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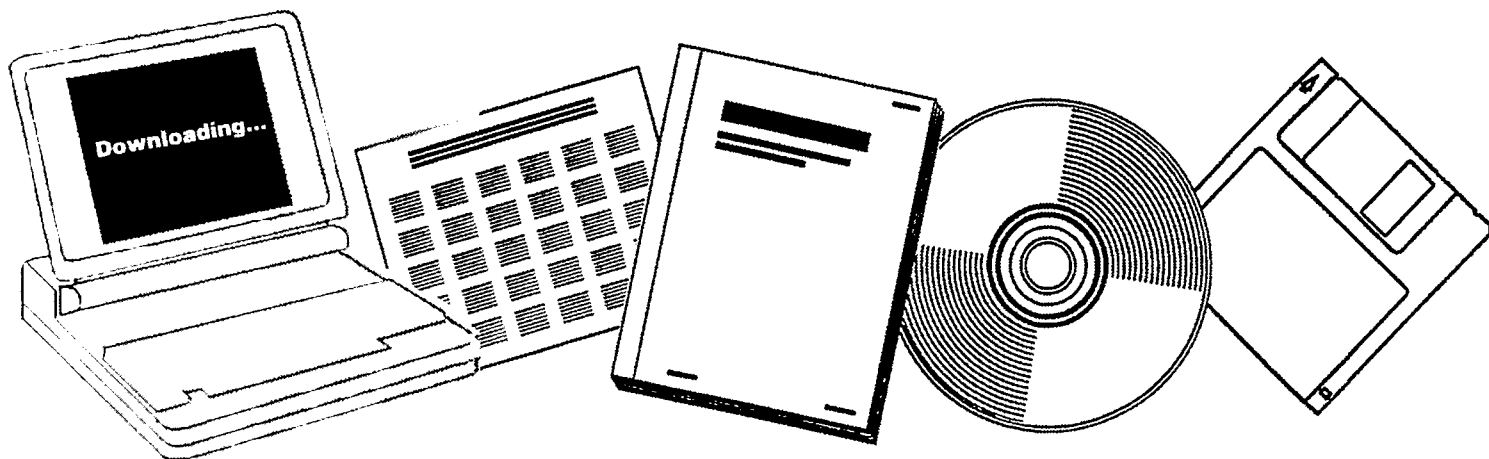
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**COAL LIQUEFACTION - INVESTIGATION OF
REACTOR PERFORMANCE, ROLE OF CATALYSTS AND
PCT PROPERTIES. QUARTERLY PROGRESS REPORT,
OCTOBER 1, 1983-DECEMBER 31, 1983**

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

1984



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

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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 direct coal liquefaction
- . Role of catalysts in indirect liquefaction and direct coal liquefaction
- . Physical, chemical and thermodynamic properties of coal liquefaction products.

2. Progress During Quarter

Work during the last quarter has largely been devoted to searching the Liquefaction Technology Data Base and other relevant sources for literature citations. A detailed description of work in each of the three tasks is given below. Six abstracts which were prepared in connection with the PCT properties of coal liquids are attached as an Appendix.

Task 1. Computer Simulator for Direct Coal Liquefaction Model

During the quarter arrangements were made with Schneider Consulting Engineers to assist the University of Pittsburgh in developing a computer

simulator for direct coal liquefaction reactors. A subcontract was given to Schneider for this work.

During the quarter Schneider Consulting Engineers developed a theoretical model to simulate the behavior of the preheater and dissolver for direct coal liquefaction. The model accounts for both the mass and energy balances for the two units. An interactive computer program (FORTRAN language) is being developed to solve the model equations. The parameters (hydrodynamic, mixing, transport and kinetics) needed for the simulation are estimated from the correlations incorporated in the program. The user is also provided the option to input these parameters.

Task 2. Indirect Coal Liquefaction and the Role of Added Catalysts in Direct Coal Liquefaction.

In this quarter, open literature and government reports on the SASOL Fischer-Tropsch process have been collected including the gasoline and possible diesel fuel yields obtainable from this process. In addition, data obtained on the thermal efficiency of the Sasol process are compared with corresponding values for processes utilizing direct liquefaction of coal. Literature on the general mechanism and technology of improved versions of Fischer-Tropsch technology has been assembled.

Data on the use of methanol as a fuel and as a chemical is almost complete and ready for a first draft report. The Mobil (MTG) process data have also been gathered. Information on the integration of this process with the Fischer-Tropsch process is still being gathered. Work on the synthesis of higher alcohols from synthesis gas has progressed to

the point where we estimate that about 80% of the available data has been collected.

Task 3. The Physical Chemical and Thermodynamic Properties of Coal Liquefaction Products.

Final reports on two properties of coal liquids have been prepared in this quarter. The viscosity peak occurring as a bituminous coal goes into solution is the most significant factor in the design of a demonstration plant. A number of different types of viscometers have been used to measure the viscosity of coal liquids. Further experimental work needs to be done to develop a viscometer to extend its application to more concentrated slurries. To date, a capillary flow viscometer appears to be the most suitable instrument available. The measurements to date indicate that the viscosity of coal liquid fractions increases with increasing boiling point and decreases in an exponential manner with increasing sample temperature. In general, the viscosity of vacuum bottoms increases with both the soak time and the soak temperature. The vacuum lower bottoms viscosity resembles a pseudoplastic fluid with thixotropic behavior. Viscosity decreases with increasing shear rate at constant temperature and decreases with increasing temperature at constant shear rate.

Gray has reported that the viscosity measurements for coal liquid fractions and the graphical data in the SRC-II process Physical Properties Data Book agree only for temperatures below 250°F. Current petroleum fraction viscosity data and those for pure compounds appear to have only marginal applicability to coal liquids. New correlations are needed to predict the viscosity behavior. Measurements above 500°F are needed to extend the correlations.

The thermal conductivity of coal liquids decreases with increasing temperature and with an increase in the boiling point of the coal liquid fraction. The effect of specific gravity is inconclusive. Recent measurements reported by Gray indicate that the thermal conductivity increased with increasing specific gravity for some but not for all cuts. The data for coal liquid fractions showed that most of the data were grouped in a narrow band over reduced temperatures between 0.33 and 0.9.

3. Personnel

The project tasks are supervised by Dr. Brainard (Task 3), Dr. Shah (Task 1), and Dr. Wender (Task 2). Dr. Tierney is providing overall coordination and computer consultation. During the quarter, Dr. Albal (Task 3) and Dr. Kulkarni (Task 2) left the project. Dr. Seshadri (Task 2) and Mr. Bhattacharjee (Task 3) joined the project. In addition personnel at Schneider Consulting Engineers, principally Dr. Abichandani worked on Task 1.

Title: P-99 Vacuum Column Test Series
Author: Steven T. Mathias
Source: Gulf Science and Technology Company, Report No. 627RK012, September 1979, PETC LTDB Accession No. 004814

This report covers a study to determine the effect of the flash zone temperature in the vacuum column on the recovery of distillate and the properties of the tower's product streams. The SRC-II process employs distillation for product recovery. One part of the distillation sequence is a vacuum column. In this study, primary emphasis was placed on the experimental determination of the viscosity of the bottoms product using a Brookfield laboratory model LVT viscometer. The vacuum tower bottoms samples were taken as the column temperature was being raised gradually. The viscosity tests on these samples at various temperatures (100 to 575°F) and shear rates (16.8 to 0.084 sec⁻¹) demonstrated the product to be a non-Newtonian pseudoplastic fluid with thixotropic behavior. Viscosity decreased with increasing shear rate at constant temperature, and decreased with increasing temperature at constant shear rate. As the vacuum column conditions became more severe, an increase in the viscosity was observed. The thixotropic behavior indicated that to maintain a constant shear rate with time required an ever decreasing shear force.

Abstract prepared by: Rajendra S. Albal

Title: Effect of Temperature, Residence Time, and Coal Concentration on SRC-II Feed Slurry Viscosity and Shear Stress-Valley Camp Coal and Robinson Run Coal.

Authors: Venturino, A.P. and Gall, W.

Source: Gulf Science and Technology Company, Report No. 624RJ054, File No. FT07-30-30, December 1978.

This report summarizes the results of a study on the effects of temperature (80-120°C) coal concentration, (29 to 34 wt. %) residence time (2 and 4 hours) and shear rate (16.8 to 0.08 sec⁻¹) on viscosity and shear stress of feed slurries using Pittsburgh seam coals from Valley Camp and Robinson Run mines. A laboratory Brookfield viscometer was used for these measurements. Details of the experimental apparatus operating procedure are given.

Similar results were observed for both coals. Viscosity was found to decrease with increased shear rate and to increase with increasing coal concentration and residence time. Temperature increases were found to decrease viscosity at lower coal concentrations and shorter residence times (2 hours). Higher temperatures, however increased the viscosity at higher coal concentrations and longer residence time. This indicated greater coal swelling and solvation at higher temperatures. Both coal slurries were found to be non-Newtonian, pseudoplastic, with viscosity decreasing as shear stress increased. It was concluded that these coals could cause mixing problems for the P-99 process development unit operations at coal concentrations above 30 wt % unless the recycle solids level was cut back.

Abstract prepared by: Rajendra S. Albal

Title: Feed Coal Slurry Viscosity

Author: Spearhac, R.G.

Reference: Letter to Sobernhiem, J.R., Reference No. RGS1DD1, April 29, 1980.

In this Rheology Topical Report, the author has mentioned that the most significant variable affecting the viscosity of coal feed slurry was the particle size of the coal. It was found that the coal particles finer than 400 mesh contributed substantially to the viscosity of the coal feed slurry. It is mentioned by the author that although -30 mesh coal was easier to handle, it accelerated the erosion of the process equipment. This increased erosion may be a function of slurry viscosity. It may be possible to operate at elevated slurry blend tank temperatures (375°F -425°F) where the slurry would be viscous enough to reduce erosion. This would lead to improved thermal efficiency and a slurry preheater of reduced size.

Abstract prepared by: Rajendra S. Albal

Title: Solvent Refined Coal (SRC) Process: Selected Physical, Chemical and Thermodynamic Properties of Narrow Boiling Range Coal Liquids for SRC-II Process.

Author: Gray, J.A.

Source: Interim Report for March 1980 - February 1981, Report No. DOE/ET/10104-7, April 1981.

This report presents the viscosity data for various coal liquid fractions from SRC-II process. Data for cuts 1 to 16 with boiling range (50 wt % off) temperatures between 152 to 757°F are given. Data for cuts 17, 18 and 19 could not be measured because of equipment limitations. These data were measured by Fluid Properties Research, Inc. using an absolute capillary viscometer. Measurement pressure was adjusted to approximate saturated liquid conditions, and measurement temperatures were limited to a maximum of 500°F because of equipment limitations. The coal liquid fractions were assumed to approximate Newtonian fluids in these measurements.

Stable measurements above 305°F were not possible for cuts 1-3 because the pressure drop across the capillary viscometer gradually increased with time even though the flowrate was held constant. Although not conclusive, it appeared that the samples may have degraded and fouled the wall of the capillary. The coal liquid viscosity increased with increasing boiling point and decreased in an exponential manner with increasing sample temperature. Graphs are included, with a word of caution for extrapolation to temperatures as high as the critical point or 900°F whichever comes first.

Comparison of the viscosity data with the SRC-II Physical Properties Data Book indicated excellent agreement at temperatures below 200°F for the lighter fractions (cuts 5-10) and below about 250-260°F for the heavier fractions (e.g. cut 13). At temperatures higher than 200-260°F, the viscosity data tend to be well below (10-20%) the Data Book curves.

The viscosity data were well-correlated by the following equation:

$$\ln \mu = A + \frac{B}{T+C}$$

The values of constants A, B, and C are given for all coal-liquid cuts.

Abstract prepared by: Rajendra S. Albal

Title: Solvent Refined Coal (SRC) Process: Selected Physical, Chemical and Thermodynamic Properties of Narrow Boiling Range Coal Liquid Fractions, Supplemental Property Data.

Authors: Gray, J.A., and Holder, G.D.

Source: Report No. DOE/ET/10104-44, April 1982

This report describes the evaluation of some correlations with respect to their ability to predict the viscosities of narrow boiling coal liquid fractions from the SRC-II process. The multiparameter equation of state and associated correlations, developed by Starling et al. (1980) for predicting the thermodynamic and physical properties of coal liquids were evaluated. In this analysis, separate correlations for the critical volume, the critical temperature and the orientation parameter were used. Other correlations for the liquid viscosity were also developed and evaluated.

The experimental data used in this analysis were reported by Gray (1981) and Gray et al. (1981) for 15 narrow boiling coal liquid fractions with boiling points (50 wt% off temperatures) ranging from 346 K to 724 K. Since densities are needed in calculation of viscosities, the method of calculating densities was important. Two methods to calculate the densities were used; one based on Starling's equation of state, and the other from the modification of the Rackett equation.

For the Starling et al. correlations, the experimental and predicted viscosities were in fair agreement for the lighter cuts, but discrepancies became larger as the cut became heavier. This was true regardless of whether the orientation parameter was determined from the boiling point or from Starling's general correlation. The average absolute error for cuts boiling above 590 K was generally in excess of 40%. In these calculations, the densities were based upon Starling's equation of state. When the densities were determined from the modified Rackett equation, the average absolute

errors were much worse. This occurred despite the fact that the Rackett equation give more accurate density predictions.

Gray and Holder have developed and evaluated some other correlations for prediction of saturated liquid viscosity. The most successful correlation had the following form

$$\ln (\mu/\rho^{0.5}) = f_1 + \omega f_2$$

where

$$f_1 = -5.180477 + 0.64578 \alpha + 0.102428 \alpha^2$$

$$f_2 = 0.49886 \alpha + 2.35539 \alpha^2$$

and $\alpha = (1-T_r)/T_r$

The viscosity, μ , is in mPa.s; ρ is the density in kg/m³ as determined from the modified Rackett equation; ω is the acentric factor which is determined from the boiling point and the Wilson et al. (1981) vapor pressure equation, and T_r is the reduced temperature determined from the Starling et al. (1980) correlation for critical temperature. This correlation gave an absolute average deviation in predicted viscosities of 11.92% and a bias of 1.2%. These results were considerably better than those obtained using the correlation of Starling et al., and this correlation has been recommended for estimating the viscosity of SRC-II coal liquid fractions.

References cited in this abstract:

Gray, J.A., "Selected Physical, Chemical and Thermodynamic Properties of Narrow Boiling Range Coal Liquids," Report No. 627RM049, DOE/ET/10104-7, April, 1981.

Gray, J.A., Brady, C.J., Cunningham, J.R., Freeman, J.R., and Wilson, G.M., "Selected Physical, Chemical and Thermodynamic Properties of Narrow Boiling Range Coal Liquids," paper presented at the 1981 Annual AIChE Meeting, New Orleans, LA, November 1981.

Starling, K.E., et al., Coal-Calc Project Report to DOE, Coal Conversion System Technical Data Book Project, IGT Report No. OU/IGT/S-14366-1, Published by the School of Chemical Engineering and Material Science, University of Oklahoma, Norman, OK, August, 1980.

Wilson, G.M., Johnston, G.H., Hwang, S.C., and Tsonopoulos, C., Ind. Eng. Chem. Proc. Des. Dev., Vol. 20 (1), p. 94 (1981).

Abstract prepared by: Rajendra S. Albal

Title: Density, Viscosity, and Surface Tension of Coal Liquids at High Temperatures and Pressures

Authors: Hwang, S.C., Tsonopoulos, C., Cunningham, J.R., and Wilson, G.M.

Source: Industrial and Engineering Chemistry, Process Design and Development, Vol. 21 (1982), pp. 127-134.

This paper presents the viscosity data for coal liquids at temperatures up to 730 K (850°F) and pressures up to 22 MPa (3200 psia). Measurements were made on liquids produced with the Exxon Donor Solvent process on Illinois and Wyoming coals. The viscosity was measured by using a rolling ball viscometer. Several measurements were also made to determine the effect of dissolved hydrogen on the physical properties of coal liquids.

Two methods of estimating the viscosity data were evaluated. The first one was a petroleum fraction liquid viscosity correlation developed by Abbott et al. (1971), and the second correlation was based on the application of corresponding states concepts to a large amount of experimental pure component data by Abbott and Kaufmann (1970). A comparison of the experimental and calculated viscosities indicated that neither the petroleum fraction nor the pure component correlations could correctly predict the effect of pressure on viscosity. The values predicted by the petroleum fraction correlations were appreciably higher than the experimental results at temperatures as high as 800-900°F, the absolute average deviation was 45% in the absence of hydrogen and 25% under a high pressure hydrogen atmosphere.

Although better results were obtained for the viscosity of coal liquids not containing dissolved hydrogen when the coal liquid fractions were simulated as pure components rather than as petroleum fractions, the reverse was true for coal liquids with dissolved hydrogen. In the case of the pure-component correlation, the critical viscosity of hydrogen was used in all the viscosity calculations of the coal liquids containing dissolved hydrogen.

Clearly, this blending procedure was poor for hydrogen/high-boiling compound mixtures. In order to clarify this problem created by the blending procedure used in the viscosity predictions for coal liquids containing dissolved hydrogen, calculations were also made by ignoring the hydrogen dissolved in the coal liquid. The results of those calculations indicated that the pure-component correlation was markedly superior to the petroleum-fraction correlation.

References cited in this abstract:

Abbott, M.M., and Kaufmann, T.G., Can. J. Chem. Eng., Vol. 48, p. 90 (1970).

Abbott, M.M., Kaufmann, T.G., and Domash, L., Can. J. Chem. Eng., Vol. 49, 379 (1971).

Abstract prepared by: Rajendra S. Albal

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