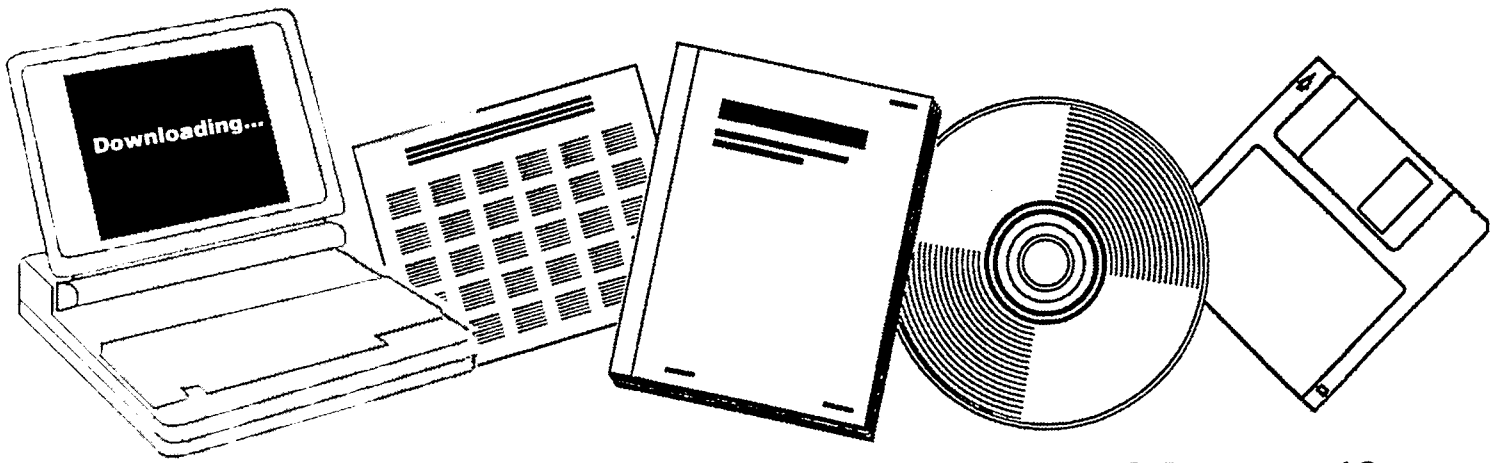
INVESTIGATIONS OF REACTOR PERFORMANCE, ROLE OF CATALYSTS, HYDROGEN DONOR SOLVENTS, AND PCT PROPERTIES OF COAL LIQUIDS AND SLURRIES. QUARTERLY PROGRESS REPORT, OCTOBER 1, 1982-DECEMBER 31, 1982

PITTSBURGH UNIV., PA

1982



DE83008188

DOE/PC/50057--T1

DE83 008188

Quarterly Progress Report

Investigations of Reactor Performance, Role of Catalysts, Hydrogen Donor Solvents, and PCT Properties of Coal Liquids and Slurries

Alan Brainard
Yatish T. Shah
John W. Tierney
Irving Wender

Rajendra Albal
Sanjay Godbole
Amol Kulkarni

University of Pittsburgh
Pittsburgh, PA 15261

Prepared for the Department of Energy
Contract No. DE-AC22-82PC50057

October 1, 1982 to December 31, 1982

1. Objective of Work

The objective of this work is to investigate areas of science and technolcgy which have been defined as being of prime interest to coal processing technology development. These areas include:

- Reaction kinetics and reactor performance in direct coal liquefaction
- Roles of catalysts and hydrogen donor solvents in direct coal liquefaction
- Physical, chemical, and thermodynamic properties of coal liquids and slurries

Reports will be prepared for each of these subjects.

2. Progress to Date:

Activity during the first quarter was directed to selecting a research team, outlining the nature of the reports which will be prepared, and initiating searches for literature references in the PETC Liquefaction Technology Data Bank (LTDB) and other sources.

A. Research Team.

Three postdoctoral students will work with Professors Brainard, Shah, Tierney, and Wender in carrying out this investigation. They are Sanjay Godbole, who will work with Dr. Shah on Task 1; and Amol Kulkarni, who will work with Dr. Wender on Task 2; and Rajendra Albal, who will work with Dr. Brainard on Task 3. Resumes for new members of the team are attached as Appendix B.

B. Structure of reports of investigation.

The work has been divided into three tasks, with one co-investigator and one postdocotral student working on each task. Overall coordination and computer assistance is being provided by Dr. Tierney. Based on discussions with Dr. Peters and Dr. Haynes at PETC, a general framework for the reports has been prepared and is presented in Appendix A. Faced with the desire to do a thorough and complete investigation and the limited time available, the decision has been made to concentrate for the first year on the SRC-II process. It is hoped that the type of investigation undertaken for SRC-II can later be extended to other coal liquefaction processes.

C. Literature searches.

The largest and most important source of data for the SRC-II process is the PETC LTDB, and a thorough search of the documents there was initiated.

3. Future work.

The primary emphasis during the next quarter is the identification and acquisition of important documents on the SRC-II process for each of the three task areas. Members of the team plan to spend considerable time at PETC reviewing the LTDB. They will also review the open literature as appropriate.

APPENDIX A

Proposed Structure for Research Reports

Task 1: Reaction Kinetics and Reactor Performance in Direct Coal Liquefaction:

In this task, data available through the PETC LTDB and at PETC and other sources will be used to carry out an investigation of reaction kinetics and reactor performance for the SRC-II process. The published data for other coal liquefaction processes may be used for comparison. Since the data available on reactions in the preheater are scarce, main emphasis will be given to the dissolver. If the data permit, some recommendations regarding future work on reactor scaleup will be outlined. The work will be carried out in three parts.

A. Kinetic Models for Coal Liquefaction

During the past decade numerous efforts have been made to evaluate and model the kinetics of coal liquefaction. Kinetic models can be subgrouped under two separate headings.

1. Lumped Kinetic Models Based on Distillation or Extraction Fractions.

Since there are many chemical species present during liquefaction, kinetic modelling involving individual chemical species has been impossible. Kinetic modelling of petroleum refinery processes has been carried out based on lumped fractions containing chemical species of similar activity. In direct coal liquefaction lumped fractions have been either on an extraction basis or on a boiling point (distillation fraction) basis.

2. Statistical Models

Many regression models have been proposed for the SRC-II coal liquefaction process. These statistical models relate product yields to process variables, coal type, and other properties. Development of these models was done in two steps, i.e. a coal property function was superimposed on basic yield models which were developed as a function of process variable data. These statistical models will be tested if any other SRC-II data are available.

B. Hydrodynamic, Mixing and Mass Transfer in Various Sized Reactors.

The performance of a coal liquefaction reactor depends not only on the intrinsic kinetics but also on prevailing hydrodynamic, mixing and mass transfer characteristics of the reactor. The scaleup of the reactor depends on the accuracy with which the design parameters can be estimated. Bubble column reactor models used for design of coal liquefaction reactors will be briefly described. The performance of the model depends upon the accuracy with which the design parameters can be predicted. These parameters include phase holdups, radial and axial distribution of phases, dispersion and mass transfer coefficients. A critical analysis of the estimation of these design parameters will be made. A large literature for simple air-water, two and three phase bubble columns for hydrodynamic mixing and mass transfer

characteristics is available. The data obtained from SRC-II as well as other published literature will be used for evaluating the applicability of these data to the design, modeling and scaleup of coal liquefaction reactors.

C. Hydrogen Consumption Kinetics and Thermal Behavior of Coal Liquefaction Reactors

Because of the inter-relationship between hydrogen consumption and thermal behavior of large scale reactors, these two topics are considered together. The dependence of hydrogen partial pressure, nature and concentration of catalyst, nature of solvent and coal, and residence time will be reviewed. The data obtained in the SRC-II coal liquefaction process under various operating conditions and in a variety of reactor sizes would be useful in analyzing the relationships for the hydrogen consumption kinetics. The effect of reactor scaleup variables such as gas velocity, reactor diameter, and length to diameter ratio on the thermal behavior of the reactor will be evaluated. The heat of reaction data along with the heat dispersion coefficient estimation will be considered as a part of the model parameter evaluations.

Task 2: Role of Catalysts and Hydrogen Donor Solvents in Direct Coal Liquefaction

In this task, the role of catalysts and hydrogen donor solvents in coal liquefaction will be investigated. The work will be essentially restricted to the SRC-II process. However, information that may become available from the EDS and H-coal processes will be incorporated if it provides a better understanding of the coal chemistry during liquefaction. Besides the information in the LTDB at PETC, some open literature findings relevant to the subject, will also be included. The work will be carried out in two parts. Promising areas for future investigations will be identified where possible.

A. Inherent Cataysts and the Effect of Hydrogen Sulfide and Sulfur Compounds.

1. The role of mineral matter and sulfur compounds in the mechanism of hydrogen transfer in coal liquefaction

2. The catalytic activity of the mineral matter

3. The effect of mineral matter and sulfur compounds on the yields and product distribution during liquefaction

B. The Relationship Between Coal Conversion and Hydrogen Transfer

1. The mechanisms involved in the transfer of hydrogen to coal in the presence of a) donor solvents such as tetralin and bottoms recycle, b) non-donor solvents such as naphthalene phenanthrene, and phenols; and c) molecular hydrogen

2. The role and effect of rank of coal and quality of donor solvents on the product quality and yields during liquefaction. Since a fundamental understanding of the chemistry of hydrogen donor solvents is

desirable this report may include hydrogenation studies with some model compounds.

Task 3 Physical, Chemical and Thermodynamic Properties of Coal Liquids and Slurries

In this task we will locate, tabulate, analyze, evaluate and correlate some of the physical, chemical and thermodynamic properties of coal liquids and coal slurries that are of paramount importance to the design of coal liquefaction plants. Properties both of model compounds and of narrow boiling range cuts of coal liquids will be considered. At least seven properties are considered necessary: enthalpy and heat capacity, vapor-liquid and vapor-liquid-solid equilibria, viscosity, surface tension, vapor pressure, heat of reaction and density. Work on all of these properties will be too extensive to be completed within the time frame of this project. Work will therefore proceed on each property one at a time.

The following subtasks provide further details concerning this work.

A. Study of Characterization Parameters

It is essential that a third independent parameter other than boiling point and specific gravity be identified and utilized in correlations, as experience has shown that two parameters are not sufficient.

B. Enthalpy and Heat Capacity.

1. Identification, Tabulation and Evaluation of Data

Data for the enthalpies and heat capacities of the coal liquids, cuts of these coal liquids and coal slurries will be located, tabulated, analyzed and evaluated. The effect of variables such as temperature, pressure, coal type, specific gravity, molecular weight, normal boiling point, presence and absence of solids will be studied. The trends in the values and possible explanations for trends will be reported. It also will be noted which data were actually measured and which were either extrapolated or obtained from correlations.

2. Experimental Methods

The experimental techniques used for the measurements will be summarized.

3. Models and Correlations

The attempted models and correlations to predict the properties or describe the behavior will be evaluated for their validity and limitations.

4. Identification of Missing Data

The analysis will also identify the areas where additional property measurements may be necessary.

C. Vapor-Liquid and Vapor-Liquid-Solid Equilibria in Coal Liquids and Coal Slurries

An analysis similar to that in substask B will be performed.

1. Identification, Tabulation and Evaluation of Data

2. Experimental Methods

3. Models and Correlations

The modified Grayson-Streed equation based on activity coefficient approach, the conformal solution theory based on the BWR equation of state, and the ASPEN modified Redlich-Kwong-Soave equation of state will be excluded from this analysis as they are being studied elsewhere.

4. Identification of Missing Data

APPENDIX B

RESUMES

Rajendra Albal
Sanjay Godbole
Amol Kulkarni

RAJENDRA ALBAL

1249, Benedum Hall
University of Pittsburgh
Pittsburgh, PA 15261

Office: (412) 624-5272
Home: (412) 683-8114

EDUCATION: **Ph.D. in Chemical Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania. February 1983.**
Cumulative QPA- 3.8/4.0.
Thesis Topic- *"Study of Mass Transfer, Power Consumption and Suspension Characteristics of Surface Aerated Agitated Contactor."*
Advanced courses include: Design of Multiphase Reactors, Heterogeneous Catalysis, Mathematical and Numerical Methods of Analysis.

M.S. in Chemical Engineering, Indian Institute of Technology, Bombay, India, 1979.
Cumulative QPA- 4.0/4.0.
Thesis Topic- *"Studies on an Industrial Vanadium Pentoxide Catalyst for Oxidation of Sulfur Dioxide with a Flow Circulation Reactor."*
First in the Merit List of I.I.T., Bombay for M.S. in Chemical Engineering.
Advanced courses include: Optimization, Fertilizer Technology, Air Pollution Control and Petroleum Refining.
Extracurricular Activities: Executive Member of I.I.T. Film Club and Hostel Committee.

B.S. in Chemical Engineering, University of Bombay, Bombay, India, 1977.
Maintained **Merit Distinction** throughout.
Extracurricular Activities: Representation as Honorary General Secretary of the University Hostels, Bombay (1976-1977).

Extensive knowledge of batch and timesharing computer services.

Supported most of the High School and College Education through scholarships. Recipient of High School Merit Scholarship (1967-1971) and Govt. of India National Merit Scholarship (1971-1977). Received Tuition and Research Assistantship from I.I.T., Bombay (1977-79) for the masters program and from University of Pittsburgh (1979-1983) for the Ph.D. program.

EXPERIENCE:

present **Postdoctoral Research Associate** - Working on "Investigations of Physical, Chemical and Thermodynamic Properties of Coal Liquids and Slurries for Coal Liquefaction," a project sponsored by Pittsburgh Energy Technology Center.

1981-1983 **Research Assistant** - Studied the effect of hydrodynamic and geometric parameters of the system, and physical properties of the various phases involved on the mass transfer coefficient, interfacial area and power consumption in multiphase agitated reactor

systems. Project sponsored by Gulf Research and Development Company. Data have proved to be of significant industrial importance.

Fall 1980 **Research Assistant** - Worked on oxydesulfurization of coal, a project sponsored by Pittsburgh Energy Technology Center. Results were implemented in "PETC Oxydesulfurization Process" at DOE Research Center, Pittsburgh.

1977-79 **Resarch Assistant**- Indian Institute of Technology, Bombay. Assessment on utilization of a differential reactor to study the kinetics of oxidation of sulfur dioxide, a project sponsored by Larsen and Toubro, India, Ltd. Data were adopted for design of commercial sulfur dioxide convertors. Also, it allowed me to observe and interact with a diverse cross section of people in industry.

PUBLICATIONS: *"Effect of pH on the Removal of Pyritic Sulfur from Coal by Oxydesulfurization,"* **Ind. Eng. Chem. Process Des. Dev.** Vol.21(No.4), October 1982, pp. 594-600.

"Kinetics of Oxydesulfurization of Minshall, Indiana Coal," **Chem. Eng. Commun.** Vol.11(4-5), August 1981, pp. 201-218.

"Chemical Cleaning of Coal- The Oxydesulfurization Process," Proceedings of NATO School, Paper III(13-1), Izmir, Turkey, Aug. 1981.

"Mass Transfer, Power Consumption and Suspension Characteristics of Surface Aerated Agitated Contactor," submitted to the **Chemical Engineering Journal.**

"Mass Transfer Coefficients and Solubilities for Hydrogen and Carbon Monoxide Under Fischer-Tropsch Conditions," submitted to the **Chemical Engineering Science.**

"Mass Transfer Coefficients in a High Pressure Agitated Contactor," submitted to the **Chemical Engineering Communications.**

"Determination of Rate Expression for SO_2 Oxidation," submitted to the **Indian Journal of Technology.**

SOCIETIES: AIChE

SANJAY GODBOLE

1249 Benedum Hall
University of Pittsburgh
Pittsburgh, PA 15261

Office: (412) 624-5272
Home: (412) 683-8114

PERSONAL: Age 25, Single, Excellent Health

EDUCATION:

Ph.D. **Chemical Engineering** **Expected April 1983**
University of Pittsburgh, Pittsburgh, PA
Dissertation: Hydrodynamic and Mass Transfer Characteristics of Multiphase Bubble Column Reactors.
Established dependencies of phase holdups, specific interfacial area and volumetric mass transfer coefficients on the solids, internals and physical properties of liquid. Developed new experimental correlations for the scaleup of multiphase bubble columns used in fermentation and Fischer-Tropsch synthesis. Modified an experimental method to measure the bubble size distribution.
Received **Coull Award** for being the best graduate student, 1982.
Quality Point Average: 3.93/4.0

M.S. **Petroleum Engineering** **December 1982**
University of Pittusburgh, Pittusburgh, PA.
Acquired skills in Reservoir Simulation using Numerical Techniques. Extensive course work in Reservoir Engineering, Enhanced Recovery Processes and Well Logging Techniques.
Quality Point Average: 4.0/4.0

M.S. **Chemical Engineering** **April 1981**
University of Pittusburgh, Pittusburgh, PA
Thesis: Dissociation Pressures of n-Propane and i-Butane Hydrates Below the Ice Point.
Designed a novel experimental technique and obtained data to predict three phase thermodynamic equilibria for large hydrocarbon molecules below the ice point. Numerical modelling techniques were used to determine molecular parameters.
Quality Point Average: 4.0/4.0

B.S. **Chemical Engineering** **July 1979**
University of Bombay, Bombay, India
Ranked in top 5% of the class throughout the undergraduate career. Received industrial training.

EXPERIENCE:

Jan.1983 -To date — **Research Associate**
University of Pittsburgh, Pittsburgh, PA 15261
Analysis of Reaction Kinetics and Reactor Performance in Direct Coal Liquefaction.

Oct.1980 -To date — **Research Assistant**
University of Pittsburgh, Pittsburgh, PA.
Modeling and experimental work in multiphase bubble column reactors to establish scale up criteria. Applications: Fischer-Tropsch synthesis, fermentation reactors. Sponsored by Gulf Research and Development Corporation, Pittsburgh, PA.

Sept.1979 -Sept 1980 — **Research Assistant**
University of Pittsburgh, Pittsburgh, PA.
Experimental and Numerical work in predicting thermodynamic phase equilibria for natural gas hydrates. Sponsored by National Science Foundation.

June 1978 -Aug 1978 — **Trainee Engineer**
National Organic Chemicals India Ltd., Bombay, India.
Designed heat exchangers and separation units for a Naptha-Cracker system.

PUBLICATIONS:

Co-author
(1) *"Design Parameters Estimations for Bubble Column Reactors"*, JOURNAL REVIEW, **AIChE J.**, Vol.28, No.3, p.353 (1982)
(2) *"Gas Holdup Stucture in Highly Viscous Newtonian and Non-Newtonian Liquids in Bubble Columns"*, **Chem.Eng. Commun.**, Vol 16, p119 (1982)
(3) *"Effect of Addition of Alcohols on the Gas Holdup and Backmixing in Bubble Columns"*, accepted, **AIChE J.** (1982)
(4) *"Measurement and Prediction of Dissociation Pressures of Iso-butane and Propane Hydrates below the Ice Point"*, **AIChE J.**, Vol 28, p930 (1982)
(5) *"Hydrodynamics and Mass Transfer in Non-Newtonian Solutions in a Bubble Column"*, submitted to **AIChE J.**(1983)
(6) *"Oxygen Mass Transfer in CMC-Solutions in a Large Diameter Tower Fermenter"*, Submitted to **Chem.Ing.Tech.**(1983)
(7) *"Hydrodynamics and Mass Transfer in Bubble Columns:Effect of Solids"*, Submitted to **Chem.Eng.Commun.** (1983)
(8) *"Bubble Column Reactor Model For the Churn Turbulent Regime:Applied to Fischer-Tropsch Synthesis"*, to be submitted to **Chem.Eng.Sci.** (1983)
(9) *"Simulation of Gas Production from a Resevoir Containing Gas Hydrates and Free Natural Gas"*, Submitted to **SPE** (1982)
(10) *"Progress Reports on the Thermal and Hydrodynamic Behavior of Multiphase Reactors"*, **DOE Publication**, DOE/ET/10104-29(1982)
(11) *"The Effect of Structural Assymetry on Potential Interactions in the Hydrate Phase"*,A paper presented at the 73 Annual **AIChE Meeting**, Chicago, November(1980)

SOCIETIES: **AIChE, SPE**

AMOL KULKARNI

1249 Benedum Hall
University of Pittsburgh
Pittsburgh, PA 15261
(412) 624-5272

EDUCATION:

Ph.D. Chemical Engineering, University of Pittsburgh, Pittsburgh, Pa. (will be completed by January, 1983).

M. Chem. Chemical Engineering, University of Bombay, Bombay, India, 1979. Q.P.A. 3.7-3.8/4.0.

B. Chem. Chemical Engineering, University of Bombay, Bombay, India, 1977. Q.P.A. 3.6-3.7/4.0.

WORK EXPERIENCE:

1982 Fall — **Research Associate**, Chemical and Petroleum Engineering Department, University of Pittsburgh.

1981 Summer-1982 Fall — **Research Assistant**, Chemical and Petroleum Engineering Department, University of Pittsburgh. Working with Multiflow Processing group, sponsored project of Gulf Research and Development. Studying the hydrodynamic and mass transfer characteristics of two-phase and three-phase mixtures in cocurrent downflow column. These parameters are useful for design and scaleup purposes and affect conversions, selectivity, etc. in gas-liquid and gas-liquid-solid reactions.

Teaching Assistant, Chemical and Petroleum Engineering Department, University of Pittsburgh. Responsible for computer programming and grading graduate course in Mathematical Modelling.

1980 Summer-1981 Winter: — **Research Assistant**, Chemical and Petroleum Engineering Department, University of Pittsburgh. Involved in studying the effect of heat of reaction on the kinetic parameters used for modelling of hydrogasification of bituminous coal. Extensive use of computer programming was required.

1980 Winter: — **Teaching Assistant**, Chemical and Petroleum Engineering Department, University of Pittsburgh. Responsible for recitation and grading of 4-credit-hour Transport Phenomena course.

1977-79: — **Research Assistant**, Department of Chemical Technology, University of Bombay. Involved in studying the kinetics and process development of diisopropylbenzenes to dihydroxybenzenes and methyl ethyl ketone.

1977 Summer: **Design Engineer**, CIPLA, Bombay, India. Involved in the design of heat exchangers, and agitated contactor for leaching of steroids from naturally occurring plants.

1976 Summer: **Trainee Engineer**, Standard Alkali, Bombay, India. Studied the operations of caustic soda and chlorine manufacturing plants.

PUBLICATIONS: **"Kinetics of Liquid Phase Oxidation of Diisopropylbenzenes".** M.S. Thesis University of Bombay. 1979

Co-Author **"Gas Holdup in Two and Three Phase Downflow Bubble Column"**, accepted in Chem. Engng. Jl., (1982)

"Hydrodynamics and Mass Transfer Characteristics of Three Phase Systems in Cocurrent Downflow Bubble Column", Paper presented at the AIChE meeting, Low Angeles, November (1982)

"Effective Interfacial Area and Volumetric Mass Transfer Coefficient in Two Phase Downflow Bubble Column", Part I, submitted to Chem. Eng. Commun., (1982)

"Effective Interfacial Area and Volumetric Mass Transfer Coefficient in Three Phase Downflow Bubble Column", Part II, submitted to Chem. Eng. Commun., (1982).

"Gas Phase Dispersion in a Downflow Bubble Column" submitted to Chem. Eng. Sci. (1982).

"Thermal and Hydrodynamic Behavior of Multiphase Reactors" DOE publication, DOE/ET/10104-29 (1982)

SOCIETY: American Institute of Chemical Engineers
American Chemical Society

HONORS: Scholarship awarded by the University Grants Commission, New Delhi, India, 1977-79.

Secretary, student chapter of Indian Institute of Chemical Engineers, Bombay Division, India, 1978.

PERSONAL: Married, Good Health

REFERENCES: Available upon request.

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