RECEIVED
USDOE/PETC

93 MAY -4 AM 10:51

ADDITIONAL INFORMATION

DE/PC/89788--714

NOVEL PROCESS FOR DEPOLYMERIZATION
OF COAL TO C₂-C₄ HYDROCARBONS

Progress Report No. 14
(Covering the Period December 1, 1992 - February 28, 1993)

Wendell H. Wiser, Principal Investigator
Alex G. Oblad, Co-Principal Investigator

Department of Fuels Engineering
University of Utah
Salt Lake City, Utah 84112

Prepared for the United States Department of Energy
under Grant No. DE-FG22-89PC89788

March, 1993

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

PERSONNEL

In addition to the Principal Investigators, research personnel participating in this project during the reporting period included:

Mr. Annapragada Rao, Graduate Student

OBJECTIVES AND SCOPE OF THE RESEARCH PROJECT

An envelope of parameter values has been experimentally identified in our laboratory, heretofore unexplored, for the catalytic depolymerization of coal which leads to yields of C_2-C_4 hydrocarbons in excess of 50 weight percent of the coal, in a direct, single-stage process under mild conditions. The chemistry observed is fundamentally different from all coal conversion processes, both liquefaction and gasification, previously reported in the literature. The process-derived recycle liquid solvent will be characterized, and is expected to constitute a super-critical phase under conditions of temperature and pressure imposed by the chemistry of the system. Using a special reactor incorporating windows for visual observation, the operation of a catalyst bed fluidized by super-critical, coal-derived fluids will be examined. The capability of such a super-critical, coal-derived fluid to control agglomeration of a strongly caking coal, in the catalyst bed, will be evaluated, and satisfactory control developed. Solvent upgrading of the recycled liquids will be applied as may be required.

Information obtained from a coal liquefaction project proceeding under my direction indicates that a two-stage system may be advantageous for the present work. A two-stage

gasification system will be constructed and operated. Kinetic data will be obtained from the two-stage system, reaction velocity constants and activation energies determined, and these data compared with the kinetic data from a single-stage system obtained by us in a companion project in my laboratory. Using these data, and other information obtained in these projects, an evaluation will then be made concerning which type of system would best serve as a basis for recommendation for further development of a prototype for possible scaleup.

ACTIVITY FOR THE REPORTING PERIOD

Analyses of experimental data produced in a single-stage system for direct conversion of coal to a product containing more than 50% by weight of the coal as C_2-C_4 gases, revealed that the conversion of coal to liquids occurs much more rapidly than the follow-on conversion of the liquids to hydrocarbon gases. The analyses revealed further that most of the hydrocarbon gases are produced from the coal-derived liquids, as opposed to direct production from the coal matrix. Examples of those data were contained in the previous Progress Report No. 13. It is for that reason that it was deemed necessary to conduct experiments in a two-stage reactor system, before a prototype reactor system could be designed.

Large amounts of experimental data concerned with conversion of coal to liquids, including kinetic data, are already found in the literature. Primary interest in this portion of the work of this project, namely production of C_2-C_4 hydrocarbons, therefore is focussed upon the conversion of the coal-derived liquids to C_2-C_4 gases. Since the first step of conversion of coal to liquids is not to be studied kinetically, that step of the overall process is performed in the simplest manner possible, utilizing a one-gallon autoclave. The liquids from the autoclave are then separated from the solids, consisting of unreacted coal, mineral matter, and catalyst when used, and the liquids passed to the second stage. Solids separation is performed by filtration.

A schematic flow diagram of the second stage is presented in the attached Figure. The reactor proper consists of a 316

stainless steel tube, 0.495 inch inside diameter and 24 inches long. The upper portion of the tube, approximately 12 inches, is filled with glass beads and serves as a preheater. The lower portion, approximately 12 inches, is filled with catalyst, and serves as the reaction portion of the reactor. A temperature controller is attached to the preheater section, at approximately the vertical center of that section. A second temperature controller is attached at approximately the vertical center of the reactor section.

Inasmuch as the liquid feed to the reactor is to be essentially solids free, the reactor is to operate as a fixed bed. This mode of operation is selected because of its simplicity of operation. Liquids combined with a hydrogen stream will be fed to the top of the reactor. Based upon prior experience with feeding coal-derived liquids, it is expected that there will be some formation of solids associated with the gasification reactions. However it is believed the fixed catalyst bed will be able to accomodate such solids formation for the duration of an experimental run, which will be of the order of one hour.

The catalyst selected for this work is sulfided nickel-moly supported on alumina, mixed with silica-alumina, in a ratio 4/1 by weight. In the prior work in a single stage, the chemistry involved was observed to follow a carbonium ion mechanism, and requires both a hydrogenation/hydrogenolysis function and a cracking function in the catalyst. The prior work utilized a pressure of 1800 psi, so the kinetic work in this program will

commence with that same pressure, in order that a comparison may be made between the two systems. However a few prior experiments in work somewhat related to this work indicates that, in the continuous system, pressures considerably lower than 1800 psi may be adequate, and pressures as low as 1000 psia will be examined. Five temperatures are to be utilized for examining the kinetics, to determine activation energies, namely 440, 455, 470, 485, and 500 °C.

A sampling manifold containing nine sampling ports is incorporated into the system. Valves to the individual ports are operated by the computer. In each experimental run, nine samples are to be collected at various times during the run. The samples are to be analyzed by GC. Initially a GC was to be placed on line, to permit on-line analysis, but it has been found that the time required for analysis of a single sample (about 20 minutes) is too long to permit analysis of the samples as they are collected (about nine samples during the one-hour run). Hence the samples are collected in the sampling manifold, and held for analysis upon completion of the experimental run. Examination of the results of the analyses enables determination of the time required to achieve steady state operation (in shake-down runs, observed to be of the order of 20 minutes). Following reaching steady state, the results of the remaining samples will be averaged to obtain the analysis of the individual run.

The computer is also used for logging of the data. A few experimental runs have been completed. Following a few minor adjustments, the complete system now operates in a satisfactory

manner. Experiments are now in progress for obtaining data to be used in determining the kinetic parameters for conversion of coal-derived liquids to a product in which the sum of C_2 , C_3 , and C_4 hydrocarbons represents more than 50% by weight of the coal fed to stage 1 of the system.

Schematic Flow diagram of 2nd Stage of
2-Stage Coal Gasification Process

END

**DATE
FILMED**

8 / 26 / 93