I.A., D.N. Rundell, K.E. Megiris, and G.J. Tjatjopoulos, "Holdup Correlations in Slurry-Solid Fluidized Beds," AIChE J., 28, 346 (1982).

SATISFACTION GUARANTEED

NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.

▶ **E-mail: info@ntis.gov**

▶ **Phone: 1-888-584-8332 or (703)605-6050**

Reproduced by NTIS

National Technical Information Service
Springfield, VA 22161

This report was printed specifically for your order from nearly 3 million titles available in our collection.

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

About NTIS

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at <http://www.ntis.gov>.

NTIS

**Ensuring Permanent, Easy Access to
U.S. Government Information Assets**



U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000
