CHAPTER II

CONTINUOUS COMPONENT
2.0 Composition distribution function

Matter is discrete. Expression of composition as a continuous distribution is therefore unnatural or even improper. Yet this concept has its advantages over the method of lumping or using pseudocomponent. This, for example, avoids the inherent arbitrariness in choosing the representative component and also preserves the dispersion of properties better.

The computational procedures for mixtures containing continuous components, though similar to the methods for multicomponent mixtures, are not quite the same and differ in several respects. A brief account is therefore being presented.

2.1 Composition representation and distribution function

The continuous component method requires that the composition be expressed as a distribution function of a parameter and this parameter has to be chosen. In many situations, more than one parameter may be required. Usually the nature of the problem suggests the parameters pertinent for a specific mixture. Thus for petroleum fractions, normal boiling point is a natural choice for one parameter.

The rationale for choosing parameter has been presented in the first chapter, section 1.1.1 and distribution functions used by different workers have been mentioned. Here the mathematical formulation is outlined in brief.

In a generalised situation, let there be $p$ parameters designated by $\tau_1, \tau_2, \ldots, \tau_p$ called "composition parameters" and let the
distribution function for the number of moles in the mixture be
\( n(\tau_1, \tau_2, \ldots, \tau_p) \), that is \( n(\tau) \, d\tau \) is the number of
components with parameter values between \( \tau \) and \( \tau + d\tau \). Then the
total number of moles of mixture will be given by

\[
N = \int \int \cdots \int n(\tau_1, \tau_2, \ldots, \tau_p) \, d\tau_1 \, d\tau_2 \cdots d\tau_p \tag{2.1}
\]

the limits of integration being the minimum and maximum values of
\( \tau_i \)'s. The distribution function \( n(\tau) \) is obviously a single
valued nonnegative, integrable function for any physically real
situation.

The mole fraction distribution function may now be defined as

\[
x(\tau_1, \tau_2, \ldots, \tau_p) = \frac{1}{N} n(\tau_1, \tau_2, \ldots, \tau_p)
\]

\[
= \frac{n(\tau_1, \tau_2, \ldots, \tau_p)}{\int \int \int n(\tau_1, \tau_2, \ldots, \tau_p) \, d\tau_1 \, d\tau_2 \cdots d\tau_p} \tag{2.2}
\]

In some cases, the distribution function may be represented by a
summation of impulse functions over a particular parameter. Let,
in a particular situation, the number of parameters be two, and
let the distribution be described as a sum of delta functions in
one of the parameters. Then the distribution function can be
written as:

\[
n(\tau_1, \tau_2) = \sum_i \frac{n_i(\tau_1)}{n_1(\tau_1)} \delta(\tau_2 - \tau_{2i}) \tag{2.3}
\]
where \( \tau_{2i} \)'s are the impulse coordinate values for the parameter \( \tau_2 \), or in other words, \( \tau_2 \) can take only discrete values given by \( \tau_{2i} \)'s. For each of these values of \( \tau_2 \), the distribution function in parameter \( \tau_1 \) is given by \( \bar{n}_1(\tau_1) \). The term "ensemble" is often used to describe a distribution function of this type. In this case, the total number of moles is given by:

\[
N = \sum_i \int \bar{n}_1(\tau_1) \, d\tau_1 \tag{2.4}
\]

while the number of moles of the \( i \)th member of the "ensemble" will be

\[
N_i = \int \bar{n}_1(\tau_1) \, d\tau_1 \quad \tag{2.5}
\]

The composition distribution will naturally be given by:

\[
x(\tau_1, \tau_2) = \frac{\sum_i n_i(\tau_1) \delta(\tau_2 - \tau_{2i})}{\sum_i \int \bar{n}_1(\tau_1) \, d\tau_1} \tag{2.6}
\]

In this case one may define the mole fraction of the \( i \)th element of the ensemble as:

\[
x_i = \frac{\int \bar{n}_i(\tau_1) \, d\tau_1}{\sum_i \int \bar{n}_1(\tau_1) \, d\tau_1} \tag{2.7}
\]

A complex mixture may also contain well defined components. For such components, it is clearly advantageous to use the normal method of representation, and such components are termed
"discrete" components.

If several discrete components be present, and if \( n_{d_j} \) be the number of moles of the \( j \)th discrete component in the mixture, then the total number of moles of the mixture will be given by:

\[
N = \sum_j n_{d_j} + \int n(\tau) \, d\tau
\]

and the corresponding composition expressed in terms of mole fraction will be:

\[
x_{d_j} = \frac{n_{d_j}}{N}
\]

\[
x(\tau) = \frac{n(\tau)}{N}
\]

It is quite important to ensure that the parameters chosen are appropriate for the specific field. For petroleum fluids, one of the most natural choices is the normal boiling point. Molecular weight or carbon number may also serve in place of boiling point. Other important factors deciding properties of petroleum fractions include aromaticity, degree of branching, and occasionally it is convenient to use these as parameters for defining ensembles.

2.2 Thermodynamic formulations

Mixtures with continuous component representation require certain modifications of definition of thermodynamic properties. The basis has been discussed in details by Salacuse and Stell (1982), Briano and Glandt (1983), Kehlen, Ratzsch and Bergman (1985). It
has been shown that the thermodynamic relations are quite similar and normally the summation over mole fraction has to be replaced by an appropriate integral. In phase-equilibrium studies, the most important property is the chemical potential. Kehlen, Ratzsch and Bergmam (1985) express chemical potential as:

$$\mu(r, T, P; x) = \mu^*(r, T, P) + RT \ln f(r, T, P; x) \quad (2.10)$$

where \( \mu^* \) is the standard state chemical potential including the standard state fugacity term of the distribution and \( f \) is the fugacity. The fugacity can be written in the usual manner:

$$\ln f(r, T, P; x) = \ln x(r) + \ln \gamma(r, T, P; x) \quad (2.11)$$

This equation just states that the fugacity of material with value of parameter between \( r \) and \( r + dr \), at temperature \( T \), pressure \( P \) and mole fraction distribution \( x(r) \), is given by the product of mole fraction distribution function and activity coefficient. This is useful for the liquid phase. For the gas phase, the fugacity is usually expressed in terms of fugacity coefficient:

$$\phi y P = f \quad (2.12)$$

This relation also is identical in form to the relation for mixtures with discrete components. But it is to be noted that there is one basic difference. In the expression for chemical potential equation (2.10), for example, the standard state chemical potential contains a hidden term, whose value remains indeterminate. This however is not a handicap in calculating
phase equilibria, as generally this term will appear on both the sides and cancel off. This discrepancy has been clearly stated by Briano and Glandt (1983) and it gives a clue as to when the distributed component method will not be applicable. An example of such a situation would be the separation of a single pure material which is also included in a continuous description. Most of the workers, who have applied the continuous component concept to petroleum fluids, have primarily investigated vapour-liquid equilibria and flash calculation. Ratzsch and Kehlen (1985), Cotterman and Prausnitz (1985), Wang and Whiting (1987), Abbasian and Weil (1988), all have calculated equilibrium flash vapourisation or constant pressure-temperature (P-T) flash. Ratzsch and Kehlen showed, assuming ideality for both vapour and liquid phases, that if the distribution function for the equilibrium vapour phase be Gaussian, the distribution function for the corresponding liquid will also be Gaussian. The same result has been found by Prausnitz and Cotterman to apply when the composition is described by a distribution. It has also been found that the distribution functions for all the three streams — feed, vapour and liquid — can not be represented by the same type of distribution function. Wang and Whiting (1987) avoided this problem by using a completely numerical procedure.

2.3 Flash vapourisation equations

The basic equations for flash vapourisation may be summarised as
follows:

$$y_d = K_d x_d$$ \hspace{1cm} (2.13a) for discrete components

$$y(T) = K(T) x(T)$$ \hspace{1cm} (2.13b) for the distribution

with mole fraction summation equations

$$\sum y_d + \int y(T) d\tau = 1$$ \hspace{1cm} (2.14a)

and

$$\sum x_d + \int x(T) d\tau = 1$$ \hspace{1cm} (2.14b)

The equation for calculation of \( P - T \) flash becomes

$$\sum \frac{[K_d - 1]}{1 + \frac{V}{P} K_d} x_f + \int \frac{[K(T) - 1]}{1 + \frac{V}{P} K(T)} x_f(T) d\tau = 0$$ \hspace{1cm} (2.15)

The equilibrium ratio values can be calculated using the usual procedure for vapour-liquid equilibria. The simplest way is to assume both the vapour phase and liquid phase mixtures to be ideal. This has been used by Hoffman (1968), Ratzsch and Kehlen (1985). Cotterman and Prausnitz (1985) have used SRK equation of state. Wang and Whiting (1988) used the UNIFAC model for the liquid phase and virial equation of state for the vapour phase. Wang and Whiting (1988) found the cubic splines to be best for numerical representation of the distribution. Abbasian and Weil (1988) assumed ideal phase behaviour, but they assumed a distribution in the form of a summation of Gaussian density functions.

2.4 Batch distillation

The problem of batch distillation of a continuous mixture may now
be analysed as an example. This also is a problem that, despite its considerable importance, has received little attention. Hoffman (1969) treated this problem assuming ideal behaviour of both vapour and liquid phases, and with several additional approximations.

Let the batch distillation of a mixture be considered whose composition can be described by a single composition parameter. Let the initial amount of liquid be $L_0$, and feed composition distribution be $x_0(\tau)$, and let at any particular instant during batch distillation, the amount of residual liquid be $L$, and the composition distribution of the liquid be $x(\tau,L)$. It should be noted that the distribution will be a function of $L$, the amount of residue.

A material balance for the component specified by the value of the parameter between $\tau$ and $\tau + d\tau$, yields:

$$d\left[L x(\tau,L)d\tau\right] = y(\tau,L)\, dL\, d\tau$$

(2.16)

where $y(\tau,L)$ is the composition distribution of the vapour.

Since the parameter $\tau$ is independent of the amount of liquid $L$, the equation can be written as:

$$L \frac{dx}{dL} = y - x$$

(2.17)

Replacing $y(\tau,L)$ by $K \, x(\tau,L)$, this equation can be rewritten as

$$\frac{L}{x} \frac{dx}{dL} = K - 1$$

(2.17a)

where $K$ is the vapour - liquid equilibrium ratio. This should properly be expressed as $K(T,P ; x(\tau,L))$ as $K$ is a function of
temperature, pressure and the equilibrium liquid distribution. In addition to the above relation, two mole fraction constraint equations - one for the liquid phase and other for the vapour phase must be satisfied:

\[
\int x(\tau, L) \, d\tau = 1 \quad \text{for all } L \quad (2.17b)
\]

\[
\int K x(\tau, L) \, d\tau = 1 \quad \text{for all } L \quad (2.17c)
\]

It will be shown that the second constraint determines the bubble point, which is also the temperature of the residue. There is no analytic method for solution of these equations - the function \(x_0\) may be quite arbitrary and generally a closed form expression for the function \(K\) may not be available. It is therefore necessary to use numerical methods for solution. The equations can be simplified if both gas and liquid phase mixtures are assumed to behave ideally. Even then no analytic solution can be obtained. However some of the interesting features of batch distillation may be deduced by analysing the equation properties. The qualitative conclusions remain valid for a large class of nonideal solutions, which do not exhibit phenomena like azeotropy or liquid phase splitting.

Let the parameter representing the composition distribution be normal boiling point, i.e let \(\tau\) denote normal boiling point. If both the gas and liquid mixtures be ideal, then \(K\) will be a function of normal boiling point \(\tau\), temperature \(T\) and pressure \(P\) in the following manner:

\[
K(\tau, T) = \frac{P_s(\tau, T)}{P} \quad (2.18)
\]
where \( P_s(\tau, T) \) is the saturation pressure of the component with normal boiling point \( \tau \) and at temperature \( T \).

As a further simplification, let
\[
\ln P_s(\tau, T) = A(\tau) + \frac{B}{T}
\]
where \( B \) is a constant for all the components. This type of relation is quite representative of various hydrocarbon homologous series.

Then
\[
K(\tau, T) = \exp \left[ A(\tau) + \frac{B}{T} \right]
\]

Let the relative volatility \( \alpha(\tau : \tau_0) \) be defined as
\[
\alpha(\tau : \tau_0) = \frac{K(\tau, T)}{K(\tau_0, T)}
\]
so that
\[
\alpha(\tau : \tau_0) = \exp [A(\tau) - A(\tau_0)]
\]
Assuming that the pressure is expressed in units of atmosphere and that the batch distillation pressure is also atmospheric,
\[
A(\tau) = - \frac{B}{\tau}
\]
and
\[
\alpha(\tau : \tau_0) = \exp B \left( \frac{1}{\tau_0} - \frac{1}{\tau} \right)
\]
as
\[
K(\tau, T) = \exp B \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)
\]
using this value of \( K \), the equation (2.17c) becomes
\[
\int K(\tau_0, T) \alpha(\tau : \tau_0) x(\tau, L) d\tau = 1
\]
or,
\[
K(\tau_0, T) \bar{\alpha} = 1
\]
where \( \bar{\alpha} \) is the average relative volatility defined by
\[
\bar{\alpha} = \int \alpha(\tau : \tau_0) x(\tau, L) d\tau
\]
and \( K(\tau_0, T) \) is the equilibrium ratio of component with normal boiling point \( \tau_0 \) at temperature \( T \).

Since \( K(\tau_0, T) \frac{a}{\alpha} = 1 \), the temperature is given by

\[
T = \frac{1}{\tau_0} + \frac{1}{B} \ln \frac{1}{\alpha}
\]

(2.28)

when the amount of residue is \( L \).

The material balance equation (2.17a) now becomes

\[
\frac{L}{x} \frac{dx}{dL} = \left[ \frac{\alpha}{\alpha} - 1 \right]
\]

or,

\[
\frac{d \ln x}{d \ln L} = \left[ \frac{\alpha}{\alpha} - 1 \right]
\]

(2.29)

This equation on integration will give the variation of \( x \), that is the composition distribution function, with \( L \). No analytic solution of this equation is possible and generally, numerical methods have to be used.

Differentiation of the vapour phase mole fraction summation equation (2.26) with respect to temperature leads to a relationship for the slope or derivative of the differential distillation curve:

\[
\frac{d}{dT} \int K(\tau_0, T) \alpha(\tau : \tau_0) x(\tau, L) d\tau = 0
\]

(2.30)

Noting from equation (2.25) that \( K(\tau_0, T) \) is independent of \( \tau \) and \( L \), and using the differential material balance equation (2.17), it can be shown that

\[
\frac{1}{L} \frac{dL}{dT} \left[ K(\tau_0, T) \frac{a^2}{\alpha^2} - 1 \right] = \frac{B}{\tau^2}
\]

(2.31)
where
\[
\overline{\alpha^2} = \int \alpha^2 \, d\tau
\]
that is the average of the square of relative volatility.

The equation (2.31) may also be written as:
\[
\frac{1}{L} \frac{dL}{dT} \left[ \frac{\overline{\alpha^2}}{(\overline{\alpha})^2} - 1 \right] = \frac{B}{T^2}
\]
(2.32)
Thus the slope of the differential distillation curve is a measure of \(\overline{\alpha^2}\).

It can be easily shown that the second derivative \(\frac{d^2L}{dT^2}\) is similarly a measure of \(\overline{\alpha^3}\). This concept will be useful later for the inversion of batch distillation curve.

The behaviour during batch distillation can be qualitatively explored from equation (2.29) which describes the differential distillation curve and allows calculation of composition of residual liquid at any stage of distillation.

Assuming the lower and upper limits of \(\tau\) to be \(\tau_0\) and \(\tau^*\) respectively, \(\alpha\) will be a monotonically decreasing continuous function of \(\tau\), with a value 1 at \(\tau = \tau_0\). At any instant of distillation \(\overline{\alpha}\) will have a value bounded by \(\alpha(\tau^*: \tau)\) and 1, that is
\[
\alpha(\tau^*: \tau_0) < \overline{\alpha} < \alpha(\tau_0: \tau_0)
\]
As the distillation proceeds, \(\overline{\alpha}\) changes, decreasing from its initial value to its final value \(\alpha(\tau^*: \tau_0)\). At any specific \(L (L > 0)\), therefore the following must be satisfied:
\[
\overline{\alpha} = \alpha(\tau^+: \tau_0)\]
for some $\tau^+$, such that $\tau_0 < \tau^+ < \tau^*$

Now consider the integral of equation (2.29) for a fixed value of $\tau$, with $\tau < \tau^+(L)$ during distillation from $L_0$ to $L$. Then there will exist a positive number $q$ such that

$$\left(\frac{\alpha}{\alpha} - 1\right) > q$$

and then the lower bound of integral will be $\ln\left[\left(\frac{L}{L_0}\right)^q\right]$.

Thus we get:

$$\frac{x}{x_0} < \left(\frac{L}{L_0}\right)^q$$

which indicates that on the average $X$ varies approximately as

$$\left(\frac{L}{L_0}\right)^q$$

where $\left(\frac{\alpha}{\alpha} - 1\right) < q < \left(\frac{\alpha}{\alpha(\tau^* - \tau_0)} - 1\right)$, and in the limit as all liquid vapourises:

$$\lim_{L \to 0} x \propto \left(\frac{L}{L_0}\right)^{\left(\frac{\alpha}{\alpha(\tau^* - \tau_0)} - 1\right)}$$

Now consider a value of $\tau$, such that $\tau^+(L_0) < \tau$ for the particular value of $\tau$. Analysis similar to the one made before shows that is then

$$\frac{x}{x_0} > \left(\frac{L}{L_0}\right)^{-q}$$

where $q$ is some positive number. With progress of distillation, $L$ will decrease, so that $L/L_0$ is always less than 1. Therefore $x/x_0$ will become greater than 1. This means that $x$ will first increase
till \( r^+ \) equals \( r \). Then \( x \) will start to decrease in the manner discussed earlier. There will be only one value of \( r \), \( r = r^* \) for which the second phase will not exist and \( x(r^*) \) will become indefinitely large, as \( L \) becomes zero.

Thus we get the well known result that in a batch distillation, the maximum temperature reached will be the boiling point of the least volatile component and that the last drop to be evaporated will be "pure least volatile material". For continuous mixtures, this implies that the composition distribution in the last drop will be a \( \delta \) function.

2.5 Batch distillation computation results

For illustrating the main features of batch distillation, results of computation for a wide boiling mixture with boiling point range from 40°C to 430°C with uniform composition distribution are presented in figures 2.1 to 2.6. The mixture has been assumed to behave ideally, with vapour pressure following the relation:

\[
\ln P^s(r,T) = A(r) + \frac{B}{T}
\]

The TBP and the batch distillation curves are shown in figure-2.1. It is interesting to note that the batch distillation curve is nearly a straight line, showing a strong curvature and change of slope only near the FBP. Accurate experimental determination of this region of the curve would be difficult, with column holdup presenting a major difficulty.

In figures 2.2 to 2.6 changes in composition distribution as distillation progresses are shown. The changes conform to the
analysis presented here. Initially the volatile parts of the feed distill off quite rapidly, while all the higher boiling components register almost similar increases in composition in the residue. The distribution curve becomes S shaped, and finally when most of the material has evaporated, it approaches a delta function form.

The figure - 2.6 shows how the concentration of any specific component changes with the progress of distillation. The most volatile components show a rapid and almost exponential decrease. The fraction with relative volatility equal to average relative volatility of the feed starts to decrease very slowly, and all components more volatile than this fraction shows monotonic decrease as expected. But components with lower relative volatilities show an initial increase in concentration, passes through a maximum, then decreases in the same manner as the more volatile parts. Only the maximum boiling component shows a continuous rise as shown in the analysis.

The final boiling point that is the point at zero residue is thus a singular point.

2.6 The inverse problem

The inverse problem, that is finding out the composition distribution of the feed mixture given the batch distillation curve, is also of interest. There is no theoretical analysis of this problem in literature. Hoffman (1969) presents a similar problem for continuous mixture, but uses empirical methods. The inverse problem can not be solved if the general nature of
behaviour is not known, that is if the functional relationship of the vapour liquid equilibrium ratio with temperature and the composition parameters be unknown. Such relationships will therefore have to be assumed.

Before attempting the inversion problem for continuous mixture, it would be instructive to investigate the situation for simple mixtures. The simplest situation is of course that for an ideal binary mixture. It will be assumed that the vapour-liquid equilibrium is given by:

\[ K = \frac{1}{T} \exp B \left( \frac{1}{\tau} - \frac{1}{T} \right) \]  

(2.33)

where \( B \) is same for all the components, and \( \tau \) is the normal boiling point and also that the pressure is atmospheric. Then the relative volatility \( \alpha \) will be independent of temperature and composition.

The inverse problem may now be stated as follows:

Given the batch distillation curve, it is necessary to find out the components and the composition of the feed. The components will be identified by their normal boiling points. The initial boiling point of the batch distillation curve will be the bubble point of the mixture, and the final boiling point will be the boiling point of the heaviest component. Since the final boiling point is known, the heaviest component can be identified. The problem now is to identify the lighter component and also to find the composition.

Let the relative volatility be expressed with respect to the
heaviest component. Let \( T_{\text{in}} \) indicate the initial boiling point in the batch distillation curve.

One can therefore write, at \( T_{\text{in}} \)

\[
\alpha K^* x_1 + K^*(1 - x_1) = 1
\]  

(2.34)

where \( K^* \) is the V-L-E ratio of the heavy component at \( T_{\text{in}} \) and \( x_1 \) is the composition in mole fraction for the light component and \( \alpha \) is its relative volatility.

Rearrangement of equation (2.34) gives:

\[
x_1 = \frac{1}{\alpha - 1} \left[ \frac{1}{K^*} - 1 \right]
\]

(2.35)

while the batch distillation equation is:

\[
\frac{1}{L} \frac{dL}{dx_1} = \frac{1}{x_1} \left( \frac{1}{\alpha K^* - 1} \right)
\]

(2.36)

The equation (2.34) remains valid all along the path of distillation.

Differentiating equation (2.34) with respect to distillation temperature \( T \), and using equation (2.36) one obtains:

\[
\frac{1}{K^*} \frac{dK^*}{dT} + \frac{1}{L} \frac{dL}{dT} \left[ \frac{\alpha^2}{K^* - 1} \right] = 0
\]

(2.37)

where \( \alpha^2 = (\alpha^2 x_1 + x_2) \), is the average of the square of relative volatility for the binary mixture. Rearranging

\[
\frac{\alpha^2}{(\alpha')}^2 = 1 - \frac{L}{K^*} \frac{dK^*}{dT} \frac{dT}{dL}
\]

(2.38)

This equation, along with equation (2.34) and the explicit expression for \( K^* \), can be solved to find out both \( \alpha \) and \( x_1 \). The explicit value of \( \alpha \) if \( K \) be given by equation (2.33) will be
\[ \alpha = \frac{1}{K_{T_{in}}^*} \left[ 1 - \frac{1}{\frac{T_{in}^2 B}{L} \frac{1 - K_{T_{in}}^*}{dL/dT}} \right] \]  

(2.39)

where \( K_{T_{in}}^* \) is the vapour-liquid equilibrium ratio for the heaviest component at initial boiling point \( T_{in} \).

Since \( \alpha \) is given by:

\[ \alpha = \exp \left[ B \left( \frac{1}{\tau_0} - \frac{1}{\tau^*} \right) \right] \]

where \( \tau_0 \) is the boiling point of the lighter component, the component is identified. The results of this analysis for the binary system can therefore be summed up as follows:

i) The boiling point of the heaviest component is given by the end point temperature of the batch distillation curve.

ii) The boiling point of the lighter component and the composition are given by the starting slope of the distillation curve and \( T_{in} \), the initial point on the distillation curve.

Since the distillation curve is unique, the following corollary may be stated:

For a binary mixture the initial boiling point and the slope of the distillation curve at the initial boiling point decides the curve completely.

The existence of a unique distillation curve also follows from the fact that for a binary mixture, every intermediate composition will be attained by the residue.

For multicomponent system the situation is somewhat different.
The situation for a ternary system is now presented.

In this case also, the solution of the inverse problem requires evaluation of boiling points of the three components, that is \( \tau_1, \tau_2, \tau_3 \) and the composition \( x_1, x_2, x_3 \). Of these the boiling point of the heaviest component will be given by the final point of the distillation curve. Also out of three compositions, two are independent. Thus, four quantities \( \tau_1, \tau_2, x_1 \) and \( x_2 \), need to be determined. For a multicomponent situation with \( n \) components, the number of unknowns will be \( 2(n - 1) \). The explicit equation for the ternary system will be:

\[
K^*(\alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3) = 1 \quad \text{or} \quad K^* \alpha = 1
\]

\[
L \frac{dx_1}{dL} = (\alpha_1 K^* - 1) x_1 dL \quad \text{or} \quad \frac{dx_1}{dL} = \frac{1}{L} (\alpha_1 K^* - 1) \quad (2.41a)
\]

\[
L \frac{dx_2}{dL} = (\alpha_2 K^* - 1) x_2 dL \quad \text{or} \quad \frac{dx_2}{dL} = \frac{1}{L} (\alpha_2 K^* - 1) \quad (2.41b)
\]

\[
L \frac{dx_3}{dL} = (\alpha_3 K^* - 1) x_3 dL \quad \text{or} \quad \frac{dx_3}{dL} = \frac{1}{L} (\alpha_3 K^* - 1) \quad (2.41c)
\]

Now along the distillation path

\[
\frac{d}{dT} \left[ K^* \left( \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 \right) \right] = 0 \quad (2.42)
\]

i.e. \( \frac{d}{dT} \left\{ K^* \alpha \right\} = 0 \)

The relation given by equation (2.38) remain valid and may be written as

\[
\frac{\alpha^2}{(\alpha)}^2 = 1 - \frac{L}{K^*} \frac{dK^*}{dL}
\]

(2.43)

It may be noted that by direct differentiation of the average of
m th power of $\alpha$, one gets the recurrence relation:

$$\frac{d}{d \ln L} \alpha^m = K^* \alpha^{m+1} - \alpha^m$$  \hspace{1cm} (2.44)

Continued differentiation of equation (2.42) gives:

$$\overline{\alpha^3} = \overline{\alpha^2} \cdot \overline{\alpha} - \frac{L}{K^*} \frac{d}{dL} \left( \frac{L}{K^*} \frac{dK^*}{dL} \right)$$  \hspace{1cm} (2.45)

$$\overline{\alpha^4} = (\overline{\alpha^2})^2 - 2 \overline{\alpha} \overline{\alpha^3} - 2(\alpha)^2 \overline{\alpha^2} - \frac{L}{K^*} \frac{d}{dL} \left[ \frac{L}{K^*} \frac{d}{dL} \left( \frac{L}{K^*} \frac{dK^*}{dL} \right) \right]$$  \hspace{1cm} (2.46)

where $\frac{d}{dL}$ is differentiation along the path of distillation, and may be replaced by the operator

$$\frac{d}{dL} = \frac{dT}{dL} \frac{d}{dT}$$

Thus $\overline{\alpha^3}$ of the feed is related to the second derivative and $\overline{\alpha^4}$ to the third derivative of the distillation curve at the initial boiling point. These therefore can be evaluated if the specific relationship between temperature and $K^*$ be known, using equations (2.43) to (2.48).

Now since,

$$\overline{\alpha} = \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3$$  \hspace{1cm} (2.47)

$$\overline{\alpha^2} = \alpha_1^2 x_1 + \alpha_2^2 x_2 + \alpha_3^2 x_3$$  \hspace{1cm} (2.48)

$$\overline{\alpha^3} = \alpha_1^3 x_1 + \alpha_2^3 x_2 + \alpha_3^3 x_3$$  \hspace{1cm} (2.49)

$$\overline{\alpha^4} = \alpha_1^4 x_1 + \alpha_2^4 x_2 + \alpha_3^4 x_3$$  \hspace{1cm} (2.50)

these equations can in principle be used to evaluate the four quantities $\alpha_1$, $\alpha_2$, $x_1$ and $x_2$. It may be noted that $\alpha_3 = 1$ and
The results can be extended directly to mixture containing larger number of components and finally to the case of continuous mixtures. In this case the same equations hold, but the averages are to be expressed as:

\[ \overline{a_3} = \int \alpha x \, d\tau \]  \hspace{1cm} (2.51)

\[ \overline{a_2} = \int a_2^2 x \, d\tau \]  \hspace{1cm} (2.52)

etc

It is therefore observed that these integrals are related to higher order derivatives of the distillation curve at initial point. It is obvious that for a continuous mixture, all the derivatives, that is infinite number of these will be required to evaluate the function \( x \). The starting point for the composition distribution or the relative volatility of the lightest component will be given by:

\[ \alpha_{r0} = \lim_{m \to \infty} \left( \frac{\alpha^m}{m!} \right) \]  \hspace{1cm} (2.53)

This statement can be proved quite easily for discrete systems, and is assumed to be valid for continuous systems as well.

The framework for inversion of the batch distillation curve for a continuous mixture can now be presented. In this thesis only the theoretical analysis is being provided.

For the continuous system, the normal boiling point \( \tau \) is chosen as the composition parameter. The vapour and liquid phases are assumed to behave ideally. Then the relative volatility function
\( \alpha \) is a monotonic continuous decreasing function of \( \tau \). It may therefore be assumed that the series of function 1, \( \alpha \), \( \alpha^2 \), \( \alpha^3 \), will span the function space of all non negative, bounded, piecewise continuous distribution functions defined over the specific range of values of \( \tau \). Let \( F_1, F_2, F_3 \), etc denote the elements of the orthogonal basis set extracted by Gram Schmidt procedure. That is:

\[
\begin{align*}
F_1 &= \frac{1}{\|1\|} \\
F_2 &= \frac{\alpha - \langle \alpha, F_1 \rangle F_1}{\| \alpha - \langle \alpha, F_1 \rangle F_1 \|} \\
F_3 &= \frac{\alpha^2 - \langle \alpha^2, F_1 \rangle F_1 - \langle \alpha^2, F_2 \rangle F_2}{\| \alpha^2 - \langle \alpha^2, F_1 \rangle F_1 - \langle \alpha^2, F_2 \rangle F_2 \|} \\
&\quad \text{etc}
\end{align*}
\]

The symbol \( \langle p, q \rangle \) stands for the inner product defined as:

\[
\langle p, q \rangle = \int_0^\tau p(\tau) q(\tau) \, d\tau
\]

which is just a real valued function of \( p \) and \( q \).

The symbol \( \| p \| \) stands for norm of \( p \), defined as:

\[
\| p \| = \| \langle p, p \rangle \|^{1/2}
\]

The distribution function \( x \) may now be obtained as series expansion:

\[
x(\tau) = \langle x, F_1 \rangle F_1(\tau) + \langle x, F_2 \rangle F_2(\tau) + \ldots
\]

where

\[
\begin{align*}
\langle x, F_1 \rangle &= \frac{\langle x, 1 \rangle}{\| 1 \|} \\
\langle x, F_2 \rangle &= \frac{\langle x, \alpha \rangle - \langle \alpha, F_1 \rangle \langle x, F_1 \rangle}{\| \alpha - \langle \alpha, F_1 \rangle F_1 \|}
\end{align*}
\]
\[
\langle x, F_3 \rangle = \frac{\langle x, a^2 \rangle - \langle a^2, F_1 \rangle F_1 - \langle a^2, F_2 \rangle F_2}{\| a^2 - \langle a^2, F_1 \rangle F_1 - \langle a^2, F_2 \rangle F_2 \|}
\]

and so on.

It is to be noted that

\[
\langle x, 1 \rangle = \int x(\tau) \, d\tau = 1
\]
\[
\langle x, a \rangle = \int x(\tau) \, a(\tau) \, d\tau = \bar{a}
\]
\[
\langle x, a^2 \rangle = \int x(\tau) \, a^2(\tau) \, d\tau = \bar{a}^2
\]
\[
\langle x, a^n \rangle = \int x(\tau) \, a^n(\tau) \, d\tau = \bar{a}^n
\]

These quantities are related to the derivative of distillation curve at the initial point and may be determined from there.

The above discussion is therefore a constructive proof of the existence of an unique solution to the inverse problem for a continuous mixture describable by a simple parameter - normal boiling point - and behaving ideally in both liquid and vapour phases. In actual application, the results have to be extended to mixtures containing multiple ensembles as well as discrete components and not necessarily behaving ideally, particularly in the liquid phase.
Summary
Continuous component representation requires identification of appropriate composition parameters for describing the composition distribution. A complex mixture may also contain discrete components, and in special cases, may contain several ensembles. Thermodynamics of complex mixtures is similar to the thermodynamics of systems containing discrete components, though some modifications in expressions and concepts are necessary. Several vapour-liquid equilibrium problems have been analysed, one of which - the problem of batch distillation - has been analysed in detail. The batch distillation problem has been chosen since, despite its importance, it has received inadequate attention. The qualitative features of batch distillation have been deduced from consideration of the forms of the equations and expressions. The variation of composition of the residue with progress of distillation has been computed and the singular nature of the final boiling point has been indicated.

The inverse problem, that is finding the feed composition, given the batch distillation curve, has also been addressed. It has been shown that for ideal vapour and liquid phase behaviour, the derivatives of the distillation curve at initial boiling point are related to the average of relative volatility and its higher powers. The original composition may in principle therefore be extracted from the derivatives at initial boiling point. Though no actual computation of feed composition has been presented, the conceptual framework for inversion has been provided.
<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n(r) )</td>
<td>Number of moles of element of an ensemble with parameter values between ( r ) and ( r + dr )</td>
</tr>
<tr>
<td>( x(r) )</td>
<td>Mole fraction of element of an ensemble with parameter values between ( r ) and ( r + dr ) in liquid phase</td>
</tr>
<tr>
<td>( n_d )</td>
<td>Number of moles of ( j )th discrete component</td>
</tr>
<tr>
<td>( n_i(r) )</td>
<td>Number of moles of ( i )th member of ensemble having parameter values between ( r ) and ( r + dr )</td>
</tr>
<tr>
<td>( N_i )</td>
<td>Number of moles of ( i )th member of ensemble</td>
</tr>
<tr>
<td>( x_i )</td>
<td>Mole fraction of ( i )th member of ensemble in liquid phase</td>
</tr>
<tr>
<td>( x_{d_i} )</td>
<td>Mole fraction of ( i )th discrete component in liquid phase</td>
</tr>
<tr>
<td>( x_{d_j} )</td>
<td>Mole fraction of ( j )th discrete component in liquid phase</td>
</tr>
<tr>
<td>( x_i(r) )</td>
<td>Mole fraction of ( i )th member of ensemble having parameter values between ( r ) and ( r + dr ) in liquid phase</td>
</tr>
<tr>
<td>( x(r) )</td>
<td>Mole fraction of element of an ensemble having parameter values between ( r ) and ( r + dr ) in liquid phase</td>
</tr>
<tr>
<td>( y_{d_i} )</td>
<td>Mole fraction of ( i )th discrete component in vapour phase</td>
</tr>
<tr>
<td>( y_i(r) )</td>
<td>Mole fraction of ( i )th member of an ensemble having parameter values between ( r ) and ( r + dr ) in vapour phase</td>
</tr>
<tr>
<td>( y(r) )</td>
<td>Mole fraction of element of an ensemble having parameter values between ( r ) and ( r + dr ) in vapour phase</td>
</tr>
</tbody>
</table>
\( y \) Mole fraction in vapour phase

\( T \) Temperature

\( P \) pressure

\( K_{d_i} \) Phase equilibrium ratio of \( i \) th discrete component

\( K_i(\tau) \) Phase equilibrium ratio of \( i \) th member of an ensemble having parameter values between \( \tau \) and \( \tau + d\tau \)

\( K(\tau) \) Phase equilibrium ratio of element of an ensemble having parameter values between \( \tau \) and \( \tau + d\tau \)

\( F \) Total number of moles of feed

\( x_0(\tau) \) Initial mole fraction of element of an ensemble having parameter value between \( \tau \) and \( \tau + d\tau \) in feed

\( x_{f_i} \) Mole fraction of \( i \)th discrete component in feed

\( x_f(\tau) \) Mole fraction of element of an ensemble having parameter value between \( \tau \) and \( \tau + d\tau \) in feed

\( L_0 \) Initial number of moles of liquid

\( L \) Number of moles of residual liquid

\( V \) Number of moles of vapour

\( x(\tau,L) \) Mole fraction of an element of ensemble having parameter values between \( \tau \) and \( \tau + d\tau \)

\( y(\tau,L) \) Mole fraction of an element of ensemble having parameter values between \( \tau \) and \( \tau + d\tau \) in vapour phase

\( P^S(\tau,T) \) Saturation pressure of the component with normal boiling point \( \tau \) and at temperature \( T \)

\( K(\tau,T) \) Phase equilibrium ratio of the component with normal boiling point \( \tau \) and at temperature \( T \)
A(τ) Parameter function of normal boiling point τ in the equation for saturation pressure PS(τ,T) of the component with normal boiling point τ and at temperature T

B Constant for all components in the equation for saturation pressure PS(τ,T) of the component with normal boiling point τ and at temperature T

Tin Initial boiling point

K^* Tin V-L-E ratio of the heaviest component at initial boiling point Tin

<p,q> Inner product of function p(τ) and q(τ)

||p|| Norm of the function p(τ)

F1, F2, F3 Orthonormalised basis set derived from the function 1, α, α^2

f Fugacity

Greek letters

τ_p p th parameter

δ Delta function

μ Chemical potential

μ^0 Standard chemical potential

ϕ Fugacity coefficient

γ Activity coefficient

a(τ :τ_0) Relative volatility

\bar{a} Average relative volatility
\( \tau_0 \)  
Minimum value of the composition parameter. When composition parameter is normal boiling point, it represents the boiling point of most volatile component.

\( \tau^* \)  
Maximum value of the composition parameter. When composition parameter is normal boiling point, it represents the boiling point of least volatile component.
References


Figure 2.1 Batch Distillation Curve
Figure 2.2 Composition - Initial Stages
Figure 2.3 Composition - Intermediate Stages
Figure 2.4 Composition — Intermediate stages
Figure 2.5 Composition —Final Stages
Figure 2.6 Residue Composition Evolution