Phase Equilibria of Continuous Fossil Fuel Process Oils

Fossil fuel process oils consist of such a large number of components that their only proper description is in terms of continuous distribution functions of a suitable characteristic variable. A methodology is presented to describe the oils in terms of a generalized distribution function. The characteristic variable is determined from measurements of the equilibrium ratios of two test oils, at ambient pressure. Application of the proposed methodology to a sequence of operations shows that, unlike the pseudocomponents technique, the level of accuracy can be maintained.

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Introduction

Although the fossil fuel process oils have long been thought of as continuous, the description of the vapor-liquid equilibrium (VLE) processes of these oils has often been based on the approximation that treats the oils as a relatively small set of pseudocomponents. This procedure is reasonably accurate for a simple operation. However, the loss of information will eventually lead to significant inaccuracies in the description of a sequence of operations. Nasir and Kobayashi (1981) showed that large errors would be incurred in VLE operation if the boiling point range were taken to be large in such an approach.

Various investigators have recently published suggestions for the VLE calculations of continuous materials (Kehlen and Ratzsch 1980, 1983; Ratzsch and Kehlen, 1983; Kehlen et al. 1984, 1985; Gualtieri et al., 1982; Salacuse and Stell, 1982; Briano and Glandt, 1983). However, only theoretical approaches have been stressed in these studies. Models are assumed for the equilibrium ratio, and distributions are described by particular analytical functions.

An oil can have any arbitrary distribution (usually nonanalytical), depending on the circumstances under which it was produced and pretreated. One should not expect a simple analytical expression to be so flexible as to accurately fit any oil distribution. The equilibrium ratios should be determined from the VLE processes of real continuous oils and not from their pure component constituents.

In this work, the equilibrium ratios are experimentally determined from ambient batch distillation of two real continuous oils: a shale oil and a coal oil. The oils are described by a set of distributions (fractional continuous oils) consistent with the equilibrium ratios, and the rule of transformation of the parameters is determined.

Comparison of Continuous and Discrete Analyses

To demonstrate a typical behavior of oils, computations estimating the results of a VLE process of a hypothetical continuous oil were made. To describe the oil and its properties, a distribution function F is used to represent the oil fraction with a differential range of a characteristic parameter τ. The constraint of the function is

$$\int_{\tau} F d\tau = 1 \quad F > 0 \tag{1}$$

Often these continuous oils are described in terms of relatively few pseudocomponents (Ritchey et al., 1976). When such a procedure is applied to the flashing of a continuous oil, the predicted bubble point temperatures are generally lower and the dew point temperatures are generally higher than correct values obtained from continuous descriptions.

To illustrate this point, an arbitrary distribution representing an oil cut with a 250 K boiling range was chosen and the equilibrium flash vaporization curve (bubble point to dew point curve) was calculated in terms of 5, 10, and 20 pseudocomponents. Figure 1 compares the equilibrium flash vaporization (EFV) curves predicted by the pseudocomponents technique with those of the exact method. The discrepancies in prediction of the equilibrium flash vaporization curve increase with the pseudocomponent technique in a successive operation. Figure 2 compares the EFV curves for the vapor (15%) produced at 550 K. The EFV curve is unrealistic, having as many as 10 pseudocomponents.

Another important point to be noted is that in many situations

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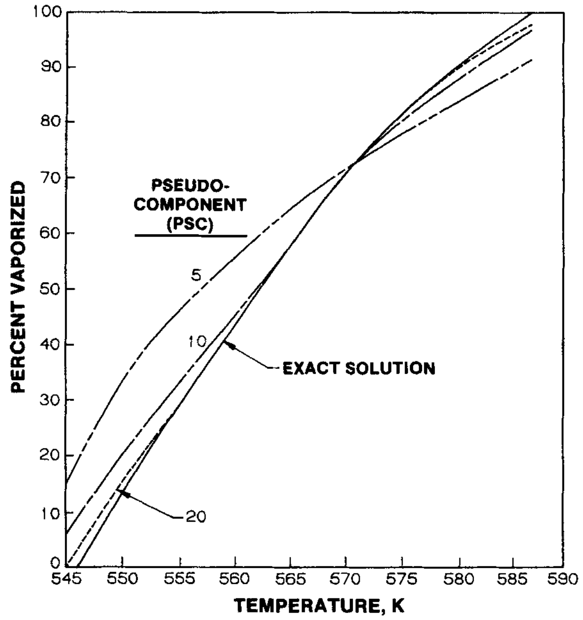

Figure 1. Equilibrium flash curve of oil cut.

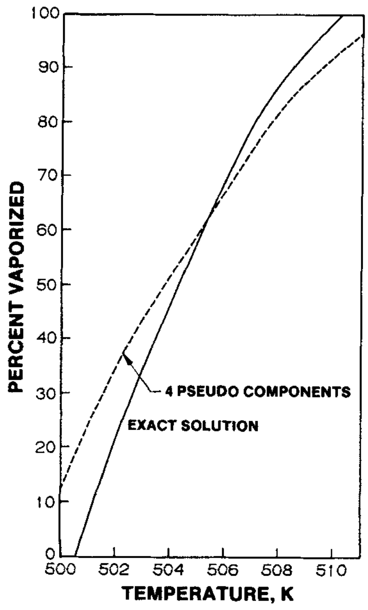

Figure 3. Equilibrium flash vaporization curve of narrow oil cut.

the necessary number of pseudocomponents does not depend on the boiling point range of the oil. For example, a narrow cut has a bubble point very close to its dew point, and the EFV curve is very sensitive to temperature. With a few pseudocomponents (e.g., four) even though the predicted bubble point and dew point temperatures are not very different from values predicted from the exact solution, the fraction vaporized can be in significant error. Figure 3 compares the EFV curve for a narrow oil cut with 120 K boiling range with the curve predicted with four pseudocomponents (30 K boiling range for each). At the bubble point, the fraction vaporized calculated by 30 K pseudocomponents is 20%, compared with 10% obtained with 10 pseudocomponents (30 K boiling range) in Figure 1.

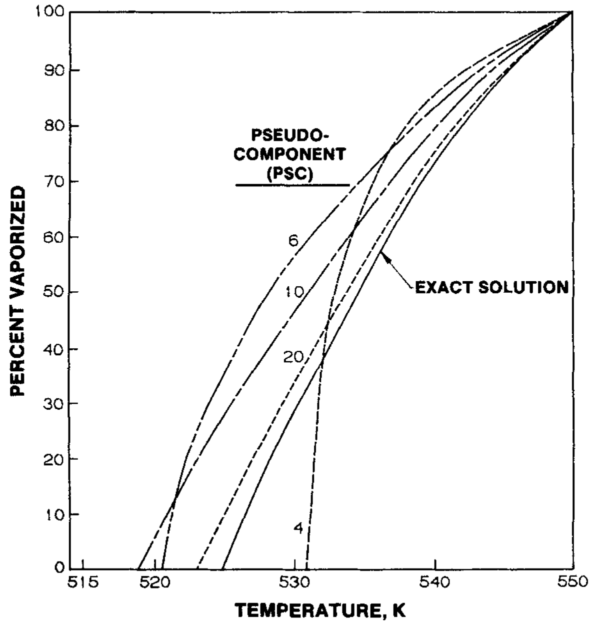

Figure 2. Equilibrium flash curve of vapor produced at 550 K.

Characteristics of Continuous Distribution Functions

It has been noted that certain distribution functions can exhibit a common form for liquid and vapor in equilibrium if the equilibrium ratios can be expressed in a particular form. Ratzsch and Kehlen (1983) examined the case of normal or Gaussian functions. They showed that if Raoult's law applies and each infinitesimal component's vapor pressure follows the Clausius-Clapyron relation, and if its heat of vaporization is proportional to the boiling point, then both vapor and liquid composition can be expressed by the Gaussian distribution; they also presented the relationship between the parameters of the two distributions.

Cotterman et al. (1985) used the Soave-Redlich-Kwong equation of state with a particular expression for its parameters and obtained a relationship for the equilibrium ratio that is first order with respect to the characteristic variable (i.e., molecular weight). These authors demonstrated that the composition of both phases can be described by the Schultz distribution, and they presented the rules of transformation of parameters.

The above concept can be generalized if the equilibrium ratios can be described by exponential terms that are linear in the parameters regardless of the appearance of the characteristic variable; that is,

$$K(\tau, T, P; F^v; F^\ell) = \frac{F^v}{F^\ell}$$

$$= C^K \exp\left[\sum_{i=1}^{n} h_i\,(T, P; F^v; F^\ell)\cdot g_i(\tau)\right] \qquad (2)$$

We can achieve the convenience of describing the distribution of the vapor and liquid composition by similar functions. Thus, if

$$F^{\ell} = C^{\ell} \exp\left[\sum_{i=1}^{m>n} h_i^{\ell}(T, P; F^v; F^{\ell}) \cdot g_i(\tau)\right] \tag{3}$$

was the mole fraction density function for the liquid phase, then

$$F^{v} = C^{v} \exp\left[\sum_{i=1}^{m>n} h_i^{v}(T, P; F^v; F^{\ell}) \cdot g_i(\tau)\right] \tag{4}$$

would describe the vapor phase at equilibrium. The rule of transformation of parameters would be found from the condition

$$h_i^v = h_i^{\ell} + h_i \tag{5}$$

for the coefficients of the $g_i(\tau)$ terms. The distribution function of F^v and F^{ℓ} must contain all the τ-dependent terms, $g_i(\tau)$, that appear in the equilibrium ratio equation but can have additional terms.

Relative Ideality in Continuous Mixture

It is obvious that a real continuous oil cannot be separated into its pure-component constituents and that there is no information available other than the distribution in terms of the characteristic variable. In this situation, where all the information comes from the collective properties of the mixture, we probably have a built-in nonideality correction. Describing each component of infinitesimal concentration in terms of the properties of its pure state is such a major extrapolation that a thermodynamic model would be developed that is much more complicated than necessary. Edmister et al. (1952) assumed Raoult's law with a simple expression for the vapor pressure of petroleum oils to describe successfully the phase equilibrium of such materials. Many investigators seem to accept the assumption of ideal mixing for petroleum oils as appropriate (Kragas et al., 1982). In an example from Wilson et al. (1981), the fact that a coal liquid has a vapor pressure curve like that of a pure component can be accounted for by assuming that each individual component obeys Raoult's law. We do not contend that therefore each component behaves ideally, but that in a true continuous oil the nonideal behavior may not be detectable. In other words, the oil can behave ideally relative to the primary measured data.

If the vapor and the liquid phases are ideal mixtures in the Lewis-Randall sense, then

$$f^v[T, P, \tau;\ F^v(\tau)] = F^v(\tau) \cdot \tilde{f}^v(T, P, \tau) \tag{6}$$

and

$$f^{\ell}[T, P, \tau; F^{\ell}(\tau)] = F^{\ell}(\tau) \cdot \tilde{f}^{\ell}(T, P, \tau) \tag{7}$$

where $F^v(\tau)$ and $F^{\ell}(\tau)$ are the distribution density function of the vapor and liquid phases, respectively, and $\tilde{f}^v$ and $\tilde{f}^{\ell}$ are the apparent fugacities of an infinitesimal component identified by τ. The term $d\tau$ was canceled out in Eqs. 6 and 7. It should be noted that the continuous representation of these materials terms, such as apparent fugacity or apparent vapor pressure of a hypothetical pure component, should be used. Even the infinitesimal fraction of a continuous oil is itself a continuous oil rather than a pure component. Therefore, whenever we speak of a property of a continuous oil component in the pure state (e.g., $\tilde{f}$ or $\tilde{P}$), it refers to the apparent property of the material. In Eqs. 6 and 7 f^{ℓ} and f^v are the fugacity density functions of an infinitesimal component in the mixture that is represented by the whole distribution, and τ is the characteristic variable.

With Eqs. 6 and 7, the equilibrium ratios are expressed as

$$K(T, P, \tau) = \frac{F^v(\tau)}{F^{\ell}(\tau)} = \frac{\tilde{f}^{\ell}(T, P, \tau)}{\tilde{f}^{v}(T, P, \tau)} \tag{8}$$

The parameters of the distribution density functions F^v and F^{ℓ} depend on the temperature and pressure.

Fractional Continuous Oil Description

The major difficulty with the above analysis lies in the fact that the original oil has a distribution function that usually is not simple. The distribution of an oil depends on the circumstances under which it was produced and pretreated. Therefore, in many situations the oil must be described in terms of linear combinations of any proposed functions that can describe the whole continuous oil to any desired degree of accuracy. In Figure 4 a typical continuous oil is shown in terms of five continuous functions.

By describing the oil as the sum of a finite number of continuous oils, unlike the pseudocomponent description, after a large number of sequential operations the essential continuous nature of the oil is not lost. The rules of propagation of parameters of Eq. 5 tend to move the distribution functions of the vapor product to the lower part of the boiling range and those in the liquid product to the higher part of the boiling point range.

We cannot expect these continuous oils to retain their identity in a sequence of operations. In this sense, they cannot be considered components that have unchanging characteristics (i.e., distribution functions). It is in view of this that they are referred to as fractional continuous oils. In this approach the original oil is described in terms of relatively few distribution functions:

$$F^f = \sum_{j=1}^{n} w_j^f \psi_j^f \tag{9}$$

$$\sum_{j=1}^{n} w_j^f = 1 \tag{10}$$

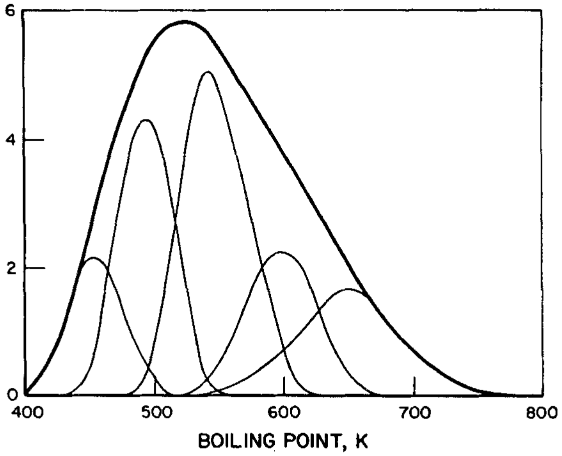

Figure 4. Representation of a continuous oil in terms of five distribution functions.

where F^f is the original distribution function of the oil and w_j^f is the weight representing the mole fraction of fractional oil ψ_j^f. The equality in Eq. 9 will not be exact for the entire range of the characteristic variable. Any procedure that would result in describing the F^f in terms of fractional oils with reasonable accuracy can be employed. The necessary quality of the approximation will probably depend on the severity of the operation in mind.

The product streams in an equilibrium process such as a flash (i.e., F^v and F^ℓ) are also described in terms of fractional oils:

$$F^\ell = \sum_{j=1}^{n} w_j^\ell \psi_j^\ell \tag{11}$$

$$\Sigma\, w_j^\ell = 1 \tag{12}$$

$$F^v = \sum_{j=1}^{n} w_j^v \psi_j^v \tag{13}$$

$$\Sigma\, w_j^v = 1 \tag{14}$$

Instead of Eqs. 3 and 4, each fractional oil would have density functions:

$$\psi_j^\ell = C_j^\ell \exp\left[\sum_{i=1}^{m} h_{ij}^\ell (T, P) \cdot g_i(\tau)\right] \tag{15}$$

$$\psi_j^v = C_j^v \exp\left[\sum_{i=1}^{m} h_{ij}^v (T, P) \cdot g_i(\tau)\right] \tag{16}$$

and

$$h_{ij}^v = h_{ij}^\ell + h_i \tag{17}$$

To use this concept in the description of real oil vapor-liquid equilibria, suitable characteristic variables and suitable equilibrium ratio functions (i.e., Eq. 2) must be established experimentally.

Experimental Approach

Equilibrium ratios were determined from a gas chromatograph simulated distillation conducted on samples obtained in batch distillation runs. A flow diagram of the ambient pressure batch distillation unit is shown in Figure 5. In operation, the oil is heated at a predetermined heat-up rate. The oil vapor is condensed, and representative sets of samples of pot liquid and distillates are obtained at several predetermined temperatures (about every 10 to 25 K).

Two types of oils were used in this study, a shale oil and a coal oil. Large samples of the oils chosen for extensive study were prepared and characterized prior to the experimental runs. Preparation included removal of water and light components that appear as discrete quantities. The characterization of an oil consisted of developing a true boiling point curve using data obtained from a Podbelniak distillation column (ASTM D2892) and measuring the average molecular weights (cryoscopy) and densities of the true boiling point distillation fractions. Gas chromatograph (GC) simulated distillation tests were conducted on the whole oils and their fractions.

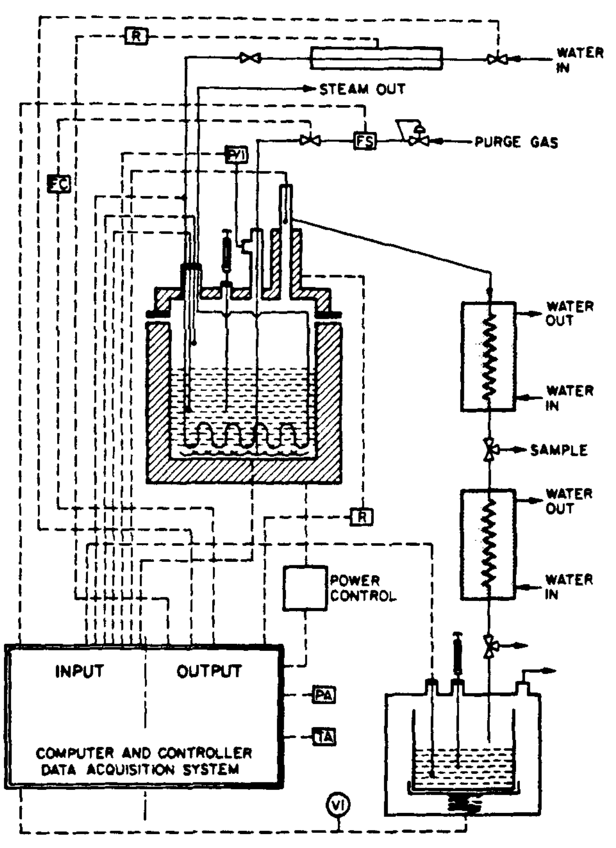

Figure 5. Flow in batch distillation unit.

A comparison of Watson's characterization factor K for the two oils (KS-1 and CTO-1) is presented in Figure 6. Watson's characterization factor is defined as

$$K_w = \frac{(T_b)^{1/3}}{SG} \tag{18}$$

where T_b is the boiling point in degrees Rankin and SG is the specific gravity. The Watson K factor for both oils is lower than 12 (normal paraffins), and the values for the coal oil are lower than those for the shale oil, implying higher aromaticity for the coal oil.

To investigate the dependence of the equilibrium ratios on the distribution of the oil a variation of liquid distribution at the same temperature is necessary. The purge gas flow rate, heat-up rate, and cooldown rate provide means of changing the liquid composition at several temperatures. Table 1 shows the range of the fraction distilled at each of the temperature levels for different sets of samples obtained during experimental runs. The equilibrium ratios were assumed to be independent of vapor composition because all the runs were conducted at ambient pressure.

Samples of vapor and liquid were analyzed by GC-simulated distillation, and the K values were determined. To account for the purge gas,

$$K = F^v \cdot \left(\frac{Q_{oil}}{Q_{oil} + Q_P}\right) / F^\ell \tag{19}$$

where Q_{oil} is the molar flow of the vaporized oil and Q_p is that of the purge gas.

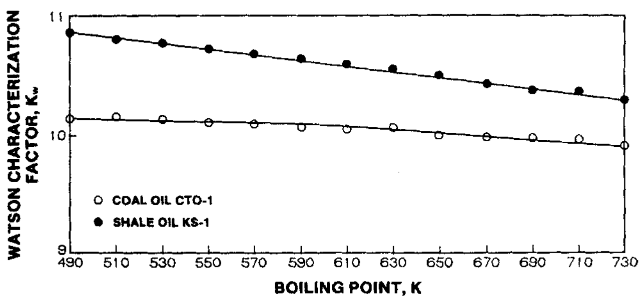

Figure 6. Comparison of Watson *K* factor for the two test oils.

The K values, when plotted against the boiling point, appeared to be independent of the composition over a wide range, Table 1. Furthermore, the K values were calculated at $T_b = T$ for all samples and appeared to be independent of temperature (or T_b). For the shale oil K ($T_b = T$) had an average value of 1.005 with an individual standard deviation of 0.060. For the coal oil, the quantity was also independent of temperature with an average value of 1.004 and an individual standard deviation of 0.047. The quantity K_i/P_i^o was calculated for the pure components added to the oil. It had an average value of 0.97 with an individual standard deviation of 0.08, implying ideal behavior in the sense of Raoult's law. It is therefore concluded that the measured K values are essentially equivalent to the vapor pressure of the two test oils.

Generalized Vapor-Pressure Equation and Characteristic Variable

To correlate the K values (or, ideally, vapor pressure) with a characteristic variable, a generalized form is desirable, a form with parameters that can be determined routinely for classes of oils. Maxwell and Bonnell (1957) showed that pure aliphatic compounds and a few petroleum cuts have a vapor pressure that can be correlated in the form

$$\frac{1}{T_6(P)} = \frac{A_i}{T_i(P)} + B_i \qquad (20)$$

where T_6 and T_i are the temperatures at which normal hexane (reference component) and the material have the same vapor pressure P. They further implied that for different materials from the same source, the curves of $T_6(P)$ vs. $T_i(P)$ have a common point (pivot point). Zudkevitch et al. (1983) used the same procedure to correlate vapor pressure of coal liquids. They used normal hexane as a reference material but obtained a different pivot point for coal liquids.

Table 1. Range of Fraction Distilled at Each Temperature Level

Temp. K	% Shale Oil Distilled Min	% Shale Oil Distilled Max	% Coal Oil Distilled Min	% Coal Oil Distilled Max
225	0.3	3	0	0
250	1	12	5.5	39.5
275	4.5	68	11	39
300	12	75	16.5	38.5
325	15	60.5	30.5	42.5
350	45.5	45.5	—	—

The location of the pivot point depends on the nature of the oil and the choice of reference material. It is more appropriate to choose as reference material a component that is representative of the oil. The reference material can also be a hypothetical infinitesimal component of the oil. If the reference component (or hypothetical component) is an appropriate representative of the oil, the ordinate and the abscissa of the pivot point will be the same. It can be shown that Eq. 20 implies

$$\left[\frac{1}{T_i(P)} - a\right] = \left(\frac{\dfrac{1}{T_{b,i}} - a}{\dfrac{1}{T_{b,ref}} - a}\right)\left[\frac{1}{T_{ref}(P)} - a\right] \qquad (21)$$

where $T_{b,ref}$ and $T_{b,i}$ are the boiling points and a is a constant apparently characteristic of the oil.

From Eq. 21 it is obvious that a convenient characterization variable of an oil, rather than T_b, is

$$\tau = T_b/(1 - aT_b) \qquad (22)$$

It can also be shown that the vapor pressure of any component would be a function only of

$$\theta = [T_b/(1 - a\,T_b)]/[T/(1 - a\,T)] \qquad (23)$$

and the plots of P^o against θ for all material with a common a would fall on a single curve.

To examine this conclusion, we used the complex empirical correlation of Wilson et al., (1981) for the superatmospheric conditions with the required properties (specific gravity as a function of T_b). A fit of the data gives a value of a for this system of 0.000310 K^{-1}. For the coal liquids that Zudkevitch (1983) studied, a is 0.000315 K^{-1}. For petroleum liquids that Maxwell and Bonnell studied, a is 0.00516 K^{-1}. The parameter a probably depends on the class of oils (petroleum, shale, coal, etc.).

Our equilibrium ratio data (and therefore the vapor pressure of the KS-1 shale oil) were correlated with the dimensionless grouping θ. A least-squares fit of the data gives a value of $a = 0.000426$. Given the nature of our test oils (about 50% aromaticity) and that this value of a lies halfway between the suggested values for petroleum and coal liquids (i.e., 0.000516 and 0.000325), this value of a was chosen for our correlation. In Figure 7 the experimental K values are of the KS-1 shale oil plotted against the dimensionless group

$$\theta = \frac{T_b/(1 - 0.000426\,T_b)}{T/(1 - 0.000426\,T)} \qquad (24)$$

The following correlation was obtained:

$$\ln(P^o/P^+) = 7.51(1 - \theta) \qquad (25)$$

where $P^+ = 101.325$ kPa.

The equilibrium ratio data of the coal oil were also correlated with θ. To compare the vapor pressure of the coal oil CTO-1 with those of the previously studied shale oil KS-1 and the vapor pressure correlations proposed by Maxwell and Bonnell (1957),

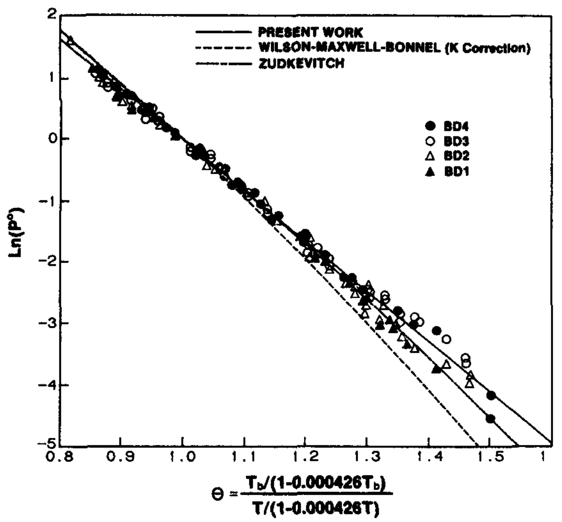

Figure 7. Correlation of experimental equilibrium ratios with θ_{GC} for KS-1-1 shale oil.

Wilson (1981), and Zudkevitch (1983), the same value of a (-0.000426 for shale oil) was chosen for the coal oil in this study. In Figure 8 the experimental K values for the CTO-1 coal oil are plotted against the dimensionless group θ. The correlation between K values of the coal oil and θ is

$$\ln (P^{\circ}/P^{+}) = 5.44 - 2.80\,\theta - 2.64\,\theta^2 \tag{26}$$

Data with samples at different temperatures that form a single curve for both oils imply that the choice of the form and characteristic variable is an appropriate one. The scatter at the higher values of θ is due to the less accurate nature of data at higher boiling points.

The experimental K values (or apparent vapor pressures) agree very well with the Zudkevitch vapor pressure correlation but are higher than the Wilson-Maxwell-Bonnel values. Equations 25 and 26 were applied to predict the experimental batch distillation rates. Excellent agreement was obtained.

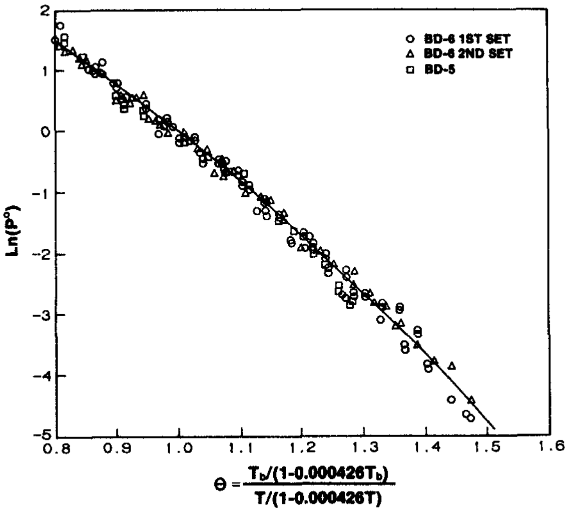

Figure 8. Correlation of experimental equilibrium ratios with θ_{GC} for CTO-1 coal oil.

The similarity of vapor pressure equations and the predicted rate of distillation implies that vapor-liquid equilibrium data of pure components, coupled with the assumption of ideal behavior, describe the behavior of continuous oils at lower pressures with reasonable accuracy. That our test oils behave ideally may be due to a built-in nonideality correction in the primary measured data (e.g., true boiling point) obtained for the whole distribution. Either way, the important point is that the systems behave ideally at ambient pressure.

Fractional Oil Analyses of Continuous Oils

Equations 25 and 26 imply that the general expression for K, Eq. 2, can be simplified to

$$\ln (K) = h_0 + h_1 \cdot \tau + h_2 \cdot \tau^2 \tag{27}$$

This requires ψ to be quadratic in τ in the exponential expressions. Although a Gaussian distribution would be appropriate for a fractional oil with the equilibrium ratio in the form of Eq. 27, it is not qualitatively consistent with the shape of a typical original oil distribution. In particular, the relatively sharp cutoff at the low end, τ_o, cannot be matched by even a truncated Gaussian distribution. A modified Gaussian distribution that, qualitatively, is more appropriately truncated at τ_o is

$$\psi = C(\tau - \tau_o)^m \exp\left[-\frac{(\tau - \bar{\tau})^2}{2\sigma^2}\right] \text{for } \tau > \tau_o \tag{28}$$

and

$$\sigma_v^2 = \sigma_\ell^2/(1 - 2h_2\,\sigma_\ell^2) \tag{29}$$

$$\bar{\tau}_v = \frac{\sigma_v^2}{\sigma_\ell^2}(\bar{\tau}_\ell + h_1\,\sigma_\ell^2) \tag{30}$$

$$m^v = m^\ell \tag{31}$$

The preexponential constant can be found by the normalization condition. If m is an integer, then

$$C = \left[m!\,(2\sigma^2) \cdot \frac{m+1}{2} \cdot \frac{(\pi)^{1/2}}{2}\, i^m \operatorname{erfc}\left(\frac{\bar{\tau} - \tau_o}{(2\sigma^2)^{1/2}}\right)\right]^{-1} \tag{32}$$

The constant must be determined numerically if m is not an integer.

With oil as an ideal mixture, it follows that each fractional oil produces the fractional oils of the product stream (i.e., vapor and liquid). If the fractional oils in all three streams have the same form, the rule of transformation of the parameters of the fractional oils can be developed in any sequence of operations. The products of any sequence of equilibrium processes can be determined only from the information of the fractional oils of the original oil (i.e., the parameters and weights).

The fractional oils of the three streams are related through the equilibrium relationship and the conservation of mass equations.

$$\frac{w_i^v\,\psi_i^v}{w_i^\ell\,\psi_i^\ell} = K(T, P, \tau) \tag{33}$$

and

$$\psi_i^f = V_i \psi_i^v + (1 - V_i)\psi_i^\ell \tag{34}$$

where V_i is the fraction of fractional oil ψ_i^f vaporized in the process.

The total amount of the oil vaporized is

$$V = \sum_{i=1}^{N} w_i^f V_i \tag{35}$$

$$w_i^v = \frac{w_i^f V_i}{V} \tag{36}$$

From Eqs. 33 and 35 it follows that

$$\frac{V_i}{1 - V_i} \cdot \frac{1 - V}{V} = K(T, P, \tau)\frac{\psi_i^\ell}{\psi_i^v} \tag{37}$$

In order to develop the rule of propagation of the parameters, the fractional oils of the original oil (i.e., ψ_i^f) and those of the product streams must have the same functional form. Given the general form of Eq. 15, Eq. 34 cannot be fully satisfied throughout the domain of τ and must be approximated. For each fractional oil, a set of k parameters for each of the two product streams and the fraction vaporized (i.e., V_i) must be determined. The parameters of the product streams are related through Eq. 17. The $k + 1$ unknown for each oil can be obtained using a variety of methods such as equating the first k moments of Eq. 34 or matching the amount of the original oil with sum of the vapor and liquid products in the k segment of the distribution.

The advantage of describing an oil in terms of continuous functions is that, unlike the pseudocomponent description, after a large number of sequential operations the continuous nature of the oil is retained. It can be shown that if the functions are chosen in a way (given equilibrium conditions T, V) that the discrepancies in the material balance are small, the same level of accuracy can be maintained in sequential operations.

To illustrate this point, this procedure was applied to a hypothetical sequence of operations on a typical oil that is described by a modified Gaussian distribution. The sequence of operations consisted of a series of partial condensations of the vapor fraction at constant pressure (1 atm) producing approximately 13% vapor. Figure 9 shows the distribution of the original oil described by a single modified Gaussian function and the first and fifth vapor distribution.

In Table 2, the estimated vapor fractions for five sequential partial condensations are shown, using a continuous distribution function, and are compared with values obtained with 20 pseudocomponents and the exact solution. After five operations, the description in terms of one continuous function is still accurate. The fraction of the original material left after the fifth operation is 3×10^{-5}.

To apply the procedure to a real oil (e.g., KS-1 shale oil) of arbitrary shape and with too wide a boiling range, the distribution must be described in terms of more than one simple continuous function (fractional oil).

To test the accuracy of this method of continuous description in terms of relatively few fractional oils, the distribution of the KS-1 shale oil in terms of three fractional oils was used.

We applied this fractional oil procedure to the three sequences of operation with ~50% vaporization at each step. The vapor fractions based on an exact calculation and on a fractional oil calculation are compared in Table 3.

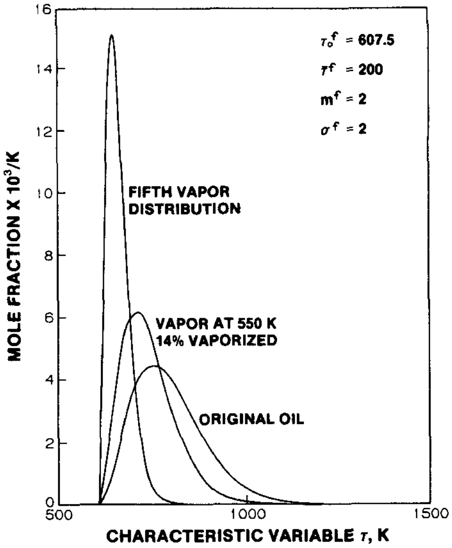

Figure 9. Representation of a distribution in sequential operation.

The alternative and flash sequences were accurately described by this fractional oil procedure. In the last step of these sequences, only about 3% of the original material is left. The accuracy is comparable to that achieved with the first fractional oil procedure with 10 fractional oils.

The condensation sequence, however, as described by the fractional oil method, was less accurate compared with the other sequences. The discrepancies become significant (>10%) when 10% of the oil is left. The difficulties with the condensation sequence are due to the differences that appear for $\tau<900$. In this sequence, the material becomes concentrated at the low end, and what might appear as minor errors in the original approximation become significant after four steps. In the other sequences, the oil concentrates in regions where the fit is very good and remains so.

In Figure 10 the relative errors are shown for the original distribution and after the fifth step in the sequential flash, sequential condensation, and in alternating series. The relative errors remain fairly constant for the sequential flash and alternating operation but are greater for the fifth vapor distribution, mainly because of lower temperature. The results lead to the conclusion that if the fractional oils are chosen properly, the initial fit of the distribution is the most important factor in determining the level of accuracy in complex processes.

Table 2. Vapor Fraction in Successive Partial Condensations of a Hypothetical Oil on Continuous and Pseudocomponent Bases

Temp. K	Exact Calc.	Cont. Func.	20 Pseudocomp.
550	0.1339	0.1360	0.1504
527	0.1330	0.1480	0.2029
512.5	0.1294	0.1528	0.2564
502.9	0.1345	0.1600	0.3244
196.1	0.1237	0.1491	0.3709

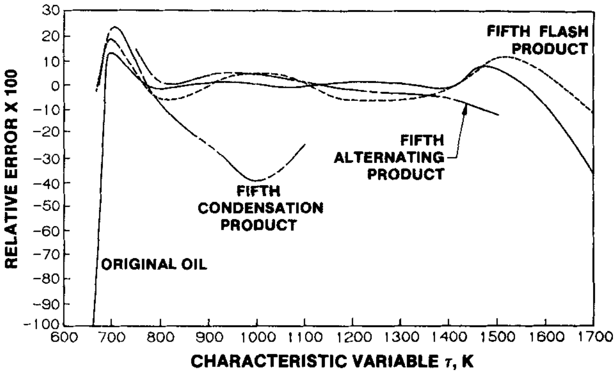

Figure 10. Relative error in distribution of KS-1-1 shale oil in sequential operations.

Conclusions

Test calculations using the pseudocomponent description of continuous oil vapor-liquid equilibrium behavior have shown that a large number is required if processes of any complexity are to be described accurately.

Description of continuous oils in terms of analytical functions of relatively convenient manipulability is possible within a certain large class of functions. Use of these functions gives an oil description that maintains the continuous nature of the oil regardless of the complexity of the process being modeled. To describe real oils, it is necessary to apply the concept of fractional continuous oils. Typical oils can be described in terms of three to ten fractional oils. If the original oil can be fitted to a set of fractional oils accurately, processes can be described even when the amounts are less than 1% of the original oil.

From the VLE measurement, a suitable characteristic variable was found that can be applied to continuous oils from several sources.

The assumptions of ideality often made with petroleum liquids were shown experimentally to apply to the shale oil and the coal oil at ambient pressure. It must be emphasized that these idealities are relative in that, in this case, the properties of pure components are never known but are deduced from properties of the continuous oil.

Table 3. Vapor Fraction in the Sequence of Operations of KS-1 Shale Oil

Temp. K	Vapor Fraction Exact Calc.	 Three Fractional Oil Basis
	Successive Flash	
640	0.595	0.603
690	0.526	0.508
730	0.498	0.493
760	0.474	0.479
790	0.562	0.571
	Alternate Flash/Condensation	
640	0.595	0.60
690	0.526	0.509
650	0.498	0.507
681	0.496	0.478
655	0.491	0.506
	Successive Condensation	
640	0.595	0.603
594	0.498	0.522
566	0.486	0.524
548	0.464	0.529
537	0.521	0.612

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Notation

C = normalization factor
F = distribution density function
f = fugacity
g = function, Eq. 2
K = equilibrium ratio
K_w = Watson K factor
m = exponent
Mw = molecular weight
N = number of components
P = pressure, atm
Q = flow rate, cm^3/min
T = temperature, K
V = mole fraction vaporized
w = weight, mole fraction
x = mole fraction, liquid phase
y = mole fraction, vapor phase

Greek letters

σ = parameter, Eq. 28
τ = characteristic variable
ψ = distribution function of fractional oil
θ = dimensionless temperature

Subscripts

b = boiling
f = feed
i = component
j = component
ℓ = liquid
p = pure
ref = reference
v = vapor
o = initial
6 = hexane

Superscripts

o = pure component
f = feed
ℓ = liquid
v = vapor
$\sim$ = pure component

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