**NTiS**

# COAL LIQUEFACTION: INVESTIGATION OF REACTOR PERFORMANCE, ROLE OF CATALYSTS AND PCT PROPERTIES. QUARTERLY PROGRESS REPORT, JANUARY 1-MARCH 31, 1984

PITTSBURGH UNIV., PA

1984

# One Source. One Search. One Solution.

**NT**_i_**S**

## Providing Permanent, Easy Access to U.S. Government Information
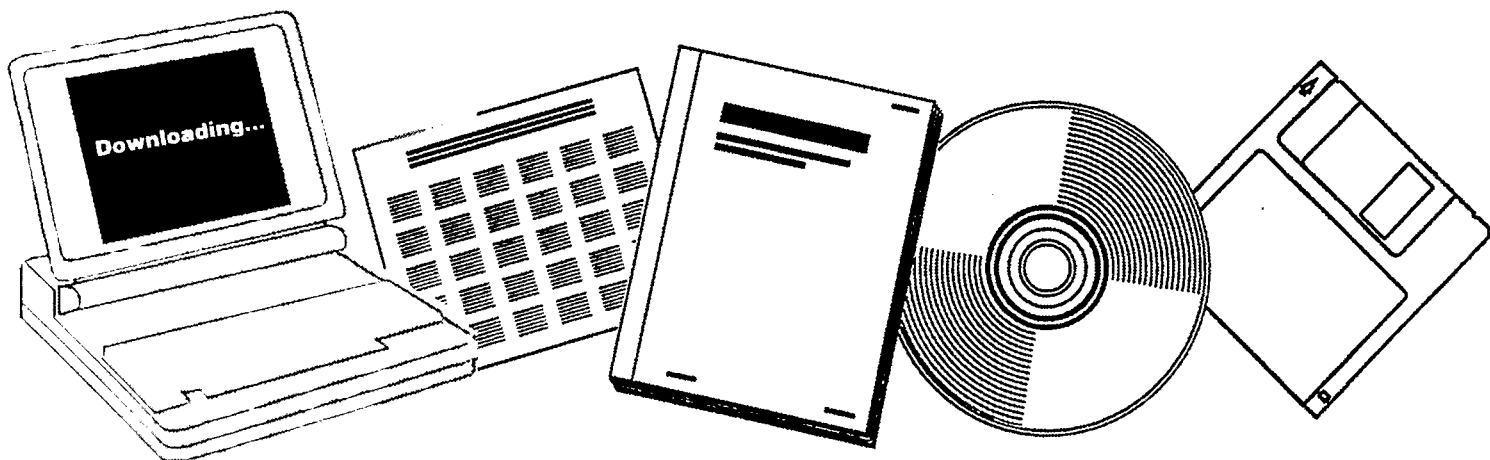
National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online 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 provides 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

DOE/PC/60054--T2

DE84 010885

Quarterly Progress Report

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

Alan J. Brainard                                    Sekhar Bhattacharjee
Yatish T. Shah                                      Sebastian Joseph
John W. Tierney                                     K. S. Seshadri
Irving Wender

University of Pittsburgh
Pittsburgh, PA   15261

MASTER

January 1, 1984 to March 31, 1984

1. <u>Objective and Scope of Work</u>

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 direct coal liquefaction

- Role of catalysts in indirect liquefaction and direct coal liquefaction

- Physical, chemical and thermodynamic properties of coal liquefaction products.

2. <u>Progress During Quarter</u>

A detailed description of work in each of the three tasks is given below. Ten abstracts were prepared and are attached as an Appendix.

Task 1. <u>Reactor Kinetics and Reactor Performance In Direct Coal Liquefaction</u>

A comprehensive program has been developed to predict the performance of coal liquefaction preheaters and reactors. The simulator is interactive and allows the user to input any linear kinetic network by specifying the reaction paths. The user must also specify the operating conditions and the physical dimensions of the units. The simulator then provides detailed information on the performance of each unit, the characteristics of each flow

stream, and an overall summary of the products leaving each unit. The simulation program is written in a modular form using FORTRAN.

Work is in progress to represent the simulator output in graphical and pictorial form. Programs are being developed on the PDP-11/70 computer at Schneider Consulting Engineers. Computer programs are also being developed to store the simulator input/output data in a database for any further processing.

Task 2  Indirect Coal Liquefaction and the Role of Added

Catalysts in Direct Coal Liquefaction

In this quarter, a first draft report on the Fischer-Tropsch (F-T) synthesis has been prepared. The following topics are discussed in the report:

The introductory section deals with the history of the F-T reaction and early German work on F-T catalysts. Items that will be included in the final report are: 1) Mobil's methanol to gasoline process, 2) methanol as a fuel and as a chemical, 3) the iso-synthesis reaction, 4) hybrid concepts and one-step processes for the conversion of synthesis gas to gasoline which are yet to be commercially proven, and 5) synthesis of higher alcohols from synthesis gas.

The next section deals with the fundamentals of the conversion of synthesis gas to fuels and chemicals. It is divided into three sub-sections dealing with, respectively, a) the thermodynamics of $CO/H_2$ reactions, b) an evaluation of proposed F-T reaction mechanisms, c) research that should be pursued to improve our understanding of the SASOL process and F-T conversion to liquid fuels in general.

The next section deals with SASOL technology and some of the developmental work that is ongoing at SASOL, in particular, work on slurry

reactors. Then this section addresses the processes at SASOL for upgrading the primary products of the F-T synthesis to gasoline and diesel fuels and improvements that can be made in this downstream operation.

The final section deals with new catalysts that have been tested in the laboratory and on pilot plant scale for narrowing the product distribution in synthesis gas conversion.

Task 3. The PCT properties of Coal Derived Liquids.

Reports on "Viscosity of Coal Liquids and Slurries" and "Thermal Conductivity of Coal Liquids and Slurries" have been prepared. Research has been initiated on two important areas of coal liquefaction, "Heat of Reaction of Direct Coal Liquefaction" and "Dimensionless Numbers for Coal Liquids." A computer search of the Liquefaction Technology Data Base at PETC and the COMPENDEX, NTIS, SCISEARCH, Chemcial Abstracts and Energy Line data bases was made. Experimental data on heat of reaction is sparse. Only one source of experimental data (Stephenson, 1981) has been identified so far. However, attempts are now being made to estimate the heat of reaction from heat of combustion data of different coal liquids and a rough draft of this subject is being prepared. Work on dimensionless groups of coal liquids has been primarily concentrated on the Prandtl number of various coal liquid fractions. Prandtl numbers have been calculated from experimental data points on viscosity, thermal conductivity and heat capacity data published by Gray and Holder (1982). Pure component Prandtl numbers for different straight chain and alicyclic compounds and aromatic compounds have also been calculated from published literature sources (Reid, Sherwood and Prausnitz, 1977) and are being compared with the Prandtl number of actual coal liquids. Our next step will be to calculate the Reynolds number and rate of heat transfer from actual coal liquefaction pilot plant operational data and to propose a semi-empirical

heat transfer correlation relating the Nusselt number, the Reynolds number and the Prandtl number.

Bibliography:

1. Gray, J.A. and Holder, G.D., "Solvent Refined Coal Processes, Selected
   Physical, Chemical and Thermodynamic Properties of Narrow Boiling Range
   Coal Liquids from the SRC-II Process, Supplemental Property Data", DOE
   Report # DOE/ET/10104-44, April (1982).

2. Reid, R.C., Prausnitz, J.M. and Sherwood, T.K., "The Properties of Gases
   and Liquids", p 629-673, McGraw-Hill (1977).

3. Stephenson, J.L., "SRC-II Process" - Exothermic Heat of Reaction
   Evaluation", Letter to Dr. F.J. Antezana, Ref # 5601FT12, February 12
   (1981).

ABSTRACTS

Title  – SRC-II Process – Exothermic Heat of Reaction Evaluation

Author – J.L. Stephenson

Source – Letter to Dr. F.S. Antezana, Gulf Science

and Technology, Ref # 5601FT12, February 12, (1981)


This letter discusses the heat balance done on the P-99 pilot plant to check the adiabatic performance of the dissolver and presents heat of reaction evaluation including data from P-99 operation with different types of coal. The net exothermic heat of reaction is evaluated from the P-99 operating data and using Gulf's CHAMP process simulator to calculate the change in enthalpy across the dissolver. Since the heats of formation of coal liquids are not known, the calculation procedure represents the coal feed as products and calculates the enthalpy change of recycle outlet temperature to the dissolver outlet temperature at the operating pressure. Based on that assumption, the folowing equation for the heat of reaction was proposed.


$$\Delta H_{reaction} = 113.551 - 13.120 \times HYCON$$


HYCON = wt % Hydrogen consumption (moisture free coal basis).


Using this equation a value of 55.4 Btu/SCF $H_2$ is calculated as the heat of reaction at the design hydrogen consumption of 4.4 st % (MF coal basis). The letter also mentions an estimation by Badger Energy Inc., who have suggested that the heat of reaction could be as high as 75 Btu/SCF $H_2$ consumed.


Number of Pages in Document:  7

Abstract prepared by: Sekhar Bhattacharjee

Title  – Prandtl Numbers for Organic Liquids

Author – Pai, M.U. and Shastri, S.R.S.

Source – Chemical Engineering, 73 (22), 131 (1966).


The Prandtl number is an important dimensionless group in heat transfer
and while Prandtl numbers for gases exhibit small changes about 0.65 – 1.00 in
the usual temperature and pressure ranges, those for the liquids vary widely
with temperature, from about 2.0 – 100,000.

In the absence of any data on thermal conductivity, viscosity or heat
capacity of a liquid, the authors propose the following Prandtl number for
non-polar and slightly polar liquids


$$\log_{10} N_{Pr} = (0.04 \, \Delta H_v / RT) - 0.22$$

$N_{Pr}$ = Prandtl number

$\Delta H_v$ = Molar Heat of Vaporization (cal/g mol)

$R$ = Gas Constant (cal/g mole K)

$T$ = Temperature (K)


This correlation is however, valid only at low temperature range (–80 –
+100°C)


Number of Pages in Document:  1

Abstract prepared by – Sekhar Bhattacharjee

Title  — Development of a Calorimeter to Determine Heats of Reaction of
         Hydrogen with Coal and Coal Slurries

Author — Fredrickson, D.R., Young, J.E., Fischer, J. and West, W.D.

Source — Argonne National Laboratory, Report # ANL/CEN/FE-78-6

A heat of reaction calorimeter was developed which was designed to
determine the heat of hydrogenation of coal and coal liquids. The calorimeter
had a constant heat flow, which at thermal equilibrium maintains a constant
temperature differential between the reaction vessel and the jacket. A heater
located in the calorimeter body is used to maintain this temperature
difference. The power for this heater is controlled and measured accurately
throughout the experiment. The unit was designed to operate at temperatures
up to 475.0°C and pressure 28 MPa. Experimental techniques were developed to
facilitate handling of coal slurries in the calorimeter and analytical
procedures were refined to enable determination of hydrogen balance for any
hydrogenation reaction to be studied in the reactor. A number of experiments
were carried out with coal slurries but some severe operational problems
prevented acquisition of any meaningful data in the reactor.

Number of Pages in Document: 15

Abstract prepared by — Sekhar Bhattacharjee

Title  — SASOL Routes to Diesel Fuel Production

Author — Mark E. Dry

Source — Tenth Annual International Conference on Coal Gasification
Liquefaction and Conversion to Electricity, 1983.


This paper reviews two downstream operations at SASOL to maximize diesel
yield. At SASOL, two types of reactors are in operation. The high-
temperature fluidized-bed reactor (Synthol) yields mainly light olefins and
gasoline. The bulk of the products of the low-temperature fixed-bed reactor
(Arge) are waxes. With current technology, it is not possible to obtain a
large yield of the diesel cut. Therefore the primary products are refined to
diesel fuel. For this purpose, olefin oligomerization and hydrocracking of
waxes are practiced at SASOL. Parenthetically, it should be mentioned that a
high quality diesel fuel has a cetane number exceeding 50 and to ensure a high
cetane number, the diesel fuel should contain a high proportion of straight-
chained hydrocarbons and be low in aromatic compounds.

$C_3$ to $C_6$ olefins can be oligomerized to gasoline and diesel fuel on
strong acidic catalytic surfaces or by a thermal non-catalytic process.

The waxes produced in the Arge reactor contain predominantly straight
chain paraffins and are hydrocracked on nickel catalysts to diesel fuel and
gasoline. At SASOL, mild operating conditions are employed. Milder operating
conditions lower the production rate but ensure long catalyst life, increase
the yield of diesel and lower that of gasoline and $C_1-C_4$ gases. At SASOL the
operating conditions are such that 80% of the products fall in the diesel
range and the cetane number is 65.

One of the primary products of the Arge reactor, albeit in low yield, is high quality diesel (cetane number 75). The diesel from different sources are blended at SASOL to obtain diesel fuel meeting all specifications.

The conclusion and recommendations of the author regarding the production of transportation fuel by the Fischer-Tropsch process are

1) The Arge route produces high quality diesel.

2) If the objective is to maximize gasoline production, the Synthol route is preferred.

3) At SASOL II and III, where only the Synthol reactor is in operation, the diesel is produced by oligomerizing olefins. This diesel does not meet all the specifications and requires cetane improvers.

4) The gasoline produced at SASOL, to be compatible with that derived from crude oil, has to be upgraded. This is done using Pt catalysts.

This paper has other pertinent information on the SASOL processes which are included in other abstracts.

Number of Pages in Document: 13

Abstract prepared by K. S. Seshadri

Title  – Synthesis Gas Conversion Over Supported Rhodium and Rhodium-Iron

Catalysts

Authors – M.M. Bhasin, W.J. Bartley, P.C. Ellgen and T.. Wilson

Source – Journal of Catalysis 54 120-128 (1978).

Raw materials for chemical industries at present are derived from

petroleum crude, which will be in short supply in the coming years.  Therefore

alternate sources of chemical feedstocks must be explored.

Synthesis gas obtained from coal and other carbonaceous materials is an

obvious choice.  The existing technology for synthesis gas conversion uses

iron-based catalysts and gives a broad product distribution.  The products are

suitable for use as fuels

Iron, cobalt, nickel and ruthenium-based catalysts, commonly used in

synthesis gas conversion, have been studied in detail, while relatively less

data are available on the catalytic properties of other group VIII elements.

Screening of these metals by the authors showed that $SiO_2$ supported rhodium

with small amounts of iron converts synthesis gas above 25 atm. to $C_2$

oxygenates, specifically to acetic acid, acetaldehyde and ethanol.

The rhodium level in the catalysts tested is held at 2.5 wt % and the

iron content is varied from 0.0 to 0.5%.  For comparison a 5% $Fe/SiO_2$ catalyst

is also tested.  The reaction is carried out in an autoclave between 200-

350°C, 25-200 atm with an $H_2$:CO ratio varying from 1:10 to 10:1.

Rhodium was used in earlier studies as a synthesis gas conversion

studies; no oxygenates more detected in the products.  In the present work,

the percent conversion of CO is low, between 1-4%.  At these low conversion

levels, with no iron, the main products are methane and $C_2$-oxygenates with

small amounts of methanol.  As the iron level is gradually increased, methane

formation decreases, the production of acetic acid and acetaldehyde is

virtually suppressed, but the production of methanol increases. The rhodium-free iron catalyst was relatively inactive and gave higher hydrocarbons.

Rhodium-based catalysts have a promising future. However, in the present study the conversion is low and there is excessive methane formation and increased conversion levels while retaining high selectivity for $C_2$-alcohols. Methanol-ethanol mixtures as such can be upgraded to fuels or, after preliminary separation, each can serve as primary chemical building blocks.

Number of Pages in Document: 9

Abstract prepared by: K. S. Seshadri

Title  — Advances in Fischer-Tropsch Chemistry

Author — Mark E. Dry

Source — Ind. Eng. Chem., Prod. Res. Dev. 15 (NO. 4), 282 (1976)

This paper deals with the product selectivity spectrum in the Fischer-Tropsch (F-T) reaction as a function of experimental conditions such as temperature, pressure, feed gas composition, basicity of iron catalyst in fixed-bed as well as fluidized-bed reactors. Plots have been prepared relating the selectivity of different hydrocarbon cuts and $CH_4$ or hard wax selectivity; these suggest that there is an interrelationship between the different carbon number cuts. Also, a theoretical product distribution, assuming stepwise growth of an adsorbed hydrocarbon complex has been computed as a function of probability of chain growth. Both the experimental and theoretical results indicate that, on iron catalysts, the maximum yield of different cuts are: 17% $C_2$ or $C_3$, 40% $C_5$-$C_{11}$, 18% diesel and 22% $C_{24}$-$C_{35}$.

The effect of temperature on product distribution apparently depends on the type of catalyst and the operating temperature range. When the catalyst and the process conditions are adjusted for wax production, as in the low-temperature fixed-bed reactor, increase in temperature significantly lowers the selectivity for wax, whereas the yields of light ends are not that much influenced by temperature changes. Gas composition also plays a part in altering the selectivity. In the fixed-bed reactor, wax selectivity is increased as the $H_2$/CO ratio increases.

The basicity of iron catalysts is an important factor in controlling product distribution and also the partial pressure of $CO_2$ in the fluidized-bed reactor, the selectivity can be varied as desired by manipulating the basicity and $CO_2$. Methane selectivity can be varied from 5-75% and that of gasoline from 0-40%.

Fischer-Tropsch systhesis is always accompanied by carbon deposition, particularly at higher temperatures, resulting in loss of catalyst activity. The basicity of the catalyst and the gas composition also influence carbon deposition. The observations of the author are: 1) as the basicity is increased, the rate of carbon deposition first decreases and then increases, and 2) the higher the reactor pressure, the lower is the carbon deposition rate.

In this paper the kinetics of the Fischer-Tropsch reaction is also briefly discussed and a method is suggested for the conversion of tail gases to high Btu gas.

Number of Pages in Document: 5

Abstract prepared by: K. S. Seshadri

Title  – Role of Vapor–Liquid Equilibrium in Evaluation of Coal Liquefaction
        Kinetics

Author – J.S. Gopal, Y.T. Shah and N.L. Carr

Source – Can. J. Chem. Eng., 61, 603 (1983).

The vapor–liquid equilibrium conditions prevailing in a coal liquefaction
reactor are incorporated into the analysis of a specific kinetic model.  The
inclusion of vapor–liquid equilibrium results in an increase in the actual
slurry residence time by a factor of 1.14 to 1.41 in the range of operating
variables investigated.  This also changes the rate expression to SRC
conversion since the partial pressure of hydrogen and the concentration of ash
in the slurry phase change.  Model simulations at typical operating conditions
(717–737 K, 13.8–20.7 MPa) found the weight fraction of liquid vaporized to be
in the range 0.1 to 0.3 which was in agreement with published data on the
volatility of typical coal liquids.  There was, however, no significant change
in the product distribution.

Number of Pages in Document:   4

Abstract prepared by:  S. Joseph

Title  — Kinetics of Short Contact Time Coal Liquefaction

  Part 1:  Effect of Operating Variables

Authors — J.S. Abichandani, J.H. Wieland, Y.T. Shah and D.C. Cronauer

Source — AIChE J., <u>30</u> (2), 295 (1984).

The preheater in a coal liquefaction process behaves as a short contact
time reactor.  This paper deals with a short contact time (<10 min.) coal
liquefaction kinetic study, which is carried out in a well mixed reactor.  The
experimental data are obtained for Powhatan No. 5 mine coal in the temperature
range of 573–723 K and pressure range of 10.3–13.8 MPa.  It was found that the
overall coal conversion increases with temperature while oil (pentane soluble)
is lost with an increase in temperature.  No effect of the initial coal
particle size distribution, total pressure and nature of gas phase
(nitrogen/hydrogen) on the production of any liquefaction product was
observed.  A lumped kinetic model is also presented to describe the product
distribution.

Number of Pages in Document:  9

Abstract prepared by:  S. Joseph

Title    – Kinetics of Short Contact Time Coal Liquefaction

        Part II:  Effect of Nature of Coal and Solvent

Authors – J.S. Abichandani, J.H. Wieland, Y.T. Shah and D.C. Cronauer

Source  – AIChE J., <u>30</u> (2), 304 (1984).

The effect of nature of coal and solvent on the kinetics of short contact time coal liquefaction is examined in this paper, which appears as a companion paper to Part I.  (Abichandani et al., AIChE J., 30 (2), 295 (1984)).  A bituminous coal (Powhatan No. 5) and a subbituminous coal (Belle Ayr) were liquefied in the presence of hydrogen donor solvents.  The hydrogen donating capacity of the solvent was varied by the addition of hydrogenated phenanthrene to SRC-II recycle solvent.  The coal conversion was not significantly different for the two coals.  However, more asphaltenes were recovered from the liquefaction of Belle Ayr coal.  Both coals when contacted with the solvent show an initial effective loss of solvent.  The results indicate that oils could be formed either directly from coal or by an indirect route via asphaltenes and preasphaltenes through adduct formation.  A kinetic model incorporating both direct and indirect routes was found to fit the data obtained with two coals and three solvents.

Number of Pages in Document:  7

Abstract prepared by:  S. Joseph

Title  – Design of Coal Liquefaction Reactors

Authors – Y.T. Shah, S.J. Parulekar and N.L. Carr

Source  – Y.T. Shah, Reaction Engineering in Direct Coal Liquefaction,

Addison–Wesley Publishing Company, Reading (1981).

Design considerations for the preheater and reactor in a coal liquefaction unit are delineated in this chapter. The peculiar nature of the slurry viscosity in the preheater is explained by dividing the preheater into three regions which chartacterize slurry heating, swelling, chemical reaction and dissolution and initial hydrogenation. An empirical correlation for the slurry viscosity is presented. Some aspects regarding the pressure drop and heat transfer in the preheater are discussed. Plug flow ror both gas and slurry phases is assumed in the preheater since the length to diameter ratio in most preheaters is large. Short contact time coal dissolution kinetics under the entire temperature range of interest is required to obtain a kinetic model for the reactions occuring in the preheater.

For the reactor, the gas phase is assumed to move in plug flow and the axial dispersion model is applied to non–volatile liquid and solid components. Kinetic models for the reactions use a generalized set of reaction pathways. Predictions from the reactor model are compared with data from existing reactors to check the validity of the model. The thermal behavior of the reactor operating under adiabatic conditions (with and without an intrareactor quench) is also evaluated. Literature correlations to determine mass and thermal dispersion coefficients and holdups for gas, liquid mass transfer coefficient are reviewed.

Number of Pages in Document:  72

Abstract prepared by:  S Joseph