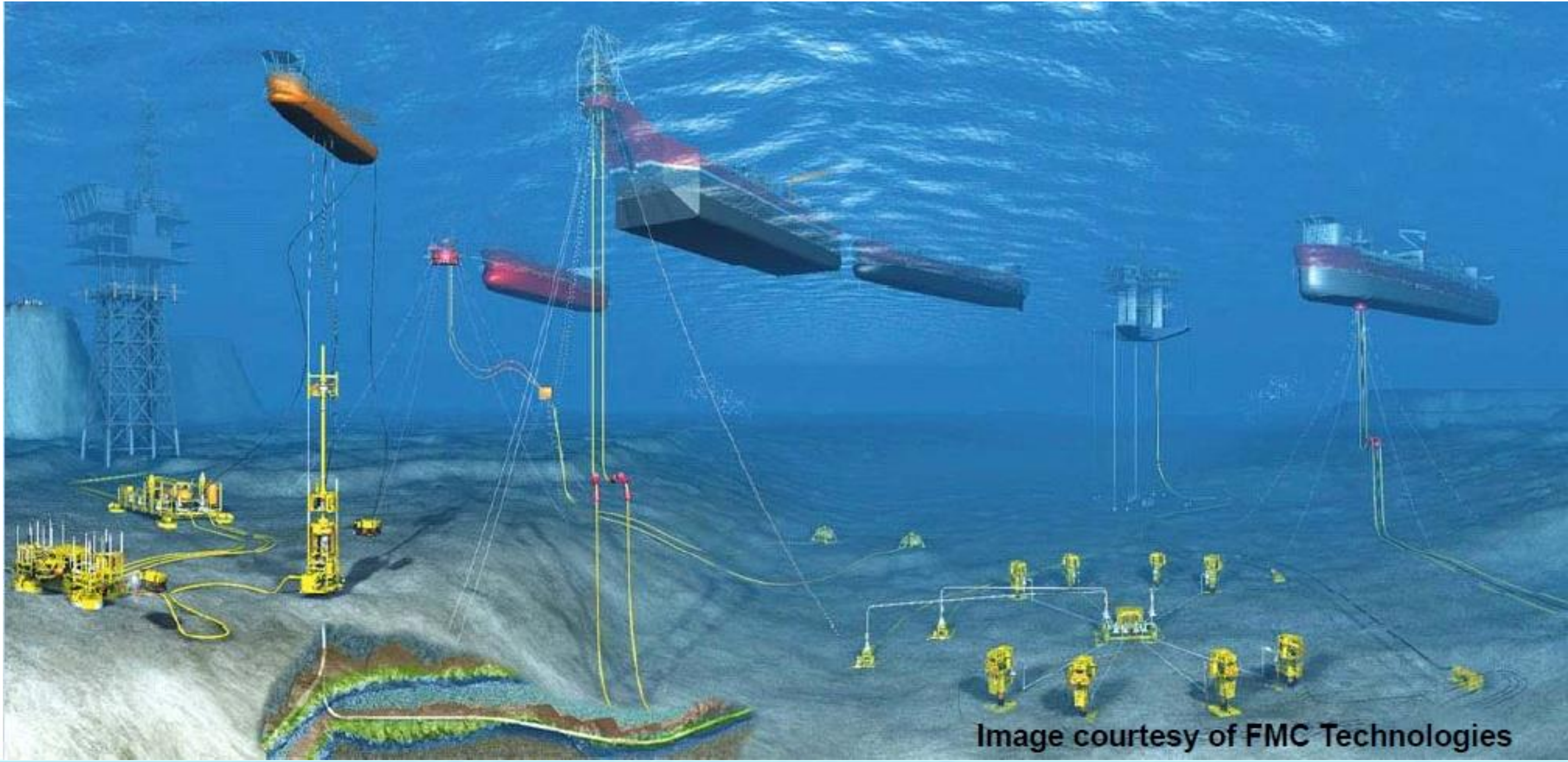
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Introduction to Offshore Engineering

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Vapor – Liquid Equilibrium (VLE)

- List of petroleum production systems that involve VLE
  - Separators
  - Reservoir
  - Pipelines
  - Wellbore
  - LNG Processing
  - NGL Processing
  - Storage
  - Oil and LNG Tankers
- Vapor/liquid equilibrium pertains to all aspects of petroleum production with which we are concerned
- Depends on the production conditions, phase changes would affect the design and operation of each production system. Ex)retrograde condensation, bubble/dew point, phases fraction

Types of VLE problems

- In a typical problem of liquid and vapor coexistence, we are usually required to know one or more of the following:
    - The phase boundaries,
    - The extent of each phase,
    - The quality of each phase.

- The main emphasis is on the quantitative prediction of the above. These three represent the three basic types of VLE problems.

Phase boundary determination

- These types of problems are either a bubble-point or a dew-point calculation. They are mathematically stated as follows:

1. <u>Bubble-point T calculation:</u> Given liquid composition (x_i) and pressure (P), determine the equilibrium temperature (T),
2. <u>Bubble-point P calculation:</u> Given liquid composition (x_i) and temperature (T), determine the equilibrium pressure (P),
3. <u>Dew-point T calculation:</u> Given vapor composition (y_i) and pressure (P), determine the equilibrium temperature (T),
4. <u>Dew-point P calculation:</u> Given vapor composition (y_i) and temperature (T), determine the equilibrium pressure (P).

Flash calculation

- Relative phase quantity determination

: In this type of problem, overall composition (z_i), pressure (P), and temperature (T) are given, and the extent of the phases (molar fractions of gas and liquid) are required.

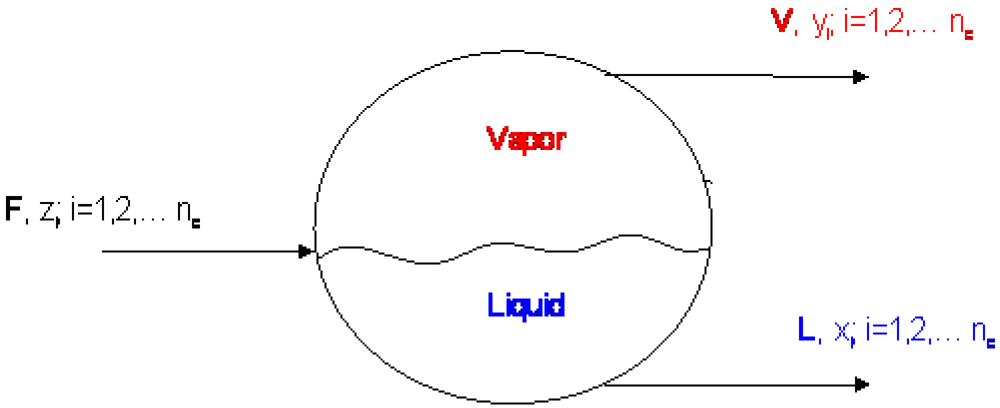
- Phase quality determination

: In this type of problem, overall composition (z_i), pressure (P), and temperature (T) are given, and the composition of the liquid and vapor phases is required.

- These two problems are referred to as *flash calculation* problems
- All three are problems that we encounter in oil and gas production engineering (Phase boundary, volume, composition)

Formulation of the VLE problem

- Consider a hydrocarbon fluid made up of known components or grouped components, for instance a certain percentage of CO2, N2 , C1, C 2-3 , C 4-6, C 7-10, C 11-15, C 16-20 and C20+.
- Place this mixture in a container such as a PVT cell, a grid block, or any other volume. Fix both the temperature and the pressure within the container. Allow enough time to reach equilibrium.
- We know the total composition {zi} of the hydrocarbon mixture. We know the pressure P and the temperature T of the mixture. What we want to know is whether there are one or two hydrocarbon phases present and what the properties of the phases are:



Where, F = L + V

- If the mixture forms a single phase, then its composition is known and it’s properties can be calculated.
- If the mixture forms two hydrocarbon phases then we need to first calculate how much is liquid and vapor (the mole fractions L and V). As part of this calculation we also calculate the relative concentration of moles in each phase (the K-values (Ki=yi/xi)). From these we can work out the compositions of each phase {xi} and {yi} and from the compositions we work out the properties of each phase.
- The same flash calculations can be used to work out the bubble point P^{bub} or dew point P^{dew} of a mixture, or more generally the saturation pressure P^{sat}. In this case we know total composition {zi} of the hydrocarbon mixture and the temperature T of the mixture. By definition, we also know that at the saturation pressure is the lowest pressure at which either (L=1 and V=0) or (L=0 and V=1). We can then solve for the K-values {Ki}) and the pressure $P=P^{sat}$.

Flash equations

- Rachford-Rice equation

$$\sum_{i=1}^{N} \frac{z_i (K_i - 1)}{1 + V(K_i - 1)} = 0$$

Where, N = number of components

Zi = overall composition, or composition of the feed

Ki = Equilibrium ratio of each components of the mixture

V = vapor fraction in the system

- This equation is a non-linear equation in one variable. The Newton Raphson procedure is usually implemented to solve it.

Summary

Type	Known information	Variables to be calculated	Equation to use
Bubble point T	P_{total}, x_i	T, y_i	(1)
Dew point T	P_{total}, y_i	T, x_i	(2)
Bubble point P	T, x_i	P_{total}, y_i	(1)
Dew point P	T, y_i	P_{total}, x_i	(2)
Flash	P_{total}, T, z_i	L/F, y_i, x_i	(3)

$$(1) \qquad 1 = K_1 x_1 + K_2 x_2$$

$$(2) \qquad 1 = \frac{y_1}{K_1} + \frac{y_2}{K_2}$$

$$(3) \qquad 1 = \frac{z_1}{1 - \frac{L}{F}\left(1 - \frac{1}{K_1}\right)} + \frac{z_2}{1 - \frac{L}{F}\left(1 - \frac{1}{K_2}\right)}$$

Equilibrium ratio - K

- A distribution coefficient used to express the ratio of the mole fraction in one phase to the mole fraction of the same component in another phase

  Vapor – Liquid: $K_i = \dfrac{y_i}{x_i}$

  where y_i and x_i are the mole fractions of component i in the phases vapor and liquid, respectively

- The values of the ratio K_i are correlated empirically or theoretically in terms of temperature, pressure and phase compositions in the form of equations, tables or graph such as the DePriester charts

Equilibrium ratio estimation

- We assumed that we knew all the equilibrium ratios. But usually we don’t. Actually, if we happen to know Ki’s, the VLE problem is soluble
- Ki value is a function of P, T, and the composition of each of the phases. If they were known, the VLE calculation would be performed by solving the Rachford-Rice objective function
- Ki’s are fairly independent of the phase composition. Numerous correlations have been developed to estimate the value of K’ for hydrocarbon component as a function of P and T.
- DePriester charts
- Wilson’s empirical correlation

$$K_i = \frac{1}{P_{r,i}} \exp\left(5.37(1+\varpi_i)(1-\frac{1}{T_{r,i}})\right)$$

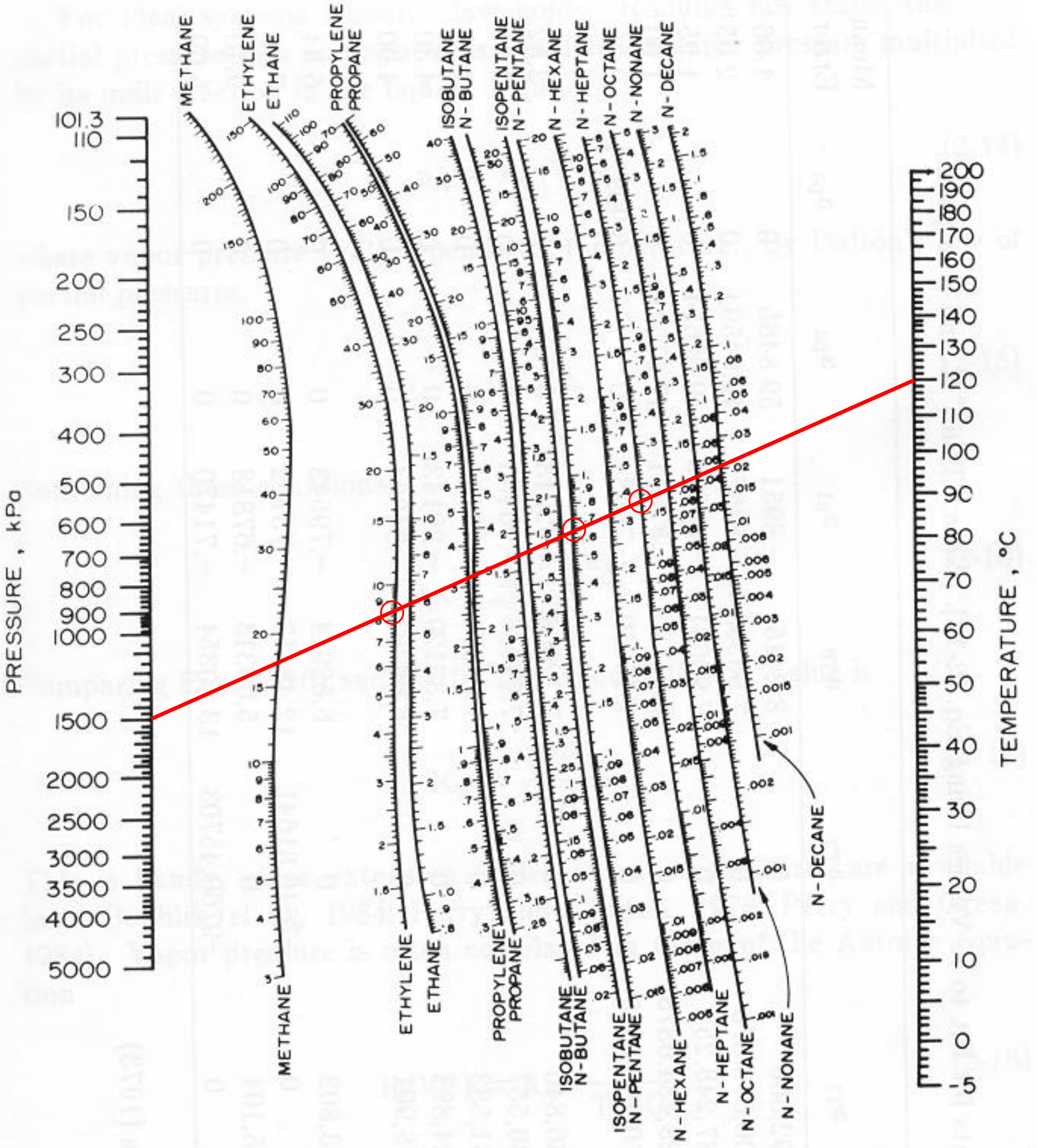


Figure 2-12. Modified DePriester chart at high temperatures. From D.B. Dadyburjor, *Chem. Eng. Prog.*, 85, April 1978. Copyright 1978, AIChE. Reproduced by permission of the American Institute of Chemical Engineers.

- at T = 120 °C and P =1500 kPa. K, are:

Ethylene	8.5
n-Pentane	0.64
n-Heptane	0.17

.

- When use K ?

- Calculate the bubble point temperature of a liquid mixture given the total pressure and liquid composition
- Calculate the dew point temperature of a vapor mixture given the total pressure and vapor composition
- Calculate the composition of the vapor and liquid, and their respective quantities, when a liquid is partially vaporized at a given temperature and pressure
- Calculate the related equilibrium vapor-liquid compositions over the range of mole fractions from 0 to 1 as a function of temperature given the total pressure

Fugacity

- For a closed system, the Gibbs energy is related to pressure and temperature as follows:

$$dG = VdP - SdT$$

- For a constant temperature process,

$$dG = VdP \qquad \text{at constant T}$$

- For an ideal gas,

$$dG = \frac{RT}{P} dP \qquad \text{at constant T}$$

- This expression by itself is strictly applicable to ideal gases. However, Lewis, in 1905, suggested extending the applicability of this expression to all substances by defining a new thermodynamic property called fugacity, f, such that:

$$dG = RTd\,ln\,f \qquad \text{at constant T}$$

- This definition implies that for ideal gases, ‘f’ must be equal to ‘P’.
- For mixtures, this expression is written as:

$$d\overline{G}_i = RT d\ln f_i \qquad \text{at constant T}$$

- where G_i and f_i are the partial molar Gibbs energy and fugacity of the i-th component, respectively.
- The definition of fugacity in terms of chemical potential becomes:
- For a pure substance,

$$d\ln f = \frac{d\mu}{RT} \quad \text{at const T}$$

(ideal gas limit)

- For a component in a mixture,

$$d\ln f_i = \frac{d\mu_i}{RT} \quad \text{at const T(16.22c)}$$

$$\lim_{P \to 0} f_i = y_i P$$ = partial pressure (ideal gas limit)

- The fugacity coefficient (Φ_i) is defined as the ratio of fugacity to its value at the ideal state. Hence, for pure substances:

$$\phi = \frac{f}{P}$$

- for a component in a mixture,

$$\phi_i = \frac{f_i}{y_i P}$$

- The fugacity coefficient takes a value of unity when the substance behaves like an ideal gas. Therefore, the fugacity coefficient is also regarded as a *measure of non-ideality*;
- The closer the value of the fugacity coefficient is to unity, the closer we are to the ideal state.

- Let’s recall, $$dlnf_i = \frac{d\mu_i}{RT}$$
- Previous expressions can be integrated for the change of state from liquid to vapor at saturation conditions to obtain:

$$\int_l^v dlnf_i = \frac{1}{RT}\int_l^v d\mu_i$$

$$ln\ f_i^{(v)} - ln\ f_i^{l} = \frac{1}{RT}(\mu_i^v - \mu_i^l)$$

- For equilibrium, $\mu_i^v = \mu_i^l$, hence

$$ln\left(\frac{f_i^v}{f_i^l}\right)_i = 0$$

- Therefore:

$$f_i^v = f_i^l \quad ; \text{i = 1, 2, … } n_c$$

- For equilibrium, fugacities must be the same as well!
- This is, for a system to be in equilibrium, both the <u>fugacity</u> and the <u>chemical potential</u> of each component in each of the phases must be equal.
- Once one of them is satisfied, the other is satisfied immediately. Using $\mu_i^v = \mu_i^l$ or $f_i^v = f_i^l$ to describe equilibrium is a matter of choice, but generally the fugacity approach is preferred.

Cubic EOS fugacity expression

- The following expressions are particularly suitable for the calculation of fugacity with cubic equations of state

SRK EOS

- Pure Substance

$$ln\phi = Z - 1 - ln(Z - B) - \frac{A}{B} ln\left(1 + \frac{B}{Z}\right)$$

- Mixtures

$$ln\phi_i = (BB)_i(Z - 1) - ln(Z - B) - \frac{A}{B}((AA)_i - (BB)_i)ln\left(1 + \frac{B}{Z}\right)$$

PR EOS

- Pure Substance

$$ln\phi = Z - 1 - ln(Z - B) - \frac{A}{2\sqrt{2}B} ln\left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right)$$

- Mixtures

$$ln\phi_i = (BB)_i(Z - 1) - ln(Z - B) - \frac{A}{2\sqrt{2}B}((AA)_i - (BB)_i)ln\left(\frac{Z + (\sqrt{2} + 1)B}{Z - (\sqrt{2} - 1)B}\right)$$

- The expressions for A, B, b_i, b_m, $(a\alpha)_m$, and $(a\alpha)_{ij}$ are the same as given before in the literature. $(AA)_i$ and $(BB)_i$ are calculated as:

$$(AA)_i = \frac{2}{(\alpha a)_m}\left(\sum_{i}^{n_c}(\alpha a)_{ij}\right)$$

$$(BB)_i = \frac{b_i}{b_m}$$

- A and B parameters and the Z-factor of each phase are needed in order to calculate the corresponding fugacity coefficients.

VLE calculation

- Consider a liquid-vapor in equilibrium. As we have discussed previously, a condition for equilibrium is that the chemical potential of each component in both phases are equal, thus:

$$\mu_i^v = \mu_i^l$$

- We showed that this is equivalent to:

$$f_i^v = f_i^l$$

- This is, for a system to be in equilibrium, the fugacity of each component in each of the phases must be equal as well. The fugacity of a component in a mixture can be expressed in terms of the fugacity coefficient.

Equilibrium and K_i

- The fugacity of a component in either phase can be written as:

$$f_i^v = y_i \phi_i^v P$$

$$f_i^l = x_i \phi_i^l P$$

- At equilibrium,

$$y_i \phi_i^v P = x_i \phi_i^l P$$

- This equilibrium condition can be written in terms of the equilibrium ratio $K_i = y_i/x_i$, to get:

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^l}{\phi_i^v}$$

- Recall the Rachford-Rice objective function.
- We demonstrated that once we know all values of K_i's, the problem of vapor-liquid equilibrium is reduced to solving the Rachford-Rice objective function, using the Newton-Raphson Procedure.
- We can now calculate equilibrium ratios, using $K_i = \frac{y_i}{x_i} = \frac{\phi_i^l}{\phi_i^v}$, in terms of fugacity coefficients. We also know that we have an analytic expression for the calculation of fugacity coefficients via EOS.
- Now you can solve the VLE problem?

- Well, Not quite.
- From the expression for fugacity coefficients in mixtures both for SRK EOS and PR EOS, they are functions of the pressure, temperature, and composition of the phases:

$$\phi_i^l = \phi_i^l(P, T, x_i)$$

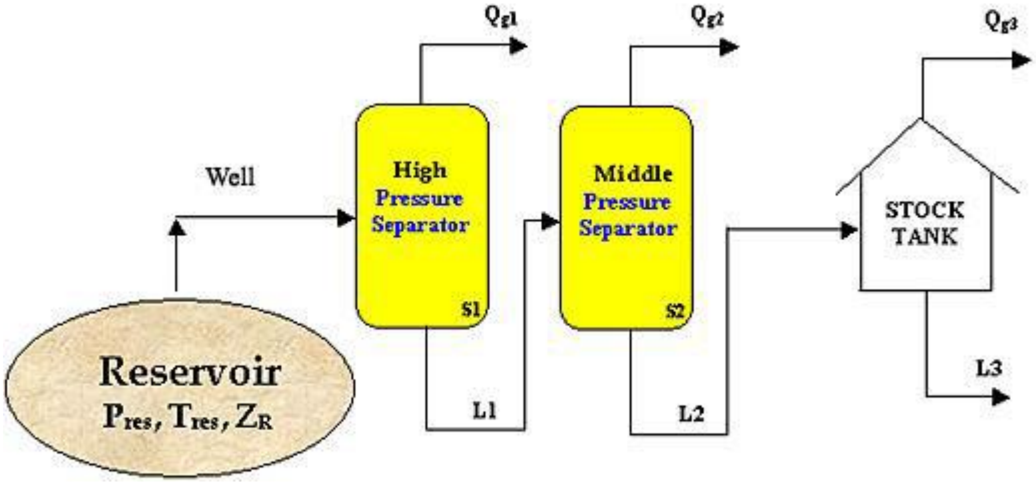
$$\phi_i^v = \phi_i^v(P, T, y_i)$$

- Do we know the composition of the phases “x_i”, “y_i” in advance? In a typical flash problem, we are given pressure, temperature and *overall* composition (z_i).
- What do we want to know? How much gas, how much liquid, and the *compositions of the phases*: α_v, α_l, y_i, x_i. So, we do *not* know those compositions in advance; therefore, as it stands, we cannot calculate above equations.

Again, iteration!

- we could try to overcome this problem by “guessing” those compositions, and proceed by solving equations for Ki and Φ_i.
- With this “rough” estimate for Ki’s, we could solve for “α_v” with the Newton-Raphson Procedure. Once “α_v” is known, we could back calculate the compositions of the phases using equations.
- If we were correct, those compositions would match each other (the “guessed” ones with respect to the “back-calculated”). More than likely, this would not happen, and we would have to make a new “guess.” This is, fundamentally, an iterative procedure. Although this is not what we do, it does illustrate that this problem is solvable by implementing the appropriate iterative scheme.
- As you see, everything that we have studied in this course is completely interlinked. That’s one of the main ideas of solving the VLE problems.

Three stage separators



- Under the assumption of equilibrium conditions, and knowing the composition of the fluid stream coming into the separator and the working pressure and temperature conditions, we could apply our current knowledge of VLE equilibrium (flash calculations) and calculate the vapor and liquid fractions at each stage.

- However, if we are looking at designing and optimizing the separation facility, we would like to know the optimal conditions of pressure and temperature under which we would get the most economical profit from the operation.
- In this context, we have to keep in mind that stage separation aims at reducing the pressure of the produced fluid in sequential steps so that better and more stock-tank oil/condensate recovery will result.
- Separator calculations are basically performed to determine:
  - Optimum separation conditions: separator P and T
  - Compositions of the separated gas and oil phases
  - Oil formation volume factor
  - Producing Gas-Oil ratio
  - API gravity of the stock tank oil

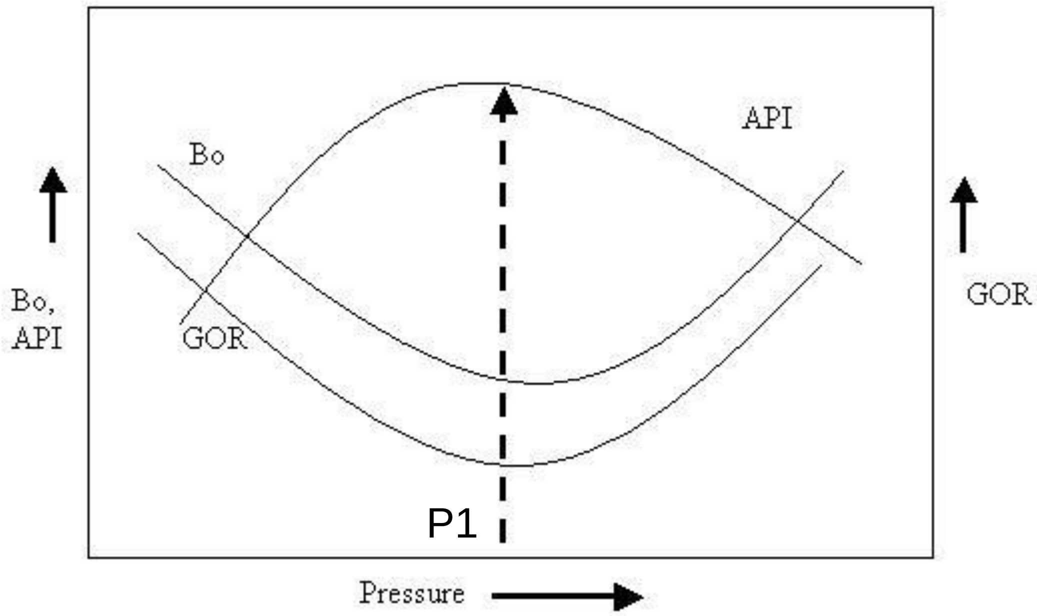
- In case of three-stage separation, temperature conditions in the surface separation facility are very much determined by the atmospheric condition and incoming stream temperatures.
- As for pressures, the very first separator pressure is controlled by the gathering lines coming from well heads, thus there is not much room for playing with pressure in the first separator. The same arguments are valid for the last stage of separation (stock tank), which usually operates at atmospheric conditions.
- Therefore, we are only left with the *middle separator* for optimization.

- As it turns out, the key to designing a three stage separation system is finding the *optimum pressure* at which to operate the *second* separator.
- The question that we would answer is “what is the pressure that will result in the best quality liquid going out of the stock tank for sales?”
- We do not want to do this empirically. That is, we do not want to play with the second stage separator pressure in the field, until we ultimately find the optimum condition.
- What we can do, using our phase behavior knowledge, is to find this optimum middle stage pressure applying our understanding of VLE equilibrium.

What we need to achieve

- Here is a typical effect of playing with the middle separator pressure on the quality and quantity of produced oil/condensate at the stock tank.
- Quality and quantity are measured in terms of properties, such as API and B_o, and the overall GOR at the separation facility.
- The optimum value of pressure for the middle stage is the one that produces the maximum liquid yield (by minimizing GOR and B_o) of a maximum quality (by maximizing stock-tank API gravity).
- The smaller the value of GOR and B_o, the larger the liquid yield. The higher the API gravity of the stock-tank fluid, the more profitable its commercialization.

- From this figure, we see that P1 is found at neither extreme (low/high) values of middle stage pressure. There is, in fact, an optimal value for middle stage pressure.



- The Phase Behavior model that we have described throughout these series of lectures provides the basic framework for the type of calculations required here.
- While doing the calculations for a 3-stage separating system, keep in mind that we have minimal control over feed pressure, as we do not want to inhibit the well (high-pressure separator). We do not control the sales line pressure (stock-tank pressure) either. The control that we do have is the operating pressure of the middle separator.

- Recall that finding the optimum pressure calls for, in part, finding the minimum gas to oil ratio (GOR, SCF/STB).
- We are dealing, in this case, with total GOR. The total GOR is the cumulative amount of gas from all three separators divided by the amount of liquid/condensate leaving the stock tank.
- During our discussion on B_o-calculations, we called “n_{st}” the moles of liquid leaving the stock tank per mole of feed entering the separation facility. This number can be obtained by sequentially flashing 1 lbmol of feed through each of the separation stages.

Thank you!