to a unique, stable, low conversion steady state.

SUMMARY

Several new regions in the CSTR parameter space, defined by additional boundaries, have been defined. The most significant new behavior is a type of hysteresis in which a stable limit cycle can be attained upon decreasing *Da* from low values. These additions to the fine structure of the CSTR parameter space once again underscore the richness of the dynamic behavior of this relatively simple model. It must also be noted that the additional subdivisions reported here will have direct analogs in other lumped and distributed parameter systems. One should be particularly aware of these boundaries when probing parameter space for specific dynamic behavior.

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Bounds on the Variation of *K*-Value with Various True Boiling Point Fractions Resulting From the Pseudo-Component Approximation: Application to a H_2-Coal Liquid System

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In H_2-coal liquid systems, the determination of H_2 *K*-value is straightforward. However, this is not so for the coal liquid. The reason is that the coal liquid components defy separation, identification, and analysis since for all practical purposes they are represented by an infinite number of components. That is to say, the heavier coal liquids represent *continua* mixtures of infinite number of "continua" components. In general, for vapor liquid equilibrium (*VLE*) measurements and calculations such liquids are divided into short boiling range *cuts*, and each of these *cuts* is identified by an average molecular weight, average boiling point, density, etc.

White and Brown (1942) obtained experimental *VLE* data for petroleum fractions boiling from 308.15K (95°F) to 672.05K (750°F) at temperatures from 422.05 to 710.95K and at pressures from 0.345 to 4.823 MPa. From the results of the equilibrium, flash vaporization runs *VLE* phase distributions were derived for arbitrary hypothetical components having a true boiling point (*TBP*) range of 27.8K (50°F). These 27.8K cuts were converted to moles using average molecular weights and gravities and were used to compute *K*-values for each of the cuts.

Grayson and Streed (1963) also used arbitrary cuts of 27.8K (50°F) (except for one cut of 13.9K) in the measurement of *VLE* data of H_2-gas oil systems up to a temperature 755.35K. These gas-oils were typical of commercial hydrocracker feed stocks.

There is some question as to whether or not experimental *K*-values of the heavy liquid *cuts* reported in the literature take into account the differences in the volatility of various components within a given cut. The literature values are reported as *average K*-values for the entire *TBP cut* and are applied independently of the degree of vaporization achieved within each *cut*.

The objective of this investigation is to assess the effect of various *TBP* widths on the error that could result in the measurement of *K*-value of this arbitrary boiling range fraction (or *cuts*). It is shown that such an approach can cause severe inherent errors in the *K*-value measurements of the *cuts* and thus reduce their utility.

ANALYSIS PROCEDURE

The Grayson and Streed (1963) (*CS*) correlation is used to compute *K*-values for several H_2—*continua* component pseudo binary mixtures. The *GS* correlation is an extension of Chao and Seader (1961) correlation for application up to about 728K. The *K*-value is computed from the relation:

$$K = y/x = \frac{\nu^0 \gamma}{\phi}$$

ϕ and γ are computed respectively from the Redlich-Kwong equation of state and from Scatchard—Hildebrand (solubility parameter) correlation. ν is given by Grayson and Streed as an empirical function of reduced temperature, reduced pressure, and acentric factor. This function was obtained from fitting of their high temperature *VLE* data on H_2-gas oil systems. These authors have also reported all the necessary parameters (viz. solubility parameter, ω, T_c, P_c, and molar liquid volume) for arbitrary "components" having *TBP* range of 27.8K (50°F) from 338.75 to 644.25K. These parameters were calculated at average boiling point of each 27.8K fraction. For this investigation, these parameters were plotted against *TBP*, and a continuous curve was drawn through these plateaus to obtain "averaged" parameter values along the entire *TBP* range. The point values representing each "continua" component were then read from such a curve for each parameter.

The coal liquid considered for analysis is the blended feed in Exxon-Donor-Solvent (*EDS*) process (Epperly, 1978). This blended feed is represented by the *TBP* curve shown in Figure 1. It was shown (Epperly, 1978) that the *TBP* curves for petroleum and coal liquids are very similar, and hence many of the correlations developed for heavy petroleum fluids can be used to predict the approximate behavior of coal liquids. Frith et al. (1979) have proposed certain empirical adjustments in petroleum correlations for making them more accurate for the prediction of *VLE* in H_2, light gases, and coal liquid systems. These

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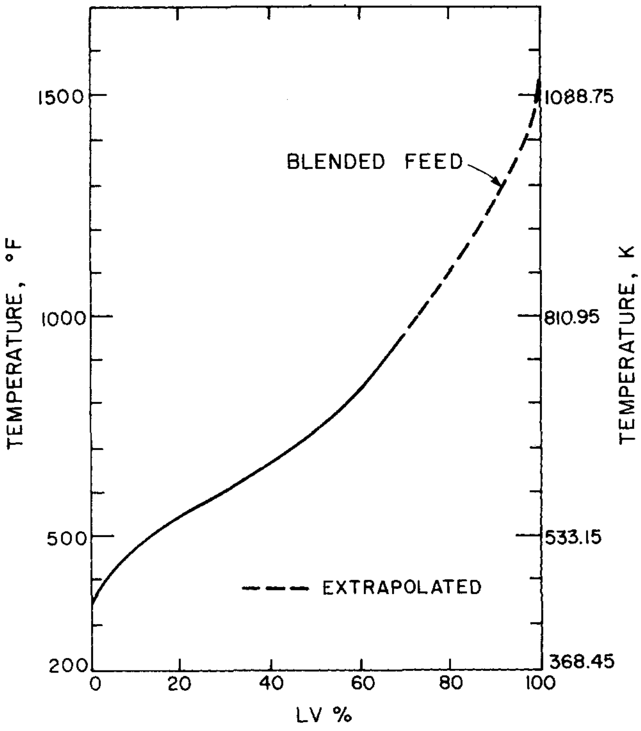

Figure 1. *TBP* **distillation of blended feed.**

empirical adjustments need specific gravity data for each *TBP* cut, but for the coal liquid considered in this investigation, such data are not available and hence the adjustments are not possible. However, it is believed that the *GS* correlation can be used to give a *qualitative indication* of the relative error in *K*-values of the pseudo *components* represented by various arbitrary boiling range fractions in calculational procedures, and to yield guidance as to how the experiments on "continua fractions" should be conducted. One also obtains guidance on how the resulting experimental data should be used in routine computations by this type of treatment.

The *TBP* curve for the blended feed (Figure 1) shows three distinct regions:

(1) region up to 477.55K, shows a slope of ca. 6.7K (12°F) per volume percent of liquid boil off (*LV%* off),

(2) region from 505.35 to 699.85K, shows a slope of ca. 3.3K (6°F) per *LV%* off, and

(3) region beyond 699.85, shows a slope of ca. 6.7K (12°F) per *LV%* off.

Only the first two regions are considered in this investigation because of the lack of experimental data on heavy liquids beyond *TBP* of 644.25K. For region-1, *TBP* fractions of 3.3K (6°F) and 27.8K (50°F) correspond to about ½ and 4.2 *LV%* off, respectively. For region-2, on the other hand, 3.3 and 27.8K boiling fractions correspond to about 1 and 8.3 *LV%* off, respectively.

To compute *K*-values, pseudo binary systems of H_2 and several *continua* components are considered. The *K*-values of these *continua* components (identified by their *TBP*) are shown in Figure 2 for equilibria temperatures of up to 644.25K and a pressure 10.335 MPa.

DISCUSSION

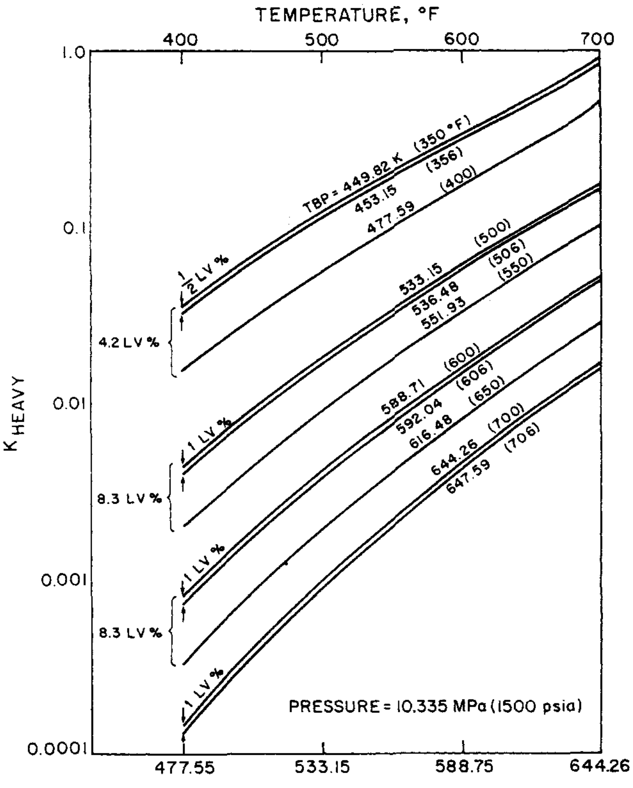

Figure 2. Possible variation of *K*-values of heavy "components" with various true boiling range of cuts.

For a *pseudo-component* having a *TBP* range and representing a fraction of the *continua* mixture, the most volatile and least volatile *continua* components bound this *TBP* range. For this fraction at some equilibrium temperature and pressure, the maximum and the minimum in *K*-value of the *pseudo-component* occurs, respectively, at the leading and the trailing edge of the fraction as far as no extraordinary interactions occur between the liquid fraction under study and the gas phase. For this fraction, the *K*-value obtained experimentally will lie somewhere between these extremes depending on how much of the original fraction (sample) has vaporized during the measurement. If, in the equilibrium cell at equilibrium conditions, the liquid to vapor molar ratio (*L/V* ratio) becomes infinite, i.e. only an infinitesimal amount of the original sample has vaporized, the system would be at its bubble-point. While for a very small *L/V* ratio (when all the original sample has vaporized) with liquid present in infinitesimal quantity, the system would be at its dew-point. Further, if there are no extraordinary interactions introduced by introduction of the light gases, the *K*-value for the arbitrary "component" will vary in a uniform way from its bubble-point value to its dew-point value. For example, consider a fraction having a *TBP* range of 533.15-536.45K (500-506°F). At 533.15K and 10.335 MPa, the *K*-value for the fraction in the presence of hydrogen would lie between 0.0167 and 0.018 (see Figure 2). If an average value of 0.01735 is considered for this 533.15-536.45K fraction, it would have an inherent error of as much as 3.7%, depending on how close the system is to the bubble point of the dew-point. For a fraction having a *TBP* range of 533.15-560.95K (500°-550°F), at 533.15K and 10.335 MPa the *K*-value would lie between 0.009 and 0.018, which means that the average *K*-value for the fraction could have an inherent error of as much as 50% depending on how much of the original fraction (sample) has vaporized during the measurement of the *K*-value. Figure 2 also shows similar bounds for *K*-values for other *TBP* conditions.

CONCLUSION

From the above analysis, it is clear that the measured *K*-values of the arbitrary *components* should be as *local* as possible, that is to say, the vaporized fraction and the remaining fraction should have boiling points as close to each other as possible. Since it would be impractical to take incremental *cuts* of 1 *LV%* or less over the entire *TBP* range, we recommend taking a narrow cut (1 *LV%* or less) followed by a rather broad cut, say an 8.3 *LV%* or less cut, and so on. A smooth curve can then be drawn through these *localized* K-values to cover the entire *TBP* range. The calculations also indicate that the variation of the liquid concentrations of the heavy *components* contribute much less to the error in the K-values from the pseudo-component treatment than the variation in the y value across the same cut. For example for the 533.15-560.95K fraction, at 533.15K and 10.335 MPa, the x-value of the heavy *component* varies from 0.8483 to 0.8473 while the y-value varies from 0.003834 to 0.007884.

Once the basic data for the equilibrium liquid and vapor compositions of acceptable accuracy have been obtained to represent the K-values as a function of pressure, temperature and composition, the latter assigned along the true boiling point cut, then the calculations can be conducted using size of cuts more consistent with the new experimental accuracy, hopefully, much smaller than are inherent in the present treatment.

NOTATION

$LV\%$ = volume percent of liquid boil off
L/V = liquid to vapor molar ratio
P_c = critical pressure
T_c = critical temperature
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

γ = activity coefficient in the liquid phase
ν^o = fugacity coefficient in the liquid phase
ϕ = fugacity coefficient in the vapor phase
ω = acentric factor

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Nitric Oxide Gas Absorption in A Limestone Packed Column

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INTRODUCTION

Absorption of nitrogen oxides into aqueous solution is an important process industrially in the manufacturer of nitric acid, and environmentally in the removal of these oxides from combustion gases and the aqueous reprocessing of nuclear fuels (Counce and Perona, 1979). Prior to the development of the Haber-Bosch process for the production of ammonia, processes in which nitrate fertilizers were produced from atmospheric air employing various types of electric arcs were widely used (Waesser, 1926). The production of nitrate fertilizer employing electric arc processes (Treharne et al, 1978) has recently received attention as a possible technique for small scale farm produced fertilizer powered by alternate energy sources (solar, wind, hydro).

In the systems being studied nitric oxide is produced by the arc from atmospheric air, oxidized to nitrogen dioxide, and subsequently absorbed into an aqueous solution containing lime of limestone. The resulting solution of calcium nitrate can be directly tied to the irrigation system during growing season, or stored for later use in the winter. The concentration of nitric oxide produced by the arc is low (1-2%), making the gas absorption process difficult. Because of the proposed farm location of the process it is desired that the system be relatively simple and inexpensive. Studies of nitric oxide gas absorption were, therefore, performed employing a column packed with limestone chips in conjunction with a gas holding tank to provide for the oxidation of nitric oxide to the more soluble nitrogen dioxide (hence N_2O_4). The studies were conducted in order to evaluate the effect of gas flow velocity, input nitric oxide partial pressure, packing height and holding tank volume on the absorption of nitric oxide—air mixtures at concentrations below 2%.

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