THE PHYSICAL, CHEMICAL, AND THERMODYNAMIC PROPERTIES (PCT) OF PRODUCTS FROM DIRECT COAL LIQUEFACTION PROCESSES

by

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SUMMARY

The PCT properties of products from direct coal liquefaction processes are of great importance to all who have to design both small scale and commercial scale process units. Material balances, energy balances, heat transfer calculations and pressure drop calculations are not possible without this information. This report continues the work reported in an earlier DOE report (Albal et al., 1983). In particular, it provides a review of the literature of the experimental measurements of the viscosity, thermal conductivity, heat of reaction, vapor pressure, and surface tension of coal liquids. While most of the information relates to products from the SRC-II process, some information on products from the Exxon Donor Solvent process is included where it is known. In addition, the report includes Prandtl numbers for SRC-II liquids.

This summary will now introduce the important findings for each of the PCT properties mentioned above.

The measurements made 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. Empirical correlations representing the viscosity of coal liquid fractions and SRC mixtures and feed coal slurries are presented. Viscosity correlations developed for petroleum fractions and pure compounds appear to have marginal applicability to coal liquids. More experimental measurements at temperatures greater than 500°F are needed to extend the present correlations to temperatures more in keeping with the higher temperatures utilized in coal liquefaction processes.

The experimental measurements of the thermal conductivity of coal liquid samples is quite limited. They show that the thermal conductivity decreases with increasing temperature and with an increase in the coal liquid fraction

boiling point. An empirical correlation relating thermal conductivity to the oxygen content and reduced temperature of coal liquid cuts is presented.

As the oxygen content is not always known, an empirical correlation relating thermal conductivity to the normal boiling point and the reduced temperature is recommended. In general, it has proven difficult to extrapolate the thermal conductivity of cuts of coal lqiuids to their critical point. At the present time the correlation hold for reduced temperatures < 0.9.

The critical temperature, T_c and the critical pressure, P_c are the independent variables most commonly utilized in various correlations representing the vapor pressure of coal liquids. Accordingly, methods of estimating T_c and P_c are first discussed. The limited experimental T_c values seem to be represented well by the Roess, Nokay, ASPEN and Kessler-Lee correlations. Five methods of predicting the P_c values were tried. The two experimental data points were best represented by the expression presented by Mathur.

Five correlations, namely the Linear, Riedel, Mobil, Starling, and Wilson correlations, were used to represent the vapor pressure of coal liquids. While all five gave a reasonable fit to various cuts of SRC-II liquid, the present authors suggest the following ranking (listed in order of decreasing ranking)

Starling
Mobil
Reidel } Approximately equal
Wilson
Linear

While Starling's correlation has the greatest complexity, it can be handled quite easily on any contemporary computer.

An extremely limited number of pieces of data for heats of reaction of coal liquids are available. The difficulty of operating a bench scale adiabatic reactor is one of the reasons why this is so. The data indicate a decreasing heat of reaction with increased H_2 consumption. Stephenson (1981) correlated the heat of reaction data with a linear relationship with H_2 consumption. He noted that the hydrogenation reactions in coal liquefaction are mainly due to the saturation of aromatic rings and not hydrocracking reactions. An attempt by the present authors to estimate heat of reaction values from heat of combustion data was not very satisfactory.

Surface tension values for coal derived liquids are very limited. Empirical expressions have been used to repsent the data. The agreement is only fair and it is clear that more experimental measurements are badly needed.

Prandtl numbers for cuts of coal derived liquids were calculated by the present authors. In general, the Prandtl number decreases with increasing temperature and increases with increasing boiling point of the coal liquid cut. Three empirical correlations representing the Nusselt number as a function of the Reynolds number and Prandtl number were tested with meaurements made by Gulf R&D. The Dittus-Boelter correlation gave the best fit both for the transition and the turbulent regions.

VISCOSITY OF COAL LIQUIDS AND SLURRIES

Introduction

The control of the coal-slurry viscosity is a crucial factor for the Solvent Refined Coal Process to maintain system operability. The viscosity data for the feed slurry, recycle slurry, vacuum bottoms, vacuum flash feed, and coal liquid fractions are required for the design and operation of the feed tank, preheater, reactor, fractionating towers, pumps, and other process equipment.

The P-99 Process Development Unit utilized at the Gulf Research Laboratories in Harmarville, Pennsylvania uses a continuous coal feed blending tank for SRC-II operation. The operation of this feed tank can be a problem because of the varying mixing properties of the different coals and the complex viscosity behavior of the feed slurry. Some coals have a tendency to swell or "gel" and form a thick, unpumpable mixture, as the mixing time increases. This gelling tendency increases with temperature, but it may be offset in some cases by the normal tendency of viscosity to decrease with increasing tempeature. Hence, it is important to know the variation of viscosity and rheological behavior of slurries of the various feed coals under the feed coal mixing conditions.

Knowledge of viscosity is very important for the operation of the preheater and dissolver to determine the degree of solubilization and depolymerization of the coal. It was found that the residence time of the coal slurry in the preheater and dissolver was critical for the success of the process. It was observed that the viscosity of the slurry first increased as the slurry was heated, especially as the caking coal passed through the temperature range of plasticity. Then, at higher temperatures, the viscosity

rapidly decreased. Prolonged heating appeared to induce a second viscosity increase. Under such conditions, turbulence may not be achievable and heat transfer may be only by conduction and may be very poor. Overheating may result in caking, i.e., plugging the pipe. It was found essential that the process be allowed to proceed until the minimum viscosity product was made, and it is undesirable for the heating to be continued to the point where the second viscosity increase becomes consequential. Thus, knowledge of viscosity can provide the means for determining the optimum values of the operating variables, and would give prompt warning if a malfunction produced an unfilterable solution.

In order to avoid the need for filtration or a similar solid-liquid separation step, the SRC-II process employs distillation for product recovery. One part of the distillation train is a vacuum column. In order to maximize the distillate product, it is desirable to cut as deeply as possible into the vacuum bottoms. On the other hand, there is the need to avoid caking in the vacuum column and the additional need to produce a vacuum bottoms product of low enough viscosity to be pumped readily. Thus, information on the effect of operating severity on the properties of the overhead and bottoms streams is important for design.

The property "Viscosity" is discussed in this report. Data from various sources for narrow boiling coal-liquid cuts, feed slurry, recycle slurry, vacuum bottoms, and vacuum flash feed are included. The available correlations to predict the rheological behavior of various streams are also included. The areas where additional experimental measurements are needed are identified.

Summary of Available Data

A large number of measurements have been reported on the viscosity of vacuum bottoms, feed slurry, recycle slurry, and the coal liquid fractions.

Most of these measurements were carried out by using laboratory instruments like the Brookfield LVT type viscometer, Haake viscometer, Capillary viscometer, Rolling-Ball viscometer, etc. More information concerning these instruments and their use may be found in Skelland (1967). In the Brookfield or Rolling-Ball viscometer, the shear rate is varied by using different stirring speeds. In a Capillary viscometer, the shear rate is varied by using different flow rates. Based on the nature of the plot of shear stress versus shear rate, the rheological behavior of the material was characterized. Figure III-1 is a general figure showing the rheological behavior of Newtonian and non-Newtonian materials. A shear diagram for a thixotropic fluid is shown in Figure III-2. The parameters varied include soak time, temperature, composition, storage time, and shear rate.

A discussion of some of the important measurements now follows.

Parimi (1981) has described the results of an extensive experimental program to study the rheological behavior and thermal stability characteristics of both the vacuum tower bottoms as well as the vacuum tower feed. The material that now follows is taken largely from this work.

Vacuum Tower Bottoms Viscosities

Five vacuum tower bottom samples were used in the test program ranging in pyridine insoluble (PI) content of 36.0 to 47.7wt%. All samples were laboratory retained samples of vacuum tower bottoms from Powhattan No. 5 coal runs for Texaco gasifier tests. In the first series of tests each sample was rapidly heated to a temperature of 600, 650, or 700 ^{o}F (soak temperatures), and held at these temperatures for 30 and 120 minutes (soak time).

Viscosities were measured using a Brookfield viscometer at shear rates ranging from 9.3 to 372 sec^{-1}. The sample was then quenched to 575°F and the viscosity measurements repeated over the same shear rate range.

In general, viscosity increased with both the soak time and soak temperature, and the increase was substantial at a soak temperature of 700°F and soak time of 120 minutes. This unusual rheological behavior was attributed to possible polymerization and thermal degradation of the sample when exposed to elevated temperatures for extended times. Further analysis and later tests, however, indicated that the high viscosities observed at elevated temperatures and exposure times were also affected by exposure to air during the process of soaking and viscosity measurement. In these later tests, the samples were sealed in sample bombs with inert gas for up to 48 hours at the test temperature, avoiding the possibility of thermal degradation due to exposure to air at the elevated temperatures. The viscosities generally increased with increasing soaking (storage) time, at all temperatures exceeding 550°F, but to a lesser extent. At 700°F, viscosity growth, however, still was substantial, indicating storage of vacuum tower bottoms at these temperatures for any extended length of time may be undesirable.

The vacuum tower bottoms samples exposed to high temperatures for different lengths of time were analyzed by Soxhlet extraction in order to characterize the chemical changes resulting from the severe conditions of exposure. The Soxhlet extraction separates the sample into oils, asphaltenes, preasphaltenes and pyridine insolubles. This analysis indicated that, in general, the IOM (Insoluble Organic Matter) and preasphaltene content increased at the expense of oils and asphaltenes, the magnitudes depending upon the severity of exposure.

A third series of tests was also conducted on one of the samples in order to characterize the effect of a distillate diluent on the thermal stability as well as the rheological behavior of vacuum tower bottoms. Heavy pump flush in quantities of 10, 20 and 30 wt% was added to the vacuum tower bottoms sample C, and viscosities were measured at shear rates ranging from 9.3 to 372 sec^{-1}. Further, the diluted samples were soaked at 575, 600 and 650 ^{o}F for up to 24 hours and the viscosities measured to determine aging effects.

The composition of the five vacuum tower bottom samples used in testing are shown in Table III-1. These samples were collected originally from vacuum flash drum B at Ft. Lewis and had been exposed to air and solidified on a water cooled Sandvik belt. Further, when each of the samples was heated to different temperatures and held for 30 to 120 minutes in the first series of tests to rheologically characterize them, they were further exposed to an oxidizing atmosphere. As a result, the viscosity data generated during the initial phase (the first series) were considered to be unreliable. The fact that the viscosity growth was substantially less for sample C in the second series of tests, where the samples were kept in inert atmospheres, substantiates that the results from the earlier work on slurry viscosities were indeed not reliable and should not be used for evaluations of their storability.

In the second series of tests, care was exercised in making the samples used in testing inert. Samples C and F were used in this phase of the study. Sample C represents the demonstration plant vacuum tower bottoms composition. These two samples were stored at 500^{o}F, 600^{o}F, 650^{o}F, and 700^{o}F for periods of 6, 12, 18, 24, and 48 hours and their viscosities measured. The viscosities generally increased with storage time. While the viscosity growth at storage temperatures of 550^{o}F to 650^{o}F was modest, the growth was

substantial at 700°F. Any storage at this high temperature appears to be undesirable.

The vacuum tower bottoms slurry behaved as a pseudoplastic fluid, with the measured viscosity decreasing with increasing shear rates at all temperatures tested. This pseudoplasticity of this material increased with temperature.

The third series of tests was conducted on vacuum tower bottoms sample C diluted with heavy pump flush. The material was fractionated into 50 degree cuts and their viscosities and densities measured as a function of temperature in the temperature range of 100° to 500°F. Also, the viscosity of the composite was measured as a function of temperature.

In this phase of the study, vacuum tower bottoms sample C, with a composition similar to that of the corresponding Demonstration Plant stream was diluted with 10, 20, and 30 wt% heavy pump flush and viscosities of the blends measured at 575, 600, and 650 °F and at several shear rates ranging from 9.3 to 372 sec^{-1}. The diluted samples were also aged for 0, 12, and 24 hours before viscosity measurements were taken. Dilution, as expected, had a positive effect on thermal stability. There was virtually no difference in the viscosity of the 30% diluted sample in the measured viscosities between the 12 and 24 hours, and even the viscosity increase between 0 and 12 hours was not significant. As stated, the viscosities of diluted vacuum tower bottoms were measured at 575°, 600°, and 650°F; however, only the data at 650°F could be used in the analysis because of the number of inconsistencies found in the data at the other temperatures.

The following conclusions can be drawn from the vacuum bottoms test program:

1) Vacuum bottoms in a liquid state must be kept in an inert environment to avoid oxidation which increases the viscosity.

2) Two vacuum bottoms samples may exhibit identical rheological behavior at one temperature but could exhibit drastically different behaviors at other temperatures.

3) Vacuum bottoms can be stored at 650°F for periods of up to 24 hours without appreciable viscosity increases. Vacuum bottoms stored at 700°F, although initially less viscous than material stored at 650°F, may become noticeably more viscous after 18 hours and unpumpable after 24 hours.

Mumford (1981) has reported the results of a program initiated to compare the rheological behavior of Ireland mine coal derived vacuum tower bottoms material which had not undergone a solidification/remelt cycle to comparable material which was solifified on the Sandvik belt and remelted. No significant change was observed in the viscosity of vacuum tower bottoms material due to a solidification/remelt cycle. While this result may not justify a similar conclusion for vacuum tower bottoms material derived from all coal types for every possible composition, it does provide a strong support for such an approximation concerning the viscosity of these materials.

Vacuum Flash Feed Viscosities

The objective of the vacuum flash feed rheological program was to determine the viscosity and thermal stability of typical vacuum flash feed used in Demonstration Plants for the design of pumping and other material handling requirements.

The viscosity data of vacuum tower bottoms sample C diluted with different amounts of pump flush were used to develop viscosity estimates of vacuum flash feed, which can be considered as diluted vacuum tower bottoms

slurry. The variables affecting the viscosity are the amount of dilution (or the amount of PI in the feed), temperature, shear rate, and storage time. The variables considered were the composition (amount of PI or amount of distillate), temperature, and shear rate.

The data on the effect of composition in terms of PI in feed are given at a temperature of 650°F and at a shear rate of 186 sec^{-1}. The temperature effect is shown on a conventional ASTM Viscosity-Temperature Chart. Here it was assumed that over a small range of temperatures, the temperature effect on viscosities of diluted vacuum tower bottoms was similar to the effect on viscosities of undiluted vacuum tower bottoms. Using the figures given by Parimi, it is possible to estimate viscosities of vacuum flash feed of a given composition at any desired temperature and shear rate.

Parimi has mentioned that the method described above in obtaining viscosities of vacuum flash feed for design purposes has one deficiency in that the characteristics of the diluent have to be similar to those used in the experimental work for the method to be valid. In order to overcome this deficiency, an alternate approach which involves application of conventional viscosity blending charts can be used. The applicability of blending charts with a minor modification was verified by Parimi for the slurry/coal liquid mixtures of interest using the existing data on the blend of vacuum tower bottoms, sample C and heavy pump flush material of known composition and rheology. It is recommended that the vacuum flash feed viscosities be obtained by using the viscosity blending chart at a temperature low enough such that the blending chart can be used and extrapolating the results to the required temperature using the ASTM viscosity temperature chart.

It should be noted that the information provided by Parimi should not be regarded as absolutely characteristic of all vacuum flash feed material. It

is useful to give the designer an approximation of the magnitude of viscosity growth and shear dependency of the mateial being tested.

A report by Mathias (1979) covers a study to determine the effect of the flash zone temperature in the vacuum column of the process development unit P-99 on the recovery to distillate and the properties of the tower's product streams. Primary emphasis was placed on the experimental determination of the viscosity of the bottoms product utilizing a Brookfield laboratory model LVT viscometer. The vacuum tower bottoms samples were taken daily for each of the periods of runs as the vacuum column's temperature was gradually raised. The viscosity tests on those samples at various temperatures and shear rates demonstrated the product to be a non-Newtonian pseudoplastic with thixotropic behavior. Viscosity was observed to decrease with increasing shear rate at constant temperature and to decrease with increasing temperature at constant shear rate. As the vacuum column conditions became more severe, an increase in the viscosity was observed.

The changes in product properties as a function of flash zone temperature provide information which can be used to define the operating limitations of P-99's vacuum column and represent process variable relationships which will be useful in the design of a commercial plant.

Due to the high viscosities and high melting points of these samples, they were prepared at room temperature in solid form. The finely ground powdered samples were melted in the Thermosel unit prior to the viscosity measurement. The shear rates varied from 16.8 to 0.084 sec^{-1}, and temperature varied was from 100° to about 575°F.

At a given shear rate, viscosity decreased with temperature which demonstrates typical pseudoplastic behavior. A linear dependence of viscosity was observed with the reciprocal of absolute temperature. The change of

viscosity with time showed a decrease in viscosity at a constant shear rate for over an hour. This thixotropic behavior indicated that to maintain a constant shear rate with time required an ever decreasing shear force.

A report from Venturino and Gall (1978) summarizes the results of a study on the effects of temperature, coal concentration, residence time, and shear rate on viscosity and shear stress of feed slurries for P-99 pilot plant using Pitt seam coals from Valley Camp and Robinson Run mines. The range of operating conditions investigated were temperature: 80 to 120°C, residence time: 2 and 4 hours, coal concentration: 24 to 34 wt%, and shear rates: 16.8 to 0.08 sec^{-1}. Viscosity and shear stress were measured using a Brookfield viscometer. 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 longer residence times (2 hours). Higher temperatures increased viscosity at higer coal concentrations and longer residence times. This indicated greater coal swelling and solvation at higher temperatures. Both coal slurries were found to be non-Newtonian pseudoplastics, with viscosity decreasing as shear stress increased. It was concluded that these coals could cause mixing problems for P-99 operations at coal concentrations above 30 wt. % unless the recycle solids level was cut back.

In a Rheology Topical Report, Spearhac (1980) 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 which were finer than 400 mesh contributed substantially to the viscosity of the coal

feed slurry. It is mentioned by Spearhac 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 slurry preheaters of reduced size.

Viscosity data for the recycle slurry are given by Gorski (1980) as a function of shear rate (18.6 to 2242 sec^{-1}) at eight different temperatures (284 to 600°F). These data were measured by a Brookfield as well as Haake viscometer. The Haake viscometer measurements were not found to be reproducible. Table III-2 lists these data.

Naylor (1980) has given data of synthetic recycle slurry material blends. The compositions of these blends, called 2, 2a, 3, 3a, are given in Table III-3. These data were measured as a function of shear rate and temperature over a range of 20 to 2000 $sec.^{-1}$ and 284 to 600°F, respectively.

Viscosity Data for Coal Liquid Fractions

Hwang et al.(1980) have presented 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 from the Exxon Donor Solvent process from 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.

Gray (1981) has summarized the viscosity data for various coal liquid fractions from the SRC-II process. 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. Gray has reported that 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 flow rate was held constant. Although not conclusive, it appeared that the samples may have degraded and fouled the wall of the capillary. The viscosity data were consistent for the most part and exhibited the expected trends, i.e., the coal liquid viscosity increased with increasing boiling point and decreased in an exponential manner with increasing sample temperature. Graphs are presented, 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 graphical data in the SRC-II Process 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 than 200 - 260°F, the viscosity data reported tend to be well below the data book curves (~ 10 - 20%). Gray has related the difference to differences in the boiling ranges of the fractions being compared. The data book samples, for example, were prepared by ASTM D-86 and D-1160 distillations, and corrections may not have been made to a true boiling point basis. Thus, the actual boiling ranges may be much wider than 50°F.

The SRC-II Process Physical Properties Data Book along with the additions and corrections by Horsak (1981) summarizes the viscosity data for coal liquid fractions derived from Powhattan coal, coal-recycle slurry, vacuum bottoms and vacuum flash feed. A procedure for estimating viscosities of SRC-II process slurry streams of various solids and coal liquid compositions is also outlined. Data are shown for 50°F cut fractions. The curves and data for

boiling points above 750°F are extrapolations of the data. These curves have been fit to an equation of the following form:

$$\ln \mu = A + \frac{B}{T + C} \qquad (1)$$

where μ is in cP, T is temperature in °R and A, B, C are constants. The values of these constants for various cuts are shown in Table III-4.

The viscosity of a mixture of coal liquids can be calculated using the blending rule recommended by the API Technical Data Book:

$$\mu_m = \left(\sum_{i=1}^{n} x_i \mu_i^{1/3}\right)^3 \qquad (2)$$

where x_i is the mole fraction of the component i.
This formula was checked against experimental data for both the light naphtha and heavy fuel oil with deviations of only 1% and 4%, respectively.

According to the Data Book, the calculations of viscosities of mixtures are not recommended for use at temperatures where the high boiling component viscosities are above 1000 cp. This limitation also must be followed in the use of the viscosity equation 1. It is suggested that a constant value of 1000 cp may be used for those heavier coal liquid fractions in mixing rule calculations where the limit of 1000 cp is exceeded, provided the mole fraction of that component is not greater than 3%.

The SRC-II Data Book also presents data of viscosity versus shear rate for SRC-II slurry obtained from West Virginia Panhandle coal with a total solids content of 45 wt% (30wt % coal and 15 wt% recycle solids). Curves are shown for a constant temperature of 350°F. Viscosity-shear rate relationships at various temperatures for Demonstration Plant Design Vacuum Bottoms are

shown. It must be stressed that these relationships were developed for a specific sample of vacuum bottoms. The composition of vacuum bottoms is known to have a substantial effect on viscosity. Distillate retention, which is highly related to vacuum tower operating conditions, will also have a major impact on viscosity. Proper care should be taken in estimating a realistic range of viscosity due to these considerations.

Based on an experimental program at the Battelle Columbus Laboratories, Droege, et al., (1980) have reported the viscosity data for coal solvent slurries in the range 300-600K. A recycle solvent from the Wilsonville SRC-I plant and a KY-9 coal were used.

This program was planned in accordance with the expected needs for the engineering design of the coal slurry heating system in the SRC-I process. The majority of the data were obtained in more dilute slurries than the plant design (i.e., at a solvent to coal ratio of 2). Since the slurry concentration substantially affects the viscosity, the results cannot be transferred directly to the preheater without exercising considerable caution. This is clear from the observation that the measurements at the design solvent to coal ratio of 1.6 gave viscosities so high that the measurements could not be completed beyond 500°F. The original reference should be seen for details.

Even though the major focus of this work was on the preheater the results obtained may be useful in connection with other aspects of the liquefaction process. These data can be applied directly to calculations for other parts of the preheating system. However, the complexity of the viscosity fluctuation and fluid mechanics will prevent the application of these data for the fired heater. In the fired heater, operating at temperatures of 560 to 700K (550-800°F), the slurry passes from a Newtonian liquid to Bingham plastic

and back to Newtonian fluid. The apparent viscosity undergoes a rapid increase followed by a rapid decrease. Turbulent flow changes to plug flow and back to turbulent flow again making development of a model almost impossible. A prerequisite for modelling would be the development of rate equations for the thickening and thinning processes. The data in this study are not sufficient for this purpose.

Effect of Solids Concentration and Temperature on Viscosity

A rheological experimental program was designed by Pittsburg and Midway Coal Mining company and described in the SRC-II Physical Properties Data Book (1980) to assess the viscosity behavior as a function of solids concentration and temperature. Using a Haake Rotovisco RV-2 viscometer, measurements were carried at atmospheric pressure at temperatures to 220°F. It was observed that for artificial slurries made from SRC-I dried mineral residue and process solvent at 57°F, added solids had a strong effect on viscosity than indicated by the Kunitz (1926) equation:

$$\frac{\mu_m}{\mu_\ell} = \frac{1 + 0.5\phi_s}{(1 - \phi_s)^4} \qquad (3)$$

where μ_m is the mixture viscosity, μ_ℓ, is the viscosity of the liquid alone, and ϕ_s the volume fraction of solids. The Kunitz equation was considered to be accurate for $\phi_s \leq 0.1$. However, Mooney's (1951) correlation:

$$\ln\frac{\mu_m}{\mu_\ell} = \frac{2.5\phi_s}{1-K\phi_s} \qquad (4)$$

was found to be applicable at times to ϕ_s as large as 0.5. The coefficient K evaluated from data usually varies from 1 to 1.5 for monodisperse systems.

It was found that the viscosity varied considerably for small temperature variations. The viscosity variation was approimately 3.8% per degree Fahrenheit. This strong effect of temperature on viscosity is supported in theory by the deGuzman-Andrade equation,

$$\frac{d\mu}{dt} = \frac{-ABe^{B/T}}{T^2}$$

$$\frac{d\mu}{dT} = -(B/T^2)\mu \qquad (5)$$

The magnitude of the temperature effect is proportional to the viscosity, μ, so that thicker material, such as recycle slurry at atmospheric saturated steam temperature should be much less sensitive to temperature change. Nevertheless, it is apparent that all experimental viscosity measurments with coal solutions will require very precise temperature control during the measurements.

Correlations

Development of a mathematical model and correlations to predict the viscosity behavior as a function of major intensive and extensive variables within the limits of commercial significance is very important. This section evaluates the work done by various investigators to correlate the viscosity data.

Correlations for Coal Liquid Fractions

Two methods of estimating the viscosity of coal liquid fractions were evaluated by Hwang, et al., (1980). The first one, a petroleum fraction liquid viscosity correlation developed by Abbott, et al. (1971), was essentially an extension of a method proposed by Watson, et al.(1935). Both correlations use the Watson characterization parameter, K_w, and the API

gravity as parameters to obtain the kinematic viscosity at 100 and 210°F. However, the new correlation was developed based on a large amount of experimental data for pure heavy components and crude fractions. The final equation for the kinematic viscosity had the form:

$$\log \nu = f_1(K_w, {}^{\circ}API) + f_2(K_w, {}^{\circ}API) \qquad (6)$$

The two functions of f_1 and f_2 and the values of the coefficients at 100 and 210°F are given by Abbott, et al. (1971). Viscosities at other temperatures were obtained from a modification of the Walther (1930) equation:

$$\log \log (\nu + E) = a + b \log T \qquad (7)$$

where E is a function of viscosity.

This correlation did not directly predict the effect of pressure on viscosity. It first calculated the kinematic viscosity for the petroleum fractions independent of pressure, and then introduced the effect of pressure only in the converson of kinematic to dynamic viscosity, through the effect of pressure on the liquid density. To obtain the mixture viscosities for systems containing petroleum fractions, the modified method introduced by Wright (1946) was used.

The second correlation used in the analysis was based on the application of corresponding states concepts to experimental pure component liquid viscosity data. It was developed by Abbott and Kaufmann (1970) by analyzing a large amount of experimental data. This correlation is applicable from the freezing point to the critical point and has the general form:

$$\ln \nu_r = \ln(\nu/\nu_c)$$
$$= A(\rho_r - 1) + B(\rho_r - 1)^{7/2} + \sum_{j=1}^{5} C_j \{\exp(\rho_r - 1)^{(j+1)/2} - 1\} \qquad (8)$$

The coefficients in this equation are functions of the acentric factor and hydrocarbon type; e.g. paraffins, olefins, aromatics. The critical kinematic viscosities required for converting the reduced kinematic viscosity were calculated from a straightforward extension of the correlation of Uhehara and Watson (1944):

$$\nu_c = 61.154 \times 10^{-4} \frac{T_c^{5/6}}{M^{1/2}} \left(\frac{RZ_c}{P_c}\right)^{1/3} \qquad (9)$$

A comparison of experimental and calculated viscosities for coal liquids is shown in Table III-5. It can be seen that neither the petroleum fraction nor the pure compenent correlations can directly predict the effect of pressure on viscosity. The values predicted by the petroleum-fraction correlations were appreciably higher than the experimental results at temperatures below 600°F. This disagreement was probably because of the fact that the correlations were based on petroleum fractions with °API's ranging from 10.6 to 54, and Kw's from 11.1 to 12.7. The coal liquids of interest had Kw's less than 11 and gravities less than 15 °API. For the measurement temperatures as high as 800-900°F, the absolute average deviation was 45% in the absence of hydrogen and 28% under a high pressure hydrogen atmosphere.

Although better results were obtained for the viscosity of hydrogen-free coal liquids when the coal liquid fractions were simulated as pure components rather than as petroleum fractions, the reverse was true for hydrogen-containing coal liquids. 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 hydrogen-containing coal liquids, calculations were also made by ignoring the hydrogen dissolved in the coal liquid. The results of those calculations are also shown in Table III-5, indicating that the pure-component correlation was markedly superior to the petroleum-fraction correlation.

Starling and coworkers (1980) have proposed a correlation based on a three-parameter corresponding states approach which is an extension of their work using a modified BWR equation of state. This correlation is very complex and requires a knowledge of the orientation parameter and the reduced density. Starling, and coworkers, have fit their correlation to the data of Hwang, et al. (1980) with average deviations of 13-24%.

Gray and Holder (1982) have described the evaluation of the Starling, et al, (1980) correlation to predict the viscosities of narrow boiling coal liquid fractions from the SRC-II process. In this analysis, separate correlations for the critical volume, the critical temperature and the orientation parameter were used. The experimental data used were obtained from 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 were needed in calculation of viscosities, the method of calculating densities was important. Two methods to calculate the densities were used. One was based on Starling's equation of state, and the other from a 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 correlations. The average absolute error for cuts boiling above 590 K was 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 gave more accurate densities.

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

$$\ln(\mu/\rho^{0.5}) = f_1 + \omega f_2 \qquad (10)$$

where:

$$f_1 = -5.180477 + 0.64578\ \alpha + 0.102428\ \alpha^2 \qquad (11)$$

$$f_2 = 0.49886\ \alpha + 2.35539\alpha^2 \qquad (12)$$

$$\text{and } \alpha = (1-T_r)/T_r \qquad (13)$$

The viscosity, μ is in mPa s; ρ is the density in kg/M^3 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.

In his earlier report, Gray (1981) has reported the use of the equation 1 attributed to Fulcher (1925), to fit the data for coal liquid fractions. This equation fit the data very well. However, this is no surprise since there are few degrees of freedom left when there are three constants and no more than six data points per fraction. The values of A, B, and C for each coal liquid fraction are summarized in Table 4. Horsak (1981), in a letter indicating corrections to the SRC-II Physical Properties Data Book, has recommended this correlation for the prediction of viscosities.

Correlation for SRC-II Recycle Slurry

In a letter to Antezana, Pitchford (1981) has reported correlations based on the analysis of the rheological behavior of recycle slurry. Multiple regression analysis of the data was perfomed using the Statistical Analysis System software. The viscosity (μ, cp) of samples with compositions near that recommended for the demonstration plant were correlated as a function of shear rate (γ, sec^{-1}) and temperature (T, ^oF). The correlations are:

$$\mu = B_o + B_1 \log_{10}(\gamma) + B_2/T + B_3/T^2 + B_4/T^3 + B_5\{\log(\gamma)/T\} + B_6\{\log_{10}(\gamma)/T\}^2;\ \gamma<1000\ sec^{-1},\ T<400^oF \quad (14)$$

$$\mu = B_o + B_1 \log_{10}(\gamma) + B_2/T + B_3/T^2,\ \gamma<1000\ sec^{-1},\ T>400^oF \quad (15)$$

$$\mu = B_o \exp\{B_1/T\};\ \gamma>1000\ sec^{-1},\ T> 350^oF \quad (16)$$

Values of B_i for equations 14, 15, and 16 are given in Tables III-6, III-7,and III-8 respectively. Because these correlations were developed with

a limited amount of data, it is difficult to estimate how accurately they can be extrapolated outside the range of the data. Also, the above equations will not accurately predict recycle slurry viscosities for samples whose composition varies significantly from that recommended for the demonstration plant. These correlations were further reviewed by Suzuki (1981) and it was found that these equations have only one function of the shear-rate when the temperature is fixed.

$\mu = 24.2976 - 2.5171 \log \gamma$ at $T = 450^{\circ}F$ (17)

$\mu = 20.0820 - 2.5171 \log \gamma$ at $T = 500^{\circ}F$ (18)

$\mu = 17.1397 - 2.5171 \log \gamma$ at $T = 550^{\circ}F$ (19)

$\mu = 15.0362 - 2.5171 \log \gamma$ at $T = 600^{\circ}F$ (20)

$\mu = 13.5037 - 2.5171 \log \gamma$ at $T = 650^{\circ}F$ (21)

$\mu = 12.3706 - 2.5171 \log \gamma$ at $T = 700^{\circ}F$ (22)

The results of these correlations and their comparison with the data in Data Book at various temperatures and shear rates are also presented by Suzuki.

Correlations for Process Solvent - SRC Mixtures and Feed Coal Slurry

The relationship between viscosity and the concentration of vacuum bottoms or SRC coal liquids was studied by Gulf R & D Company by using a Brookfield model HA viscometer and an on-line viscometer, respectively.

The Huggins equation for predicting the viscosity of dilute polymer solutions was found to provide a suitable fit of the data for Proess Solvent - SRC mixture. This equation has the following form:

$$\frac{1}{s} \ln \frac{\mu}{\mu_o} = \hat{\mu} + k'\hat{\mu}^2 s \qquad (23)$$

where: μ is the absolute viscosity of the solution

μo is the absolute viscosity of the pure solvent

s is the solute concentration

k' is a constant and,

$\hat{\mu}$ is the "intrinsic viscosity"

Rearrangement of this equation resulted in the following quadratic equation

$$\ln \mu = \ln \mu^{o} + \hat{\mu}s + k'\hat{\mu}^{2}s^{2} \qquad (24)$$

By applying polynomial regression to a data set comprised of viscosity measurements and SRC concentrations, a best fitting equation of the form:

$$y = a + bx + cx^{2} \qquad (25)$$

was obtained, where, y is the $\log_e$ of absolute viscosity at a constant temperature and x is the SRC concentration. Interpreting this by the Huggins equation, then, "a" is the $\log_e$ of the viscosity of the pure solvent and "b" is the intrinsic viscosity, μ. The constant k' can be determined as:

$$\frac{c}{b^{2}} = \frac{k'\hat{\mu}^{2}}{\hat{\mu}^{2}} = k' \qquad (26)$$

Use of the Huggins model in this case gave a good fit to the data. Also, the values of the constant a obtained from polynomial regression yield reasonable values for pure solvent viscosity. These observations lead to the conclusion that the solvent-low ash SRC system viscosity behaves in a manner quite similar to that of dilute polymer systems.

The relationship between shear rate and coal slurry apparent viscosity was studied using an on-line capillary tube viscometer using Blacksville No. 2 coal. A plot is given to show the relationship between measured apparent viscosity and shear rate. This plot indicates the coal-slurry behavior to be

non-Newtonian pseudoplastic. The following power law model describes the relationship between apparent viscosity and shear rate for pseudoplastics:

$$\mu = \overline{k}\ (\text{shear rate})^{n-1} \qquad (27)$$

$\overline{k}$ is the consistency index

n is the flow behavior index

and μ_A is the apparent viscosity.

From the data, empirical models were developed which related n and k to temperature, the concentration of coal in the feed slurry, and the concentration of SRC liquids and pyridine insolubles in the recycle slurry. These relationships are shown below:

$$n = 1.43393 \times 10^{8} C_c^{(1.0479)}\ C_{SR}^{(-7.7201)}\ C_{PI}^{-0.3974}\ \exp\left[-0.022938(T+460)\right]$$

$$k = 3.6376 \times 10^{-17} C_c^{(3.4014)}\ C_{SR}^{(-7.201)} C_{PI}^{(4.7827)}\ \exp^{[0.05667(T+460)-2.7]} \qquad (28)$$

where C_c is the feed slurry coal concentration (wt. fraction)

C_{SR} is the recycle slurry SRC concentration (wt. fraction)

C_{PI} is the recycle slurry PI concentration (wt. fraction)

T is the feed slurry temperature (^{o}F)

Summary and Recommendations

A detailed anlaysis of viscosity and its dependency on other parameters is very important for any coal liquefaction process. In order for the results to be numerically significant, they need to be broadened to include other coals and solvents.

The viscosity peak occurring as the coal goes into solution is by far the most significant characteristic of the thermophysical description in the design of a demonstration plant. It is also of great importance in developing an understanding of the chemistry of liquefaction. Therefore, viscosity mesurements need to be extended to include other coals and solvents. Further work needs to be done on developing a viscometer to extend to application to more concentrated slurries. To date, a capillary flow-meter appears to be most suitable instrument available for measurements.

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 tower bottoms increases with both the soak time and soak temperature. Also, the vacuum tower bottoms viscosity behaves as a pseudoplastic fluid with thixotropic behavior. Viscosity deceases with increasing shear rate at constant temperature and decreases with increasing temperature at constant shear rate. Since, as mentioned by Spearhac (1980), the viscosity of coal feed slurry depends largely on the coal particle size, it is necessary that this effect be studied further for other types of coals and liquefaction processes. To predict the viscosity of a mixture of coal liquids, the blending rule recommended by the API Technical Data Book is recommended.

$$\mu_m = \left(\sum_{i=1}^{n} x_i \mu_i^{1/3}\right)^3 \qquad (30)$$

where x_i is the mole fraction of the i^{th} component.

Based on the report by Gray (1981), the viscosity measurements for the coal liquid fractions agree with the data book information only at

temperatures below 250°F. The data appeared to be reasonably comparable to results published by Hwang et al. (1980). Current petroleum fraction viscosity conditions and pure compound conditions appear to have only marginal applicability to coal liquids. New correlations are badly needed to predict the viscosity behavior. Measurements are needed above 500°F to develop new correlations and to verify the extrapolations. Data in the vicinity of 800°F (coal liquefaction reactor temperature) will be the most useful.

Nomenclature

a,b	constants in equation 8
A,B,C	constants in equation 1
C_c	feed slurry coal concentration in equations 28 and 29
C_{PI}	recycle slurry pyridine insoluble concentration in equations 28 and 29
C_{SR}	recycle slurry SRC concentration in equations 28 and 29.
E	parameter defined in equation 7
K	coefficient in equation 4
K	constant in Mooney equation
K_w	Watson characterization factor
k′	constant in equation 24
$\overline{k}$	consistency index
M	molecular weight of the component
n	flow behavior index
P_c	critical pressure
R	gas constant
S	solute concentration
T	temperature
Tc	critical temperature
T_r	reduced temperature
x_i	mole fraction of component i
Z_c	critical compressibility factor

Greek Symbols

α	a parameter defined by equation 13
μ	viscosity
μ_A	apparent viscosity
μ_ℓ	liquid viscosity
μ_m	viscosity of the mixture
μ^o	absolute viscosity of pure solvent defined in equation 24
$\hat{\mu}$	intrinsic viscosity used in equation 23
ρ	density
ρ_r	reduced density
ν	kinematic viscosity
ν_c	kinematic viscosity at critical point
ν_r	reduced kinematic viscosity
γ	shear rate
ϕ_s	volume fraction of solids
ω	acentric factor

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TABLE III-1
VACUUM BOTTOMS MATERIAL SELECTED AND
VISCOSITY CHARACTERIZATION

Property	Sample B	Sample C	Sample D	Sample E	Sample F
Fusion Point, ^{o}F	350	390	280	410	350
% Ash	26.6	25.9	24.7	33.7	31.2
% Pyridine Insolubles	37.8	42.3	36.0	47.7	45.9
% Insoluble Organic Matter	11.2	14.8	11.3	14.0	14.7

TABLE III-2

RECYCLE SLURRY COMPOSITION BY WT FRACTION

Component	Composition Recycle Slurry	Recommended Recycle Slurry Composition For Demo Plant Support
<150	0.04	0.04
150-250	0.05	0.05
250-350	0.25	0.25
350-450	1.31	1.31
450-550	4.90	4.90
550-650	8.01	8.01
650-750	8.62	8.62
750-850	8.72	7.42
850-950		1.30
>900 SRC	35.74	39.17
Ash	22.71	21.38
IOM	9.65	7.55
	100.00%	100.00%

TABLE III-3

Composition Atm Boiling Point °F	Recycle Slurry Recommended Composition Weight %	Recycle Slurry Blend No. 2 Cushman Vacuum Distillation Weight %	Recycle Slurry Blend No. 2A Cushman Vacuum Distillation Weight %
Initial Boiling Point	Approx. 400°F	330°F	416°F
IBP-450	1.65	3.7	1.7
450-550	4.90	5.1	5.0
550-650	8.01	9.1	9.2
650-750	8.62	7.7	9.5
750-850	7.42	5.9	6.2
850-900	1.30	0.0	0.6
End Point	900°F	836°F	857°F
SRC	39.17	35.2	35.9
Ash	21.38	22.9	21.1
IOM	7.55	10.4	10.8
Vacuum Bottoms	68.1	68.5	67.8

TABLE III-3 continued

Composition Atm Boiling Point °F	Coal-Free Feed Slurry Recommended Composition Weight %	Coal-Free Feed Slurry Blend No. 3 Cushman Vacuum Distillation Weight %	Coal-Free Feed Slurry Blend No. 3A Cushman Vacuum Distillation Weight %
Initial Boiling Point	Approx. 350°F	370°F	352°F
IBP-450°F	3.89	3-9	4.5
450-550°F	11.54	14.2	13.5
550-650°F	13.84	14.9	15.3
650-750°F	11.19	7.0	9.3
750-850°F	7.87	5.7	7.6
850-900°F	1.13	3.5	1.0
End Point	900°F	918°F	865°F
SRC	29.10	27.9	25.4
Ash	15.84	16.4	16.1
IOM	5.60	6.5	7.3
Vacuum Bottoms	50.53	50.8	48.8

TABLE III-4

Coefficients for SRC-II Distillate Cut
Viscosity Correlations

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

where μ = centipoise

T = absolute temperature, $^{\circ}R$

Mid Boiling Point, $^{\circ}F$	A	B	C
125	-13.51667	30445.69	1952.39
175	-2.80795	628.53	-216.227
225	-5.49604	3965.64	262.456
275	-5.35386	3730.97	208.823
325	-4.32194	2080.30	-89.248
375	-3.73875	1772.63	-168.774
425	-3.43816	1529.74	-225.981
475	-3.64619	1807.16	-205.782
525	-3.56296	1735.74	-223.440
575	-3.11116	1396.64	-292.861
625	-3.01463	1462.83	-319.427
675	-3.19997	1633.81	-333.686
725	-2.9855	1426.34	-388.232
775	-3.14490	1501.65	-410.617
825	-2.75847	1211.96	-466.561
875	-2.74962	1199.41	-492.598
925	-2.65923	1147.51	-518.680
975	-2.81044	1206.37	-536.101

TABLE III-5
VISCOSITY OF COAL LIQUIDS: CORRELATION DEVIATIONS

	Petroleum-Fraction Correlations				Pure-Component Correlations			
	Dev. (cp)		% Dev.		Dev. (cp)		% Dev.	
	Ave.	Bias	Ave	Bias	Ave	Bias	Ave	Bias
Coal Liquids Without Hydrogen (70 data points)	0.610	+0.601	45.4	+41.1	0.201	-0.172	14.1	-1.8
Coal Liquids With Hydrogen (20 data points)	0.715 (0.828)	+0.696 (+0.827)	23.3 (35.4)	+26.9 (+35.1)	0.598 (0.422)	-0.598 (-0.419)	40.0 (23.4)	-40.0 (-20.8)
Total (90 data points)	0.633 (0.658)	+0.622 (+0.651)	41.6)43.2)	+38.0 (+39.8)	0.289 (0.205)	-0.267 (-0.227)	19.9 (16.2)	-10.2 (-6.0)

Values in parentheses are the results when hydrogen is ignored in the calculations.

TABLE III-6

Values of B_i for Equation (14)

i	B_i
0	-2375.0
1	224.24
2	2.3277×10^{6}
3	-7.4419×10^{8}
4	8.9642×10^{10}
5	-1.4158×10^{6}
6	3.9091×10^{6}

TABLE III-7

Values of B_i for Equation (15)

i	B_i
0	12.802
1	-2.5171
2	-10157.
3	6.8985×10^{6}

TABLE III-8

Values of B_i for Equation (16)

i	B_i
0	0.86879
1	1323.7

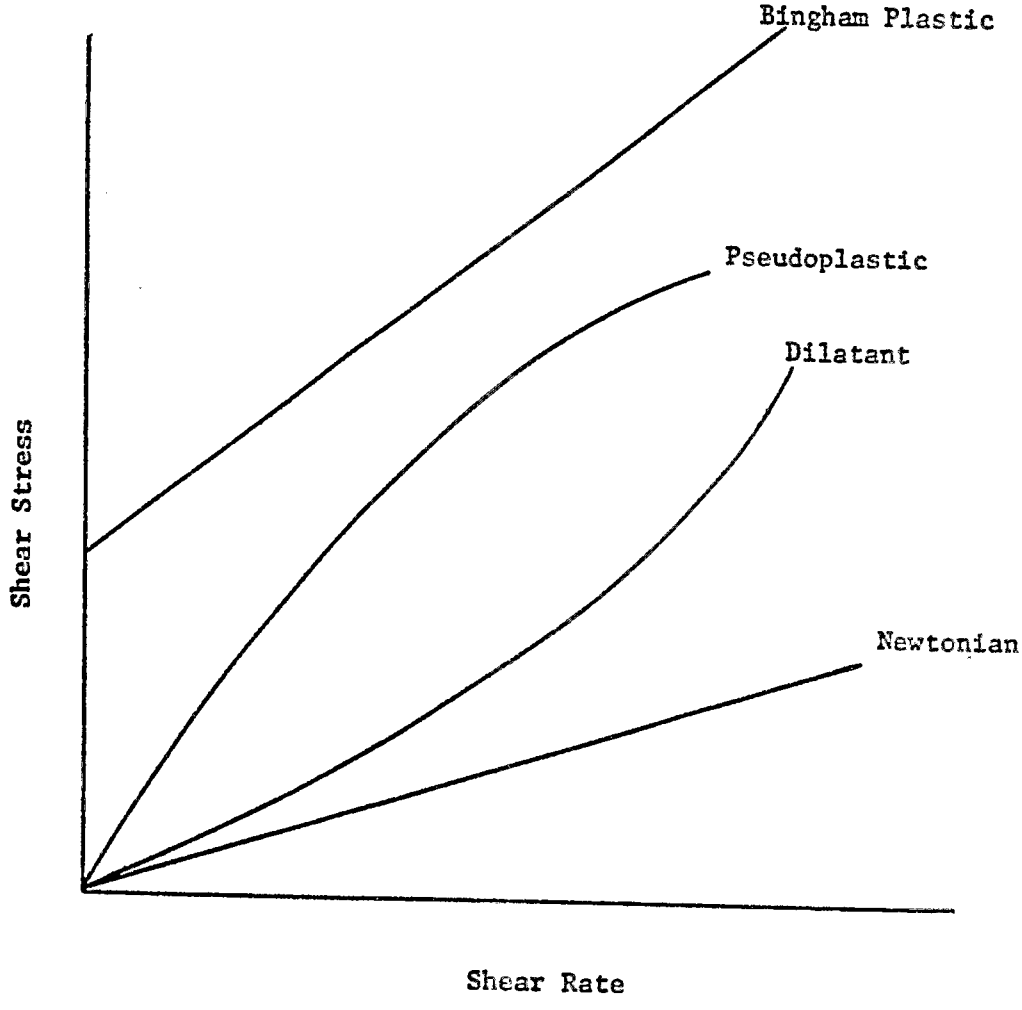

Figure III-1: Shear Diagrams for Various Fluids

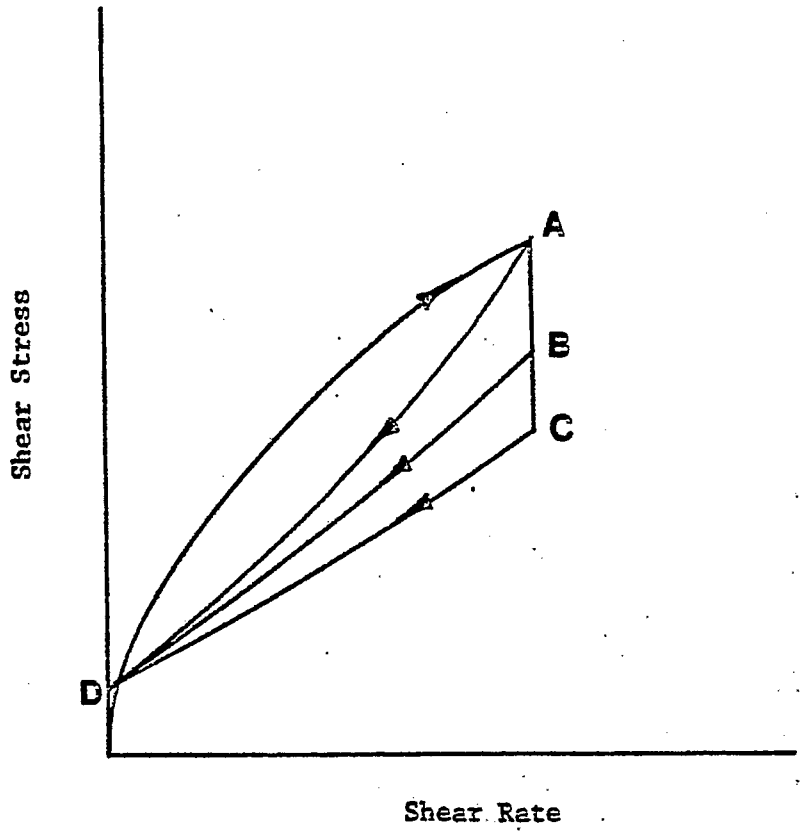

Figure III-2: Shear Diagram for Thixotropic Fluid

The area within loop DAD is an indication of the amount of thixotropy. If the shear rate is held constant after point A is reached on the up curve, the shear stress will decrease along path AB until point C is reached, beyond which no further breakdown can occur for that shear rate. If shear rate is then decreased, the down curve CD is then followed. Any number of intermediate down curves, such as BD, are possible.

THERMAL CONDUCTIVITY OF COAL LIQUIDS AND SLURRIES

Introduction

For liquids flowing through tubes, the rate of heat transfer depends on the thermal conductivity. In order to model heat exchangers and other process equipment and be able to design them for maximum efficiency, it is necessary to know the thermal conductivity of the liquid. The way in which the thermal conductivity changes with temperature in coal-solvent slurries is also important. In general, the designer will need the thermal conductivity of the coal feed slurry, recycle slurry, vacuum bottoms, and the coal liquid fractions. The property "thermal conductivity" is discussed in this report.

Measurement Technique

A number of researchers including Gray (1981) and Droege et al. (1982) have reported the successful application of a transient technique for the measurement of thermal conductivity in liquids. This method is based on the principle of unsteady state heat conduction of a continuous line source in an infinite medium. A thin straight platinum wire is heated electrically while immersed in the pressurized liquid sample, and after an initial period, the temperature-time curve can be used to calculate the termal conductivity. Droege et al. have identified the following advantages of this technique:

- small sample volume required for measurements
- fast response, minimizing setting and coking problems
- a relatively simple design compared with steady-state techniques.

Even though the transient technique can be designed to eliminate many of the problems associated with steady state techniques, new sets of difficulties must be dealt with such as the necessity to measure transient temperature and heat flux data, and more complex data reduction.

Summary of Available Data

There are no thermal conductivity data available on coal liquid fractions except those of Gray (1981) and Droege et al. (1982). In estimating thermal conductivity for petroleum fractions, Perry and Chilton (1963) suggest a single value of 0.079 BTU/hr ft. ^{o}F at 30^{o}C or the following equation at other temperatures:

$$k = \frac{0.0677}{SG} [1 - 0.003(T-32)] \qquad (1)$$

where k is in BTU/hr ft ^{o}F, SG is specific gravity at 60^{o}F/60^{o}F and T is in ^{o}F. The single value is thought to be accurate to about 13%, while equation 1 gave an absolute average deviation of 12% and a maximum error of 39% for the ranges $0.78 < SG < 0.95$ and $32^{o}F < T < 392^{o}F$. Equation 1 predicts that thermal conductivity decreases as the specific gravity increases. This fact is also shown on the thermal conductivity graph in the SRC-II Physical Properties Data Book (1980) in which parametric lines are shown for various API gravities. This figure, taken from Kern (1950), is valid for pressures less than 500 psia. In order to get the thermal conductivity values at higher pressures, the following relationship was used.

$$k_2 = k_1 \left(\frac{C_2}{C_1}\right) \qquad (2)$$

where k_2 = thermal conductivity at desired temperature and elevated pressure (> 500 psia)

k_1 = thermal conductivity at desired temperature obtained from the figure from Kern (1950).

C_1, C_2 = conductivity factors corresponding to reduced temperature and pressure conditions.

As mentioned by Gray (1981), the API Technical Data Book Figure 12A3.1 gives a single line graphical correlation of thermal conductivity versus temperature for undefined liquid hydrocarbon mixtures based on data from several sources. An equation for this correlation is

$$k = 0.07725 - 4.542 \times 10^{-5} T \qquad (3)$$

where T is in ^{o}F and $0^{o}F < T < 600^{o}F$. The API Data Book Figure 12A4.1 is used to correct for the effect of pressure. Starling et al. (1980) have derived a general thermal conductivity equation based on corresponding states principles and a large data bank of pure compounds found in coal liquids.

Gray (1981) has reported the thermal conductivity measurements performed on eight coal liquid fractions and two coal liquid slurry samples at tempratures to $450^{o}F$. Pressure was held constant at 800 psig. These data are shown in Figure III-3. The thermal conductivities of the eight coal liquid fractions exhibited unusual trends and were generally not in agreement with the petroleum fraction correlations. Thermal conductivities decreased with increasing temperature as expected, however thermal conductivity increased with increasing specific gravity except for fraction 6, 8 and 10 which gave results that overlapped somewhat. These fractions are near the normal boiling point region where a plateau occurs in the specific gravity versus boiling point curve. Therefore, it is not surprising that these particular fractions overlap. The temperature coefficients or slopes of the correlating lines also showed interesting behavior. In progressing from cuts 2 to 12 (normal boiling point increasing from 211 to $711^{o}F$) the temperature coefficients decreased and then began to increase for cuts 16 and 18. The relationship between thermal

conductivity and coal liquid fraction boiling point (50 wt. % off temperature) showed that the thermal conductivity increased with fraction boiling point (Fig. III-4) and hence with increasing specific gravities. This is just the opposite of the prediction of equation 1 and the graphical correlation in the SRC-II Data Book. According to Stephenson (1981), this coal liquid behavior is not unreasonable since the lightest cuts are mostly saturated (naphthenic in nature) while the heavier cuts are strongly aromatic. The more polar aromatic molecules are expected to have higher thermal conductivities.

Except for cuts 2 and 4, it was not easy to extrapolate the thermal conductivity data to the critical point. However, a plot of thermal conductivity versus reduced temperature showed that most of the data were grouped in a rather narrow band that extended over the range $0.33 < T_r < 0.9$. Gray has suggested that use of a plot of this type should allow reasonable extrapolation to $T_r = 0.9$ with an error of 15% or less.

Gray has also reported the thermal conductivity measurements performed on recycle slurry and coal feed slurry samples taken from the Process Development Unit P-99 situated at Harmerville, Pennsylvania. Despite their different compositions, both slurries gave essentially the same results. An approximate but somewhat conservative fit of these data is given by Stephenson (1981) as

$$k = 0.1082 - 0.36 \times 10^{-4} \times T \qquad (4)$$

where k is in BTU/hr ft ^{o}F and T is in ^{o}F.

Since the data were measured at 800 psig, it was necessary to make corrections for values at other pressures. It is suggested by Stephenson that since the slurry thermal conductivity is apparently dominated by the liquid

(or continuous) phase, it is recommended to use the same correction factor method as for the coal liquid distillates. Attempts to measure the thermal conductivity of vacuum bottoms and atomospheric flash tower bottoms were not successful because of sampling difficulties and difficutly in obtaining reproducible data. An approximate value for the vacuum tower bottoms slurry can be obtained from the following formula given by Tareef (1940)

$$k_{SL} = k_L \left[\frac{2\,k_L + k_S - 2f\,(k_L - k_S)}{2\,k_L + k_S + f\,(k_L - k_S)}\right] \qquad (5)$$

where k_L = thermal conductivity of continuous phase·

k_S = thermal conductivity of solid phase

f = volume fraction of solids

k_{SL} = thermal conductivity of a coal slurry

For mixtures of the distillate fractions, the mole fraction weighting method described in the API Technical Data Book (1976) is recommended since the data indicate that thermal conductivity at a given temperature is generally proportional to the molecular weight.

Droege et al. (1982) have used the transient line-source technique for the measurement of thermal conductivity. Data were measured for a recycle solvent from the Wilsonville SRC-I plant and KY-9 coal in the temperature range of 300-600 K. The operation of the measurement device was especially satisfactory in the high-viscosity gel region, where convection could not occur. Moreover, this is just the region in which the data are most needed.

The measurement technique was verified for toluene in the temperature range of 250 to 400 K which indicated the data to be within ± 1%. Measurements were carried out at 13.8 MPa for mixtures with various solvent-

to-coal ratio (1.6, 2.0 and 3.0 respectively). In each case, the results indicated a gradual decrease in thermal conductivity from the room temperature as the temperature increased. The measurements dropped more rapidly in the temperature range of gel formation (about 650 K). Beyond this point, the measurements remained constant as the maximum temperature was reached (about 700 K). At 700 K and above, a significant amount of solids formation occurred in the mixture and thermal conductivity data could not be measured. Data for the coal solvent used to prepare the liquid/coal mixture indicated a nearly linear drop in conductivity from room temperature up to 700 K.

Correlations

Gray and Holder (1982) have described the correlations for the thermal conductivities of several narrow boiling range coal liquids. Data measured by Gray (1981) for coal liquids with 50 wt % off temperatures (boiling point) of 372 K to 750 K (211°F to 890°F) were used in these correlations. The correlations considered included those of Riedel (1965) and Missenard (1965). The following modification of the Riedel correlation proved most successful.

$$k = 0.0518675 + 0.105376\ (1-T_r)^{2/3} \qquad (6)$$

where k is the thermal conductivty (w/mK) and T_r is the reduced temperature obtained from the correlation of Starling et al. (1980). This correlation reproduced the experimental data with an average absolute deviation* (AAD) of 2.84%, but it was unsatisfactory in that the error was not uniformly

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* $\%\ AAD = \frac{100}{N} \sum_{1}^{N} \left| \frac{Measured - Calculated}{Calculated} \right|$

distributed over all of the cuts. Cut 6 produced the worst results with an AAD of 6.61% and with one point having an error of 9.9%. This was attributed to the fact that cut 6 contained the highest oxygen content, and the greatest ability to dissolve the water. It appeared that the increased oxygen content was indicative of an increased polarity and hence an increased thermal conductivity.

Because of the systematic deviation produced by the above correlation, improved versions which related the thermal conductivity to the oxygen content were tested. This proved successful resulting in the following correlation for thermal conductivty

$$k = 0.03530133 + 0.01493397\ (1+X_o)^{2.7}\ [1 + 20/3\ (1-T_r)^{2/3}] \quad (7)$$

where X_o is the weight fraction of oxygen in the coal liquid cut. This correlation reduced the overall average absolute deviation to 1.63% and a bias* of 0.03%. This correlation was roughly as good as the correlation which did not take the oxygen content into account. The errors were fairly uniformly distributed overall cuts and were quite small. However, in order to use this correlation, the oxygen content of the cut must be known. In order to remove this difficulty, the term $(1+X_o)$ in the above correlation was replaced by a term containing only the boiling point. The following correlation was obtained.

$$k = 0.03159873 + 0.01639452\ (1+Q)\ [1+ (20/3)\ (1-T_r)^{2/3}] \quad (8)$$

---

* $\%\ \text{bias} = \frac{100}{N} \sum_{1}^{N} \frac{(\text{Measured} - \text{Calculated})}{\text{Calculated}}$

where

$$Q = \frac{T_{bf}}{[T_{bf} + (T_{bf} - 380)^2]}; \quad T_{bf} = 1.8\ T_b - 459.67 \qquad (9)$$

where the boiling point, T_{bf}, is in ^{o}F.

This correlation predicted the results with an AARD of 1.77% and a bias of 0.03%. The accuracies of the three correlations are shown in Table III-9. The present authors would like to point out that the correlations proposed by Gray and Holder have been validated only for the SRC-II coal liquid fractions and within the temperature range of measurement. Whether they are applicable to coal liquid fractions from other liquefaction processes, for other coal types, and for temperatures outside the range of the measurements is unknown. The term involving the oxygen concentration is very empirical, and even though its incorporation gave better fit to the data, its validity under different sets of conditions is questionable.

Summary and Recommendations

The thermal conductivity of coal liquid samples decreases with increasing temperature and with an increase in fraction boiling point. The effect of specific gravity is uncertain. The SRC-II Data Book predicts the thermal conductivity will decrease with an increase in specific gravity. However, Gray (1981) has reported that the thermal conductivity increased with increasing specific gravity except for cuts 6, 8 and 10 which gave results that overlapped somewhat. The temperature coefficients or slopes of the correlating lines also show interesting behavior and particle size still needs to be investigated. There are virtually no data available on vacuum bottoms. As reported by Gray and Holder (1982), data for cut no. 6 with the

highest oxygen content, was difficult to correlate. However, equations 7 and 8 can be used with sufficient confidence to predict the data for coal liquid fractions. The data for coal liquid fractions showed that most of the data were grouped in a rather narrow band that extended over the range $0.33 < T_r < 0.9$. Gray has suggested the use of such a plot for reasonable extrapolation to $T_r = 0.9$ with an error of 15% or less.

Nomenclature

C_1, C_2	correction factors defined in equation 2.
f	volume fraction of solids
k	thermal conductivity
k_L	thermal conductivity of continuous phase
k_S	thermal conductivity of solids
k_{SL}	thermal conductivity of the slurry
Q	a factor defined in equation 9.
SG	specific gravity
T	temperature
T_b	boiling point
T_{bf}	boiling point defined in equation 9
T_r	reduced temperature
X_o	weight fraction of oxygen in the coal liquid cut.

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Table III-9

Accuracy of Various Correlations to Predict the Thermal Conductivity

(Adapted from Gray and Holder, 1982)

Equation	AARD (%)	Cut Maximum Bias (%)	Point Maximum AARD (%)	AARD (%)
6	2.84	-2.43	6.61	9.86
7	1.63	0.03	2.64	5.26
8	1.77	0.03	2.94	5.64

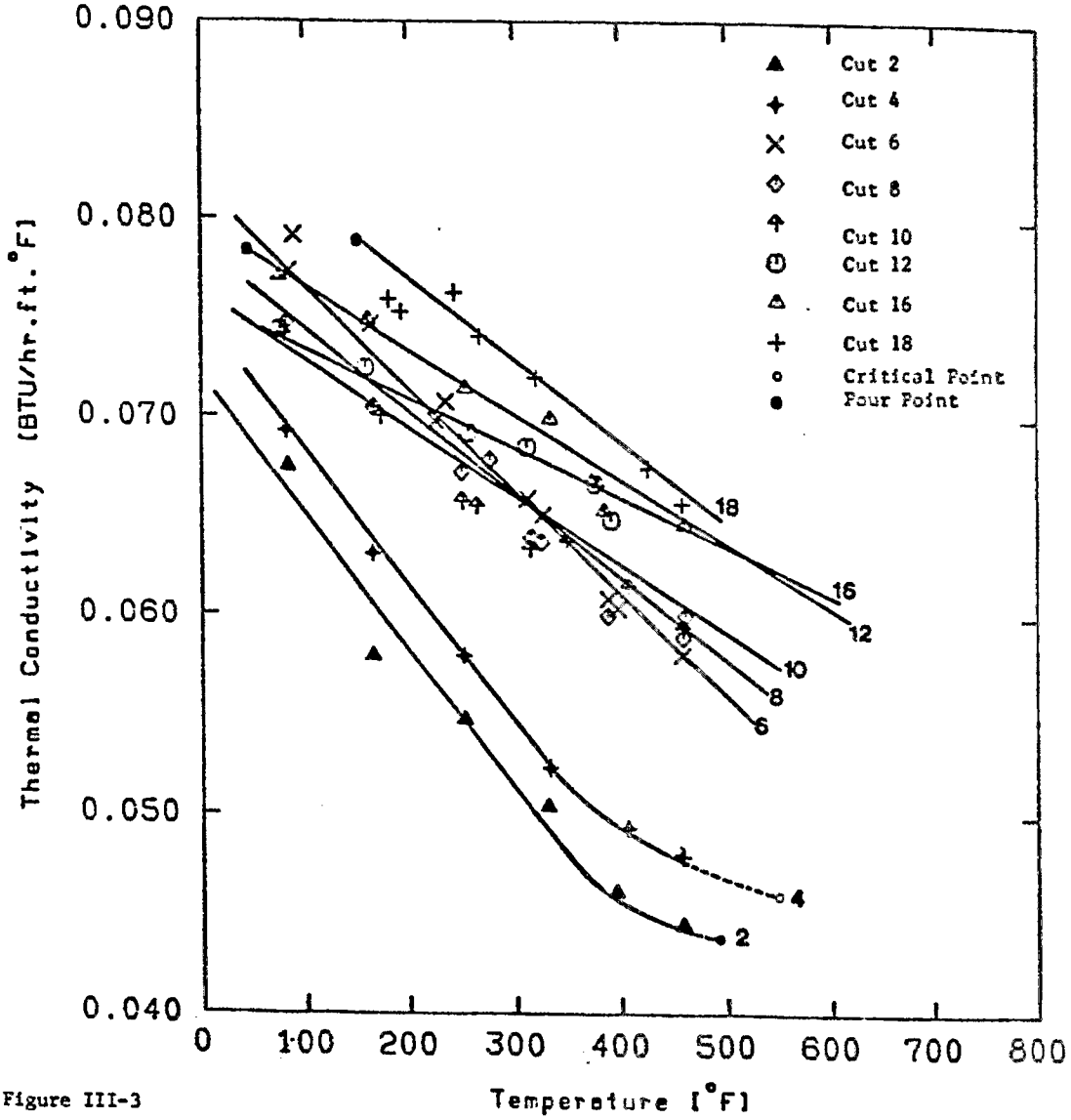

Figure III-3

Thermal Conductivity versus Temperature for Coal Liquid Fractions

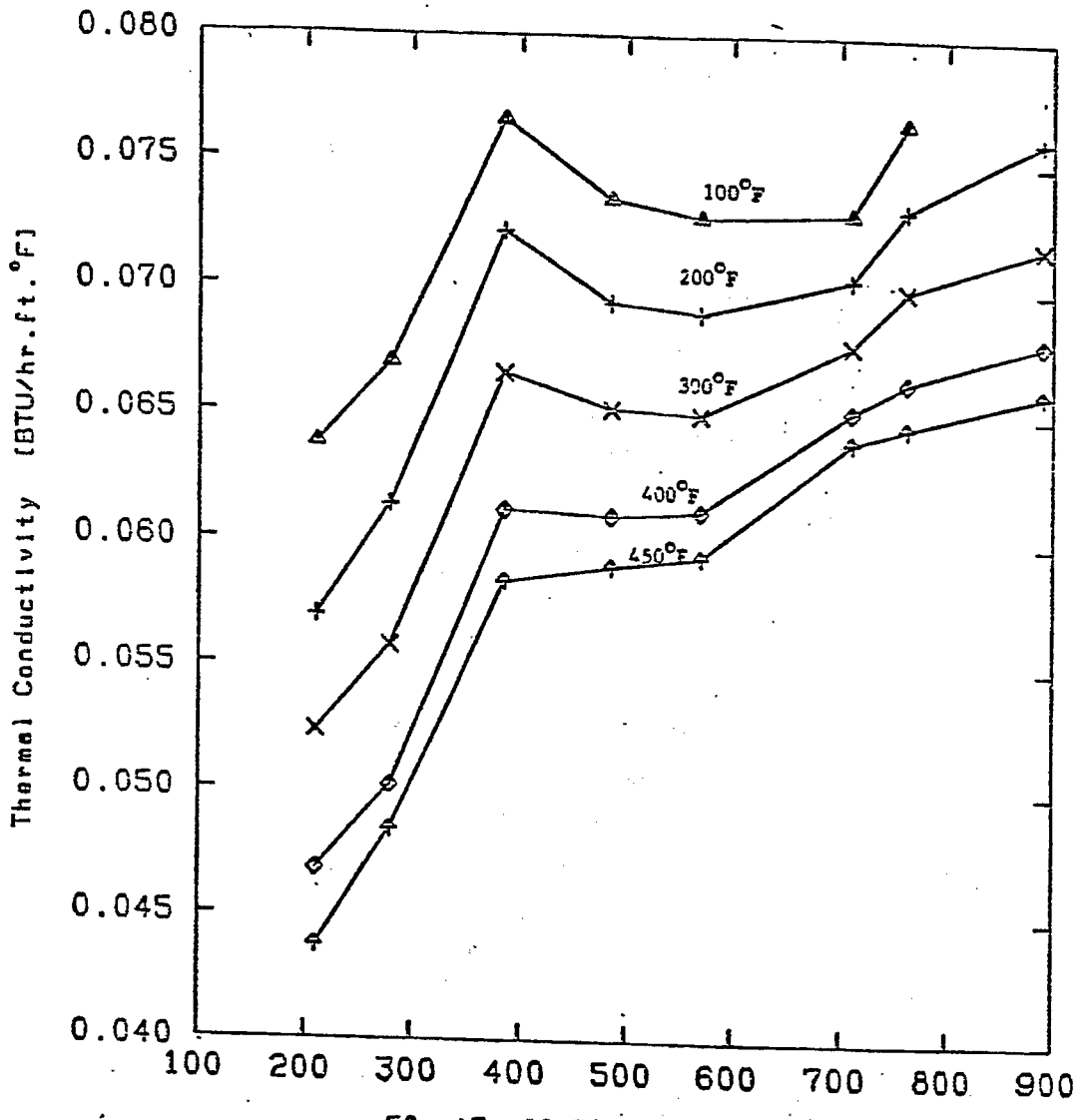

Figure III-4
Thermal Conductivity Versus Boiling Point for Coal Liquid Fractions

VAPOR PRESSURE OF COAL LIQUIDS

Introduction

Vapor pressure is the pressure of the vapor phase of a substance which is in equilibrium with the liquid phase of that substance at a specified temperature. The term is commonly used for pure substances, but it can also be applied to a mixture of liquids. For coal liquids, the composition of the vapor and liquid phases are functions both of temperature and the equilibrium pressure. Therefore, for these mixtures, the composition effect must be taken into account, either by holding liquid, vapor or overall composition constant or by focussing attention on a portion of liquid mixture which is sufficiently close boiling such that the composition changes with temperature have a negligible effect on pressure.

The SRC-II processing of coal into distillate products involves conversion and separation steps that operate at high temperatures (733 K) and pressure (to 13.9 MPa). The design and scale-up of any coal liquefaction plant requires adequate knowledge of the physical, chemical and thermodynamic properties of coal liquids at the reaction conditions. The available data in the literature on petroleum fractions can be applied to predict properties of coal liquids with caution primarily because the information on the petroleum fractions is not available at the temperatures encountered in coal liquefaction reactors. In addition, the coal derived liquids are primarily composed of aromatic and hetercyclic compounds while the petroleum fractions are primarily composed of straight and branched chain aliphatic compounds.

Coal derived liquids are a mixture of many hydrocarbons and usually boil over wide ranges of temperatures. One way to overcome this problem is to characterize the coal liquid fraction as pseudocomponents and identify these peudocomponents by some thermodynamic characterization parameters (e.g. normal boiling point and specific gravity) which are relatively easier to determine

experimentally. Based on these characterization parameters other important thermodynamic properties like critical temperature, critical pressure, and acentric factor can be estimated from available correlations. This information can then later be used to predict the vapor-liquid equilibrium data. Methods for performing these calculations and predicting the vapor pressures from the characertization parameters and their comparisons with the experimentally determined values are discussed in detail in the next section.

Estimation of Critical Temperature and Pressure

An important goal in the study of the thermodynamic and physical properties of coal liquids is the development of a model which allows many properties to be estimated using a minimum number of characterization parameters, which can be easily determined experimentally. Such models have been developed by Wilson et al. (1981) and Starling et al. (1980) and their applicability to coal liquids has been discussed by Gray and Holder (1982). There are a number of correlations available, both empirical and semi-empirical, which use easily measurable properties, namely, normal boiling point (BP), specific gravity (SG) and molecular weight (MW) to predict the critical pressure (P_c) and critical temperature (T_c). These critical properties, in turn, are used by other correlations to predict the vapor pressure of coal liquids. Some of these correlations were critically reviewed by the present authors to examine their applicability to coal liquids and they are discussed below.

Critical Temperature

Eight correlations were selected for this study (Table III-10). BP, SG and MW data were taken from Gray and Holder (1982). As expected, T_c increases with increasing boiling point of the liquids and this is shown in Table III-11 and Figure III-5. Two experimental data points are available and they are shown in Figure III-5. Depending upon the complexity of the correlations and

accuracy of the basic physical property data, we can see that the maximum deviation among the correlations is within 25% at lower temperatures (T_b < 500 K) and the deviation increases with increasing boiling point of the liquids. While the modified Guldberg model has a tendency to overpredict, Watson's correlation has a tendency to underpredict at all temperatures. The two experimental data points seem to fit very well by the Roess, Nokay, ASPEN and Kessler-Lee correlations. Some more data at higher temperatures are needed to find the best correlation applicable over the whole temperature range of coal liquids.

Critical Pressure

Five correlations, namely the Kessler-Lee, Penn-State, Mathur, Cavett and ASPEN correlations have been selected to check their applicability to coal liquids. They are shown in Tables III-12 and III-13 and Figure III-6. The critical pressure decreases with increasing boiling point and deviations among the correlations are high at low temperatures and decreases with increasing boiling point of the liquid. The two experimental data points available are shown in Figure III-6 and one of them falls directly on Mathur's correlation, which is the simplest and easy to use. The ASPEN correlation seems to overpredict critical pressures more than the rest of the correlations over the whole temperature range. Except for Mathur's, the other correlations seem to show a hump at approximately 450 K and 625 K, which is believed to be due to inaccuracy of measurement of the basic data, i.e., BP, SG or MW. In general, the Kessler-Lee, Penn-State and Cavett's correlations seem to be close to each other and predict the experimental data points relatively well.

Experimental Determination of Vapor Pressure of Coal Liquids

The experimental data reported by Gray and Holder (1982) were measured by the Wilco Research Co. and details of experimental procedure utilized to

calculate the vapor pressure of the various cuts of the coal liquids is presented in Gray (1981).

Correlations for Estimating the Vapor Pressure of Coal Liquefaction Products

A number of correlations are available to predict the vapor pressure of a liquid, which, however, were developed primarily for petroleum derived fluids and are particularly suitable for paraffinic compounds. An attempt was made in this report to review the suitability of these available correlations for predicting the vapor pressure of coal liquids.

Gray and Holder (1982) applied two different methods for correlating the vapor pressure data of coal liquids - Starling et al. (1980) and Wilson et al. (1981) and their work is described in detail by Gray and Holder (1982). Besides these we have used three other, namely the linear, Riedel and Mobil correlations to compare the available methods for the estimation of vapor pressure of coal liquids. For the purpose of comparison, we have calculated an "Absolute Average Deviation (AAD%)" for the whole set of data and it is defined as follows:

$$\text{Absolute Average Deviation} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{(\text{Measured} - \text{Calculated})}{\text{Measured}} \right| \times 100$$

a) Linear Correlation If only the normal boiling point and the critical temperature and pressure are known, a linear two-point plot of ln P^o against $1/T_r$ is often sufficiently accurate (Perry and Chilton, 1973). Based on this, the following equation was derived:

$$P^o = P_c \exp\left[-\ln\left(\frac{P_c}{P_b}\right)\left(\frac{T-T_c}{BP-T_c}\right)\left(\frac{BP}{T}\right)\right]$$

P^o = Vapor Pressure (kPa)

P_c = Critical Pressure (kPa)

P_b = Vapor Pressure at Normal Boiling Point (kPa)

T = Temperature (K)

T_c = Critical Temperature (K)

BP = Normal Boiling Point (K)

b) Riedel's Correlation (Perry and Chilton, 1973)

The vapor pressure of coal liquids was also predicted by Riedel's (1954) analytical correlation and is given by:

$$\log \left(\frac{P_c}{P^o}\right) = 0.118\ B - 7 \log T_r + (\alpha_c - 7)\ (0.0364B - \log_{10} T_r)$$

where $B = 36/T_r - 35 - (T_r)^6 + 42 \ln T_r$

where both P_c and P^o are in kPa

The parameter α_c (Riedel Factor) is defined by:

$$\alpha_c = \frac{d \ln (P_r^{\ o})}{d \ln (T_r)}$$

where $P_r^{\ o}$ = Reduced vapor pressure

α_c may calculated from the following equation

$$\alpha_c = 5.808 + 4.93\ \omega$$

where $P_r^{\ o}$ = Reduced Vapor Pressure

where ω is the acentric factor, which usually varies from 0 - 0.3 and is defined by

$$\omega = - \log P^o \text{ (at } T_r = 0.7) - 1.0$$

It may be estimated within ± 5% by the following expression:

$$\omega = \frac{3}{7}\left[\frac{\log P_c}{(T_c/BP) - 1}\right] - 1$$

where P_c is in atmosphere absolute.

c) Mobil Vapor Pressure Equation (Kessler and Lee, 1976)

$$\ln P_r^o = 5.92714 - 6.09648/T_r - 1.28662 \ln T_r + 0.169347\, T_r^6 + \omega\,(15.2518 - 15.6875/T_r - 13.4721 \ln T_r + 0.43577\, T_r^6)$$

where P_r^o = reduced vapor pressure

T_r^o = reduced temperature

ω = acentric factor

d) SWAP (Smith, 1976)

$$\ln \tilde{P} = A + B/\tilde{T} + C/\tilde{T}^2$$

where $\tilde{P} = P^o/P^*$, $\tilde{T} = T/T^*$, P^o = vapor pressure

P^* = characteristic pressure,

T^* = characteristic temperature

The coefficients A, B, and C are functions of molecular flexibity, c/n

$$c/n = 0.167 + 1.022/n - 0.189/n^2$$

$c/n = 1$, when $n = 1$

$c/n \to 0.167$ as $n \to \infty$

$$A, B, \text{ or } C = (1/\rho) \ln [(DX^E)^r + (FX^G)^\rho]$$

where $X = (c/n - 0.167)^{-1}$

ρ, D, E, F, G are coefficients. Correction functions for c/n and P^* are applied depending on what fractions of carbon atoms in the molecule are part of an aromatic ring, napthenic ring or terminal branches.

e) Exxon Maxwell-Bonnell (Maxwell and Bonnell, 1957)

$$\log P^o = \frac{A\,X - B}{C\,X - D}$$

$$X = \frac{T_b/T - 0.00286\,T_b}{748.1 - 0.2145\,T_b}$$

T_b = normal boiling point corrected to $K_w = 12$

A, B, C, D are coefficients

K_w = Watson Characterization Factor

f) Curl-Pitzer (Pitzer, 1955)

$$\log P_r^o = \log P_r^{o(o)} + \omega \log P_r^{o(1)}$$

$$\log P_r^{o(0)} = C - 1.192\,B$$

$$C = 7 \log T_r - 0.118\,A$$

$$A = 36/T_r - 35 - T_r^6 + 96.73 \log T_r$$

$$B = \log T_r - 0.0364A$$

$$\log P_r^{o(1)} = 4.93\,B$$

g) Wilson et al. (1981)

$$\ln Pr^o = A - B/T_r + \ln T_r + D\,T_r^6$$

$A = 5.671485 + 12.43960\omega$

$B = 5.809839 + 12.75591\omega$

$C = -0.867513 - 9.654169\omega$

$D = 0.1383536 + 0.316367\omega$

T_r = reduced temperature

ω = accentric factor

Discussion

We have compared five different correlations for calculating the vapor pressure of coal derived liquids-namely, the Linear, Riedel, Mobil, Starling and Wilson correlations. The rest of the correlations (Newmann, 1975) are compiled here for the sake of completeness. Parameters or data needed for these correlations were not available at present to be compared with others. Out of these five, the last two, namely Starling and Wilson, were used by Gray and Holder (1982) and we have taken the calculated data from their report for the purpose of comparison. The critical properties needed for vapor pressure calculations were again taken from Gray and Holder's report. The experimental and calculated vapor pressure data for twelve different cuts of coal liquids are given in Table III-14 and Figures III-7-III-18. From this Table and these Figures we can see that all the correlations used fit the experimental data rather closely. However, for lower cuts of liquids, namely Heart Cut 4HC, these correlations differ mainly in the lower and higher end of the curves and best matching is observed in the range of 400-450 K. As we go to higher boiling cuts, this region of overlap moves to higher temperatures and for Heart Cut 18 HC-B, this moves to 700-750K and for Heart Cut 19HC-A, we do not observe any region of overlap at all.

This fact is more clearly shown in the % relative deviation plots (Figures III-19-III-22) defined as:

$$\% \text{ relative deviation} = \frac{\text{calculated-expeirmental}}{\text{experimental}} \times 100$$

From these plots we can see that the Starling correlation gives the best fit of experimental data, while the linear correlation gives the worst fit. The Mobil, Riedel and Wilson correlations fall in between and all three of them give comparable fits. For any particular cut of liquid, the linear correlation strongly overpredicts the experimental data (~ 30%), a result which is much higher than the other correlations used in this study. However at higher temperatures, the linear correlation underpredicts when compared with the other correlations (5-10%). The total deviation between the experimental and calculated vapor pressure over the whole temperature range for any particular liquid is expressed in terms of AAD (Average Absolute Deviation) and these are plotted in Figures III-23-III-27. We can see that Starling's equation works equally well for both high and low boiling liquids in the sense that the AAD is always within 5% for all cuts of liquids. With the Wilson, Riedel and Mobil correlations we see that they work very well for the middle boiling range of liquids and the AAD increases up to 10% for high and low boiling liquids. Again, the linear gives the worst fit for the whole boiling range of coal liquids and for high boiling liquids, the deviations may increase up to as high as 20%. Therefore, we rank the correlations to predict the vapor pressure of coal liquids in the following manner (listed in order of decreasing recommendation):

Starling > Mobil, Riedel, Wilson > Linear

It must be kept in mind that this recommendation is made based on experimental results of cuts of a coal liquid product produced in the SRC-II process. It is not known whether this ranking would hold for other coal liquids produced by other coals and other processes.

The linear equation is very simple and extremely easy to use and it therefore can be used as a preliminary predictor. For the accurate design of coal liquefaction plants, Starling's equation should be used. More experimental data on critical properties and vapor pressure of coal derived liquids are needed to test the applicability of the correlations available today.

Conclusions

A systematic study of the available correlations to predict the critical properties and vapor pressure of coal liquids is given in this report. These correlations were primarily developed for petroleum fractions which are predominantly aliphatic in nature. In contrast, coal liquids are primarily composed of aromatic and heterocyclic compounds. Eight correlations for critical temperature, five for critical pressure and five for vapor pressure of coal liquids were compared with the experimental data reported by Gray and Holder (1982). Unfortunately, experimental data on critical properties were very limited and therefore no specific recommendations could be made about the superiority of one correlation over others. In case of vapor pressure, more extensive data were available and Starling's equation was found to be very satisfactory over the whole range of temperature studied. However, this equation is very complicated and not easy to use. Riedel's, Wilson's and Mobil's equations are less accurate, but extremely simple to use. In fact, the last three equations can be utilized for preliminary design purposes. More experimental data are urgently needed on the critical properties and vapor pressure of coal liquids.

Nomenclature

A	Parameter defined in Curl-Pitzer correlation
A	Coefficient defined in Exxon Maxwell-Bonnell correlation
A_i	Coefficients in Cavett's correlation
^oAPI	= (141.5/SG) - 131.5
B	Parameter defined in Riedels' correlation
B	Parameter defined in Curl-Pitzer correlation
B	Coefficient defined in Exxon Maxwell-Bonnell correlation
B_i	Coefficients in Cavetts' correlation
BP	Normal boiling point
C	Coefficient defined in Exxon Maxwell-Bonnell correlation
c/n	Molecular flexibility
D	Density at normal boiling point as defined in Roess' correlation
D	= SG(BP+100)
D	Coefficient defined in Exxon Maxwell-Bonnell correlation
i=1,2,..	Subscripts in Cavetts' correlation
K_w	Watson characterization factor
MW	Molecular weight
N	Number of data points
P	Pressure
P^o	Vapor Pressure
P^*	Characteristic pressure
$\tilde{P}$	$= P^o/P^*$
P_b	Vapor pressure at normal boiling point
P_c	Critical pressure
P_r	= P/Pc, reduced pressure
P_r^o	$= P^o/Pc$, reduced vapor pressure

SG	Specific gravity
T	Temperature
T^*	Characteristic Temperature
$\tilde{T}$	$= T/T^*$
T_b	Normal boiling point corrected to K_w=12
T_c	Critical Temperature
T_r	$= T/T_c$, reduced temperature
x	Indexed defined in ASPEN correlation
X	Parameter defined in Exxon Maxwell-Bonnell correlation

Greek Symbols

α_c	Riedel factor
ω	Acentric factor

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Table III-10: Critical Temperature Correlations

1) Nokay (1959)

$$(\log_{10} T_c = 1.057019 + 0.227320 \log_{10}(SG) + 0.0669286)*$$

where T_c = Critical Temperature, K

SG = Specific Gravity, $60^o/60^oF$
BP = Normal Boiling Point (K)

*Coefficients are Reid, Prausnitz and Sherwood's Constants

2) Roess (1936)

$$T_c(^oF) = 202.7 + 1.591(a) - (6.29 \times 10^{-4})a^2$$

a = (specific gravity, $60/60^oF$) (V.A.B.P. + 100)
V.A.B.P. = volumetric average boiling point, ^oF

3) Watson (1936)

$$T_c(K) = \frac{BP}{0.283} \left[\frac{1}{(MW/D)}\right]^{0.18}$$

where

BP = Normal Boiling Point (K)
MW = Molecular Weight
D = Density at Normal Boiling Point and is the same as given in Roess' correlation

4) ASPEN (Annon, 1978)

$$T_c = 812.0 + 1.434\ BP - 0.007577\ BP^2 - 0.01078\ API \times BP - 0.6122 \times 10^{-6} BP^3 + 0.1828 \times 10^{-4}\ API \times BP^2 + 0.3902 \times 10^{-8}\ API^2 \times BP^2$$

where

T_c = Critical Temperature (^oR)

BP = Normal Boiling Point (^oF)
API = (141.5/SG) - 131.5
SG = Specific Gravity

5) Modified Guldberg Rule (Gold 1968)

$$T_c(K) = BP/0.635$$

BP = Normal Boiling Point (K)

6) Mathur (1969)

$$T_c(K) = 87.5\ (MW)^{0.4406}$$

MW = Molecular Weight

7) Kesler-Lee (1976)

$$T_c(^oR) = 341.7 + 811(SG) + (0.4244 + 0.1174\ SG)BP$$

$$+ (0.4669 - 3.2623\ SG)\ 10^5/BP$$

SG = Specific Gravity, $60^oF/60^oF$
BP = Normal Boiling Point (^oR)

8) Eaton-Porter (1932)

$$T_c(^oF) = 180 + 1.75(D) - (8.8 \times 10^{-4})D^2$$

where $D = (SG)(BP + 100)$

SG = Specific Gravity, $60^oF/60^oF$
BP = Normal Boiling Point (^oF)

9) Cavett (1962)

$$T_c(F^o) = A_0 + A_1(BP) + A_2(BP)^2 + A_3(API)(BP) + A_4(BP)^3 +$$

$$A_5(API)(BP)^2 + A_6(API)^2IBP)^2$$

where
$A_0 = 768.07121$
$A_1 = 1.7138693$
$A_2 = -0.10834003 \times 10^{-2}$
$A_3 = -0.89212579 \times 10^{-2}$
$A_4 = 0.38890584 \times 10^{-6}$
$A_5 = 0.5309492 \times 10^{-5}$
$A_6 = 0.327116 \times 10^{-7}$
API = ^{o}API @ $60^oF/60^oF$
BP = Normal Boiling Point (^oF) @ 1 atm

10) Penn State (Annon, 1978)

$$T_c(^oF) = \exp(3.9935)(BP)^{0.08615}\ (SG)^{0.04814}$$

BP = Normal Boiling Point (^oR)
SG = Specific Gravity, $60^oF/60^oF$

Table III-11: Estimation of Critical Temperature of Coal Liquids from Available Correlations*

Cut #	BP	SG	MW	Nokay	Roess	Watson	ASPEN	Modified Guldberg	Mathur	Kesler-lee	Eaton-Porter
4HC	409.6	0.8160	110	607.16	589.92	610.32			605.15	608.52	
5HC	433.2	0.8827	116	647.76	647.69	625.53	648.86	682.20	549.95	644.3	648.84
6HC	467.6	0.9507	127	693.38	699.64	671.40	698.88	736.37	622.30	694.91	698.24
7HCB	492.6	0.9672	141	720.81	727.74	694.88	730.44	775.74	649.29	722.16	723.94
8HC	519.8	0.9718	158	748.05	753.26	717.49	763.72	818.58	679.93	741.06	746.43
10HCB	572.1	1.0021	188	803.29	803.99	766.89	766.10	900.94	729.52	800.26	787.83
11HC	612.6	1.0359	202	847.31	841.34	813.72	881.31	964.72	760.59	844.31	814.07
15HC	632.1	1.0830	220	814.05	864.75	832.57	903.09	995.40	777.30	876.7	827.61
16HC	658.7	1.0900	237	900.03	880.81	860.00	935.73	1037.32	801.27	900.41	834.62
17HC	692.6	1.1204	258	936.44	901.38	889.13	974.75	1090.70	829.30	937.6	838.9
18HC	741.5	1.1760	293	991.08	921.86	936.44	1025.41	1167.71	873.15	996.49	827.61
19HC	776.5	1.1792	315	1022.82	926.50	966.93	1070.57	1222.83	849.13	1276.33	813.19

*BP(K), SG and MW data of the coal liquids used to calculate the critical temperature (K) were taken from Gray and Holder (1982).

Table III-12: Critical Pressure Correlations

1) Kessler-Lee (1976)

$$\ln [P_c(PSIA)] = 8.3634 - 0.0566/(SG) - (0.24244 + 2.2848/SG + 0.11857/SG)^2 \times 10^{-3}(BP) + (1.4685 + 3.648/(SG) + 0.47227/SG)^2 \times 10^{-7} (BP)^2 - (0.42019 + 1.6977/SG)^2 \times 10^{-10}(BP)^3$$

where

SG = Specific Gravity
BP = Normal Boiling Point (^oR)

2) Penn State (Annon, 1978)

$$P_c(PSIA) = 3.4824 \times 10^9 (SG)^{2.4853}/(BP)^{2.3177}$$

SG = Specific Gravity
BP = Normal Boiling Point (^oR)

3) Mathur (1969)

$$P_c(atm) = 4532(MW)^{0.929}$$

MW = Molecular Weight

4) Cavett (1962)

$$\log_{10} [P_c(PSIA)] = B_0 + B_1 (BP) + B_2(BP)^2 + B_3(API)(BP) + B_4(BP)^3 + B_5(API)(BP)^2 + B_6(API)^2(BP) + B_7(API)^2(BP)^2$$

where

B_0 = 2.8290406
B_1 = 0.94120109 x 10^{-3}
B_2 = -0.30474749 x 10^{-5}
B_3 = -0.2087611 x 10^{-4}
B_4 = 0.15184103 x 10^{-8}
B_5 = 0.11047899 x 10^{-7}
B_6 = -0.48271599 x 10^{-7}
B_7 = 0.13949619 x 10^{-9}
BP = Normal Boiling Point (^oF)
API = API, $60^oF/60^oF$

5) ASPEN (Annon, 1978)

$$P_c = \frac{10^x}{14.70}$$

where

P_C = Critical Pressure (atm)

BP = Normal Boiling Point (K)

$$x = 3.067 + 0.001136\ BP - 0.5446 \times 10^{-5}\ BP^2 - 0.2837 \times 10^{-4}\ API \times BP$$

$$+ 0.4136 \times 10^{-8}\ BP^3 + 0.4178 \times 10^{-7}\ API \times BP^2 + 0.2890 \times 10^{-6}\ API^2 \times BP$$

$$- 0.8075 \times 10^{-9}\ API^2 \times BP^2$$