COAL LIQUEFACTION: INVESTIGATION OF REACTOR PERFORMANCE, ROLE OF CATALYSTS AND PCT PROPERTIES: FINAL REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL AND PETROLEUM ENGINEERING

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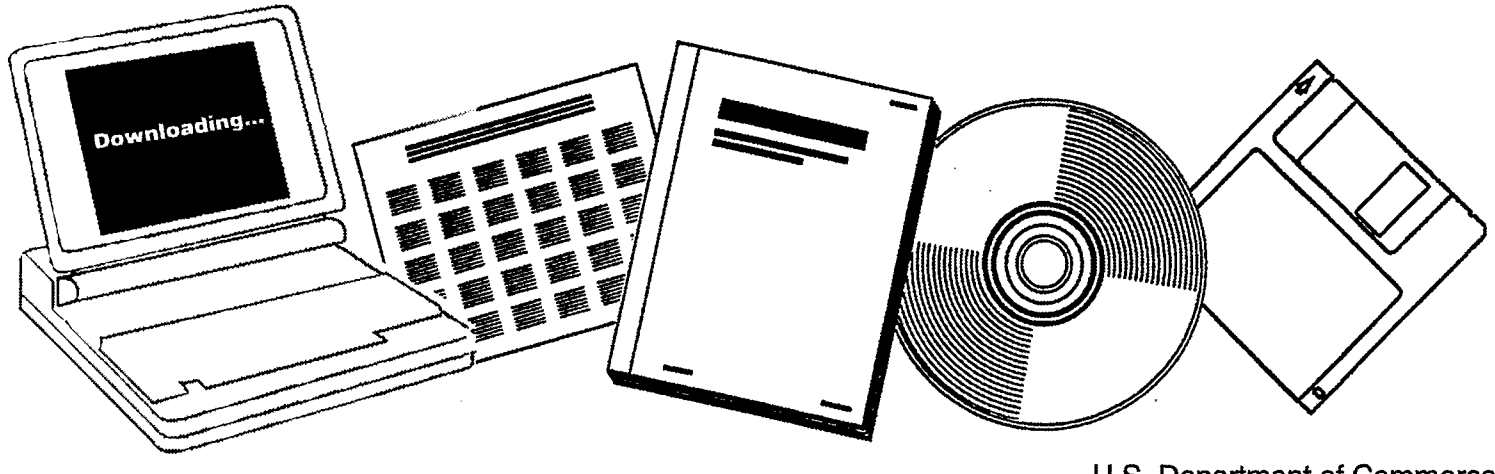

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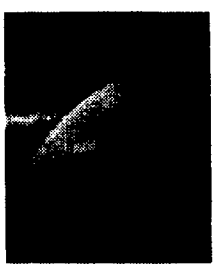

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FINAL REPORT

Coal Liquefaction - Investigation of Reactor Performance, Role of Catalysts and PCT Properties

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Introduction

This is the third and final report for a three year project in which areas of special importance to coal liquefaction have been studied. The work was done by faculty, research associates, and graduate students in the Chemical and Petroleum Engineering Department at the University of Pittsburgh. It has had as its general objective the review and analysis of recent developments in both direct and indirect coal liquefaction theory and practice. While coal liquefaction is not commercially viable at this time, it is expected that, as petroleum supplies decline, liquids derived from coal will play a key role in replacing-petroleum based liquid fuels, and it is of critical importance that the results of extensive research into coal liquefaction processes which have been carried out in recent years be systematically examined and evaluated.

The studies were carried out in three areas:

1. Coal liquefaction reactor design, performance, and modeling.
2. The role of catalysts in direct and indirect coal liquefaction.
3. The properties of coal liquids and slurries.

The results of these studies are published in this report and in two previous Technical Progress Reports[1,2]. An overview of the entire project is given in the next section. The section which then follows contains a more detailed summary of work done in the last year and reported in this document. As an aid in locating specific information in previous reports, the Summary and Contents pages from these reports are reproduced as Appendix VII at the end of this report. Both reports can be obtained from the National Technical Information Service. Another source for related information is a study published in 1983[3].

Project Overview

Coal Liquefaction Reactor Design, Performance, and Modeling

It is evident that the rational design of a coal liquefaction process requires that a suitable mathematical model of the process be available. To this end, a general process simulator such as ASPEN can be used for material and energy balances, handling of flows between units, recycle calculations, and simulation of conventional process units such as heat exchangers and distillation equipment. However, good models have not been generally available for the most important unit in a coal liquefaction process - the reactor. A major objective of this project is to make available good models for the common liquefaction reactors in such a form that they can be used with a process simulator such as ASPEN to study and design coal liquefaction processes. The models listed below have been developed on this project and reported in the document indicated. In addition to development of the model, a listing of the program and the solution of sample problems are included.

Technical Progress Report 1[1] presented models for bubble column slurry reactors used in direct coal liquefaction and appropriate for the follow processes:

SRC-I

SRC-II

H-Coal

Exxon Donor Solvent

Technical Progress Report Number 2[2] included models for indirect coal liquefaction processes in which the coal is first converted to a mixture of carbon monoxide and hydrogen and then reacted to form liquid products. The following processes were included:

Fischer-Tropsch - slurry reactor

Fischer-Tropsch - fluidized bed reactor

Fischer-Tropsch - fixed bed reactor

Methanol synthesis - fixed bed reactor

Methanol synthesis - slurry reactor

Mobil Methanol to Gasoline - fluidized bed reactor

Mobil Methanol to Gasoline - fixed bed reactor

The use of the ASPEN Plus Process Simulator

This report presents a model for a modified direct coal liquefaction process in which two stages are used to improve performance:

The Wilsonville Integrated Two-Stage Liquefaction Process

Role of Catalysts in Coal Liquefaction

The second major objective of this project was to review and evaluate the role of catalysts in coal liquefaction processes. For direct coal liquefaction, an understanding of the reaction paths and effects of catalysts is difficult because of the complex composition and structure of coal and the many different kinds of catalysts, both natural and added, which can be used. For indirect liquefaction, the chemistry is simpler, but the reactions are far from being completely understood, and catalysts play an even more important role than in direct liquefaction. Coal liquefaction is an active research area, and important advances are being made. Following is a list of the topics in direct and indirect coal liquefaction which have been studied in this project and the report in which they can be found.

Technical Progress Report Number 1[1] contained reviews of the catalysts used in the important indirect liquefaction processes including:

The Fischer-Tropsch synthesis

The Kolbel-Engelhardt synthesis

The Isosynthesis

Methanol synthesis and its uses as a fuel, a chemical, and a chemical precursor

Hydrocarbons from methanol and other substrates using shape selective catalysts: Mobil's Methanol-to-Gasoline technology

Synthesis of higher alcohols

Chemicals from syngas

Technical Progress Report Number 2[2] extended the study of indirect liquefaction by reviewing four areas of potential importance which had not been covered previously and also reviewed the coprocessing of coal and heavy oils.

Methanol synthesis via methyl formate

Role of carbon dioxide in the methanol synthesis

Methanol synthesis using noble metal catalysts

A new sulfur-tolerant synthesis of higher alcohols

Coprocessing of coal and heavy oil

This last report contains reviews of the role of three kinds of catalysts in direct coal liquefaction.

Transition metal carbonyls as catalysts

Superacids as catalysts

Liquid clathrate catalysts

The Properties of Coal Liquids and Slurries

Coal liquids are complex chemical mixtures, and the values of certain physical and thermodynamic properties are needed for design and analysis of liquefaction processes. Solid phases containing ash and unreacted coal are also present and make property determination more difficult. These methods were reviewed and recommendations were made for estimation of the following important properties.

Technical Progress Report Number 1[1]

Viscosity of coal liquids and slurries

Thermal conductivity of coal liquids and slurries

Vapor pressure of coal liquids

Heat of reaction for direct coal liquefaction products

Surface tension of coal liquids

Prandtl numbers and heat transfer of coal liquids

Final Report Summary

The work reported in this document was performed in the Chemical and Petroleum Engineering Department in the period from October 1, 1985 through February 28, 1987. The principal authors are Professors Yatish Shah, John Tierney, and Irving Wender and Research Associates Sebastian Joseph and Chaur Wen. Contributions were also made by Carlos Dassori, Zhenyu Liu and others.

In the first section of the body of this report, a mathematical model for the Wilsonville Integrated Two-Stage Liquefaction Process is presented. The first stage is a bubble column slurry reactor and has been modeled previously in this project. The second stage is an ebullated bed catalytic reactor designed to improve product quality, process flexibilty, and hydrogen utilization efficiency. The basic equations for the second stage are developed in the main body of Section I of this report. Supplementary information, a user manual, a sample problem, and a complete computer code in FORTRAN are given in Appendices I through VI.

The second, third and fourth sections of this report deal with the role of three types of catalysts in direct coal liquefaction. The second section contains an overview of the advantages, limitations, and significance of using homogeneous catalysts such as transition metal complexes for direct coal liquefaction. These catalysts have the potential for hydroliquefaction of coal at relatively mild conditions and with good liquid yields. Emphasis in this section is on review of the large body of published literature and on obtaining a perspective for where future developments using these types of catalysts will occur.

The third section is concerned with the conversion of coal to liquids using very strong acids known as superacids as catalysts in direct coal

liquefaction. The study of the direct liquefaction of coal with superacids is in its infancy and promises to yield new approaches to both coal conversion and to elucidation of the constitution of coal.

Background information on the use of liquid clathrates as catalysts for coal liquefaction is presented in Section IV. Liquid clathrates can aid in the liquefaction of coal at or near room temperature and require neither application of heat nor consumption of hydrogen. Unfortunately, yields are low, and further developments are needed to justify commercial exploitation.

Recommendations

It has become evident in the course of this project that research in coal liquefaction is ongoing and may assume great importance in the not too distant future. Dynamic and important additions to the liquefaction literature are still being made, both in direct and in indirect liquefaction. It is difficult at best for the research scientist or engineer to keep abreast of new developments, and projects such as this one are vital for summarizing and evaluating the status of liquefaction processes as well as in clean coal and other coal technologies. We recommend that more reviews of this type be made, particularly in the following areas which we judge to be of prime importance.

1. Regular updates and critical analyses of the status of both direct and indirect coal liquefaction research are needed. The most critical areas for future reviews are:

   Coprocessing of coal and heavy oils

   Novel approaches to direct coal liquefaction

   New developments in the indirect liquefaction of coal and in the rapidly expanding use of synthesis gas for fuel in the generation of electricity (integrated gasification combined cycle) and in the transportation area.

   A highly selective synthesis of ethanol and higher alcohols directly from synthesis gas is urgently needed and developments in this area should be followed.

2. A comprehensive review of the chemistry of SO_x/NO_x removal processes would be of great value. Many processes are available, but the reactions involved are poorly understood. Clarification would enable one to differentiate usable processes from those that are troublesome and inefficient.

3. Much the same can be said for H_2S/CO_2 removal processes. A critical review of methods for separating H_2S cleanly from H_2S/CO_2 mixtures is needed.

4. The chemistry and utilization of CO_2 should be examined, especially as a way to diminish the amount of CO_2 emitted to the air. Can we utilize this chemical so as to diminish the threat of the greenhouse effect? One possible route is to react CO_2 with coal in a Boudouard reaction to convert the CO_2 to the very useful CO.

5. Mathematical models for SO_2 and H_2S removal processes are needed if intelligent decisions about process selection and optimization are to be made. These models should be efficient and preferably could be used on microcomputers.

References

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