

VAPOR-LIQUID EQUILIBRIUM CALCULATION OF MULTI-COMPONENTS SYSTEM WITH ESTIMATION OF PRE- HEAT TEMPERATURE

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ABSTRACT

This general process design for multi-components vapor-liquid equilibrium flash calculation of a two- phase system comprises bubble and dew point calculations, estimation of the flash point, calculations of the vapor split and resulted compositions with flow rates in each of the liquid and vapor phases and estimation of the pre-heat temperature needed for a specific vapor split via unprecedented theories. The technique employed entails prediction of the equilibrium temperature, based on the critical temperatures of the feed's components, which in turn is used to estimate the corresponding flash pressure. The theories entail accommodate any light hydrocarbons' mixture and other molecules which are of relatively uncomplicated molecular force fields, as in the case of natural gas liquid. Appropriate gases and liquid properties correlations parameters were obtained from the literatures and used in different equations most suitable for vapor-liquid equilibrium calculations of any light hydrocarbons' mixture and other mixtures of relatively uncomplicated molecular force fields. The computer implementation put forward for this design calculation, which can handle up to twelve components, aids the calculations of vapor-split, which requires several iterations, and other results. The accuracy of the procedures entail in this work is also shown in the value of the preheat temperature which is greater than flash temperature.

KEYWORDS: Flash point, critical point, pre-heat temperature, enthalpy of vapor, heat of vaporization.

1 INTRODUCTION

Vapor-liquid equilibrium (VLE) is a state or condition where the rate of evaporation (liquid changing to vapor) equals the rate of condensation (vapor changing to liquid) on a molecular level such that there is no net inter-conversion. In simpler term, it means a condition where vapor (gas phase) and liquid are in equilibrium. Equilibrium could be practically reached in a relatively closed location if a liquid and its vapor are allowed to stand in contact with each other long enough with no interference or only gradual interference from the outside. The formulation for vapor-liquid equilibrium for a multi-component system arises from the fact that the fugacity of species I in the vapor phase equal to the fugacity in the liquid phase;

$$f^v = f^l$$
$$y_i \phi P = \gamma_i x_i p_i' \quad (i=1, 2, \dots, N) \quad (1.1)$$

Where ϕ is the fugacity coefficient, y_i and x_i are respectively vapor and liquid compositions, γ_i is the activity coefficient, p_i' is the vapor pressure and p is the total pressure.

The corresponding general vapor-liquid equilibrium equation for ideal system reduces to

$$y_i p = x p_i' \quad (i=1, 2, \dots, N) \quad (1.2)$$

An important application of vapor-liquid equilibrium is the flash calculation. The name originates from the fact that a liquid at a pressure equal to or greater than its bubble point pressure "flashes" or partially evaporates when the pressure is reduced below the bubble point pressure, producing a two phase system of vapor and liquid in equilibrium (Smith et al, 2005). The appropriate laws for vapor-liquid equilibrium calculations include Raoult's law, Dalton's and Henry's laws.

Generally, flash calculations are calculations that are applied for processes where vapor and liquid are in equilibrium. A typical process that requires the application of flash calculation is when a feed stream (F) is separated into a vapor (V) and liquid (L) product as shown in Figure 1.1. A very good example of this process is flash distillation which is partial vaporization without reflux. Possibility of vapor-liquid equilibrium data obtained at high pressure has been affirmed by Ana et al (2011).

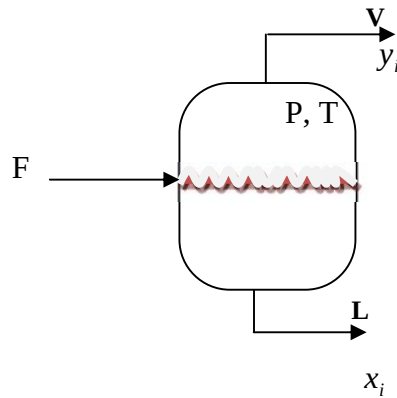


FIGURE 1.1: *Flash Tank*

2 DESIGN METHODOLOGY FOR VAPOR-LIQUID EQUILIBRIUM (FLASH) CALCULATIONS

The theories put forward on process design for equilibrium flash calculation are discussed as follows.

2.1 ESTIMATION OF THE EQUILIBRIUM TEMPERATURE BASE ON THE CRITICAL TEMPERATURE OF EACH COMPONENT OF THE MIXTURE

The critical temperature is a temperature where there is no change in the behavior of the gases no matter the alteration in the temperature. The method employed entails the prediction of the flash point base on the lowest possible critical temperature of the components of the mixture (with respect to Wagner and extended Antoine equation) and therefore the calculation of the corresponding pressure requires to ensure vapor-liquid equilibrium at the predicted or estimated temperature. This is achievable since the time of ignition is dependent on the pressure; and therefore the pressure requires for a specific flash point can be obtained.

It is important to note when this technique is employed that the flash temperature must not be higher than the lowest critical temperature of the feed's components.

Table 2.1 Critical Temperature of Natural Gas Liquid Components

Source: Polling et al (2001), the Properties of Liquid and Gases, 5th Edition, Appendix A, PP A.47-A.60

Natural Gas Liquid Components	Critical Temperature(K)
Ethane	305.33
Propane	369.85
N-Butane	425.25
I-Butane	408.14
N-Pentane	469.80
I-Pentane	460.43
Hexane	507.90

2.2 Estimation of the Flash Pressure

The major criterion that must be met in following the procedures entail in this work is that the flash pressure must lie between the bubble pressure and dew pressure. Thus, the need to calculate the vapor of each component of the mixture, bubble point/pressure and dew point /pressure . The flash pressure is the pressure (total pressure) required to achieve equilibrium at a definite temperature (flash point). Various stages entails in estimating the flash pressure are discussed in the sub-sections that follow.

2.2.1 Calculation of the Vapor Pressure for Each Component Using Wagner and Extended Antoine Equations

The major parameter needed in estimating the total pressure is the vapor pressure of each component. The other parameter is just the composition of each of the component in the feed. These are the two parameters needed to calculate bubble pressure and dew pressure (when Raoult's law holds) from which the flash pressure can be predicted.

Wagner equation represents the vapor pressure behavior of most substance over the entire liquid range and it is expressed as;

$$\ln p_{vp_r} = \frac{a^2 + b^2 \cdot 1.5 + c^2 \cdot 2.5 + d^2 \cdot 5}{T_r} \quad (2.1)$$

a, b, c and d are constants supplied by Polling et al (2001), T_r is the reduce temperature and ^{2} is one minus reduce temperature. It is expedient to note that,

$$T_r = \frac{T_F}{T_c} \quad (2.2)$$

Where T_F and T_c are respectively flash temperature and critical temperature

$$^2 = 1 - T_r \quad (2.3)$$

It is important to note that the exponential of Equation (2.1) gives the values of the reduce vapor pressure (p_{vp_r}). The value of the vapor pressure can be obtained by making use of the relation;

$$P'_i = P_{VP,i} \times P_{ci} \quad (2.4)$$

Where P'_i , $P_{VP,i}$ and P_{ci} respectively denote vapor pressure, reduce vapor pressure and critical pressure of a particular component.

Extended Antoine equation covers enough temperature and pressure range even up to the critical points of some substances and it is expressed as;

$$\log_{10} p'_{vp} = A - \frac{B}{T + C - 273.15} + 0.43429x^n + Ex^8 + Fx^{12} \quad (2.5)$$

Where;

$$x = (T - t_o - 273.15) \quad (2.6)$$

Where A, B, C, E, F, and t_o are constants which are readily available, T is the temperature in Kelvin.

For the purpose of this work, Wagner and extended Antoine equations have been employed due to the fact they are the two major equations that can be used to obtain the vapor pressure of most substances up to their critical points.

2.2.2 Bubble Point/Pressure Calculation

This stage entails the calculation of the bubble pressure of the feed for the prediction of pressure corresponding to the predicted flash point. To determine the bubble pressure of the mixture, we make use of the general equation for vapor-liquid equilibrium expressed as;

$$y_i \phi P = \gamma_i x_i p_i' \quad (i = 1, 2, 3, \dots, N) \quad (2.7)$$

If the feed sample is of relatively low molecular force field, the condition could be subjected to Raoult's law. Therefore, fugacity coefficient Φ and activity coefficient γ_i are each equal to unity and Equation (3.7) becomes;

$$y_i P = x_i p_i' \quad (2.8)$$

$$\text{Recall that } y_i P = p_i \quad (2.9)$$

Equation (3.6) therefore becomes,

$$P_i = x_i p_i' \quad (2.10)$$

Where p_i , P, and p_i are respectively vapor pressure, total pressure and partial pressure. It should be recalled that the summation of partial pressure of all components in a mixture equals the total pressure that is;

$$\sum p_i = P \quad (2.11)$$

$$\text{So that; } \sum x_i p_i' = P_{\text{bubble}} \quad (2.12)$$

Thus, the value obtained from Equation (2.12) gives the bubble pressure of the mixture. It is expedient to take note that the value of x_i in Equation (2.12) is taken equivalent to be molar composition (z_i) of each component in the feed for bubble pressure calculation. That is, Equation (2.12) could be written as;

$$\sum z_i P_i' \quad (2.13)$$

2.2.3 Dew point/Pressure Calculation

To calculate the dew point of the mixture, a suitable equation has to be derived from Equation (2.7). Equation (2.7) can be rewritten as;

$$x_i = \frac{y_i \phi_i P}{\gamma_i P_i'} \quad (2.14)$$

Since in flash calculation $\sum x_i = 1$ for liquid phase, we have;

$$1 = \frac{\sum y_i \phi_i P}{\gamma_i P_i'} \quad (2.15)$$

From Equation (2.15), the expression for dew pressure is given as,

$$P = \frac{1}{\sum (y_i \phi_i / \gamma_i P_i')} \quad (2.16)$$

For an ideal condition, Equation (2.16) becomes,

$$P = \frac{1}{\sum \left(\frac{y_i}{P_i'} \right)} \quad (2.17)$$

Also, as it was done in the case of bubble pressure calculation, the value of y_i in Equation (2.17) is equivalent to that of z_i , so that Equation (2.17) can be written as;

$$P_{dew} = \frac{1}{\sum \left(\frac{z_i}{P_i'} \right)} \quad (2.18)$$

2.2.4 Prediction of the Flash Pressure from the Result of the Bubble Pressure and Dew Pressure.

The major criteria for the validity of this vapor-liquid equilibrium (flash) calculation as stated earlier is that the flash pressure must lie between the bubble pressure and dew pressure. Hence, the need to carry out bubble pressure and dew pressure calculations. These steps help to predict a suitable pressure for the flash calculation at a specific flash point.

The predicted flash temperature will correspondingly be an equilibrium temperature once the pressure estimated (by bubble pressure and dew pressure calculations) via this temperature lies between the bubble pressure and dew pressure; and vice versa.

2.3 Calculation of the Phase Equilibrium Constant for Each Component of the Mixture

With reference to general equation for vapor-liquid equilibrium which is expressed as,

$$y_i \phi_i P = \gamma_i x_i P_i'$$

We can write,

$$\frac{y_i}{x_i} = \frac{y_i P_i'}{\phi_i P} = k_i \quad (2.19)$$

Where k_i denotes phase equilibrium constant of a component i . Base on Raoult's law, Equation (2.19) becomes,

$$k_i = \frac{P_i'}{P} \quad (2.20)$$

Where p is the predicted flash pressure (total pressure) and p_i' is the obtained vapor pressure via Wagner equation or extended Antoine equation.

2.4 Calculation of the Vapor Split (Percentage Vaporized) on Flashing by Solving Iterative Rachord- Rice Equation, Liquid Composition (x_i) and Vapor Composition (y_i)

One of the major objectives of the flash calculation is towards the optimum vapor split. One of the major factors that determine the percentage vaporized is actually the flash pressure which varies inversely with the percentage vaporized.

Obtaining an expression for relating vapor split with composition and phase equilibrium constant entails taking a material balance around an exemplified flash distillation process comprising a two phase equilibrium process as depicted in Figure 1.1. For each of the N_C components, the material balance is;

$$F Z_i = L x_i + V y_i \quad (2.21)$$

Since vapor and liquid are in equilibrium, Equation (3.19) can be written as,

$$y_i = k_i x_i$$

By substituting $y_i = k_i x_i$ in Equation (2.21),

$$F Z_i = L x_i + V k_i x_i \quad (2.22)$$

Making x_i the subject of formula in Equation (3.22) gives;

$$x_i = \frac{F Z_i}{L + V k_i} \quad (2.23)$$

Since $L = F - V$, substituting for L in Equation (3.23) gives;

$$x_i = \frac{F Z_i}{F - V + V k_i} \quad (2.24) \text{ so that;}$$

$$x_i = \frac{Z_i}{1 + \frac{V}{F}(k_i - 1)} \quad (2.25)$$

Also, by substituting $x_i = \frac{y_i}{k_i}$ in Equation (2.21) and making y_i the subject of formula for further simplification as used in deriving equation (2.23) gives,

$$y_i = \frac{Z_i k_i}{1 + \frac{V}{F}(k_i - 1)} \quad (2.26)$$

Where V/F denotes vapor split (percentage of the feed vaporized). It is a criteria for a valid vapor-liquid equilibrium calculation that $\sum_i y_i = \sum_i x_i = 1$

So that equation (2.23) can be written as;

$$\sum_{i=1}^{N_C} x_i = \sum_{i=1}^{N_C} \frac{Z_i}{1 + \frac{V}{F}(k_i - 1)} \quad (2.27)$$

To obtain a monotonic function equation in V/F , we write,

$$\sum_i (y_i - x_i) = 0 \quad (2.28)$$

So that by substituting Equations (2.24) and (2.26) into Equation (2.28), we have,

$$\sum_i \frac{Z_i (k_i - 1)}{1 + \frac{V}{F}(k_i - 1)} = 0 \quad (2.29)$$

Equation (2.29) is the so called Rachord-Rice equation and can be solved to obtain vapor split by either trial and error method or Newton- Raphson method. A physical solution must satisfy $0 \leq V/F \leq 1$.

2.6 ESTIMATION OF THE PRE-HEAT TEMPERATURE FOR SPECIFIC VAPOR SPLIT

In almost all the previous work on vapor-liquid equilibrium calculations, especially flash calculations, the major aims are to calculate the vapor split and compositions. These aims have been extended in this work to involve the prediction or estimation of the pre-heat temperature by modification of the procedure given by McCabe et al, (2005).

Pre-heat temperature is the temperature to which the feed would be subjected for a specific vapor split. An enthalpy balance is made using flash temperature in order to determine the pre-heat temperature. This entails calculations of the heats of vaporization at the flash temperature and the average heat capacities of the liquid from the flash point to a predicted temperature range. The unprecedented theories and explanations are given in the following sub-sections on different stages involve in the estimation of the pre-heat temperature for a specific vapor-split.

2.6.1 Calculation of the Heat of Vaporization at the Flash point.

The expression for estimating the heat of vaporization of a fluid at a specific temperature as predicted by Polling et al, (2001) is;

$$\frac{\Delta H_v}{RT_c} = 7.08[1 - T_r]^{0.354} + 10.95w(1 - T_r)^{0.456} \quad (2.30)$$

Where ΔH_v the needed heat of vaporization, w is the acentric factor (constant for all compounds) and R is the gas constant. The unit of measurement of heat of vaporization in equation (2.31) is determined by the unit of temperature and gas constant used.

It is important to take note that the criteria for the appropriation of Equation (2.31) is that the range of the reduce temperature of the substance should be between 0.6 and 0.99, that is, $0.6 < T_r < 1.0$

2.6.2 Calculation of the Heat Capacities for Each Component over a Predicted Temperature Range from the Flash Point

The pre-heat temperature is primarily expected to be above the flash point. The molar heat capacities for each component in the mixture are therefore calculated from the flash point to a predicted temperature of about 100°C or less above the flash point. The expression for calculating the molar heat capacities of liquid and gases; the heat capacity at a specific temperature is expressed

$$\text{as; } \frac{C_p^o}{R} = a_o + a_1T + a_2T^2 + a_3T^3 + a_4T^4 \quad (2.31)$$

Where a_o , a_1 , a_2 , a_3 , and a_4 are constants, provided by Polling et al, (2001).

2.6.3 Calculation of the Average Heat Capacity for Each of the Feed's Components

The average heat capacity is needed to be calculated for each of the components of the mixture. This is easily obtained from the average value of the heat capacities over the entire temperature range from the flash point.

$$\overline{C_{Pi}} = \frac{\sum_i C_{Pi}^o}{N_{C_{Pi}}} \quad (2.32)$$

The components average molar heat capacities are used to predict expression for the average molar heat capacity of feed as given in the next section.

2.6.4 Calculation of the Average Molar Heat Capacity of the Feed ($\overline{C_{pf}}$).

The average molar heat capacity of the feed is obtained from the feed's composition and average heat capacities of the feed's component. This relation is expressed as;

$$\overline{C_{pf}} = \sum_{i=1}^{N_c} \overline{C_{Pi}} Z_i \quad (2.33)$$

$\overline{C_{Pi}}$ is the average molar heat capacity of each of the feed's components.

2.6.5 Calculation of the Enthalpies of the Liquid and Vapor Phases.

The enthalpy of the vapor phase can be predicted from the estimated heat of vaporization and composition of each component in the vapor phase. This relation is given by,

$$H_v = f \left[\sum_{i=1}^{N_c} [Y_i \times \Delta H_{vi}] \right] \quad (2.34)$$

f is the obtained vapor split and ΔH_{vi} is the heat of vaporization of each component at the flash point.

It is expected that the enthalpy of the liquid phase should be zero since the conversion is from the liquid phase to the vapor phase.

2.6.6 Obtaining the Preheat Temperature

The pre-heat temperature, depicting the final temperature to which the feed must be heated for a definite vapor split, can be estimated in terms of the average molar heat capacity of the feed and the enthalpy of the vapor phase. This relation is given by,

$$H_v = \bar{C}_p [T_o - F_T] \quad (2.35)$$

Equation (2.35) can be expressed in term of pre heat temperature as;

$$T_o = \frac{H_v}{\bar{C}_p} + F_T \quad (2.36)$$

F_T denotes flash temperature.

2.7 CALCULATION OF THE VAPOR AND LIQUID FLOW RATES (v_i and l_i)

For complete design methodology for vapor-liquid equilibrium calculations, it is essential to estimate each component flow rates in liquid and vapor phases. These can be obtained by dividing Equation (2.21) by F so that;

$$z_i - \frac{L}{F} x_i = \frac{V}{F} y_i$$

Therefore,

$$v_i = y_i \times \frac{V}{F} \quad (2.37)$$

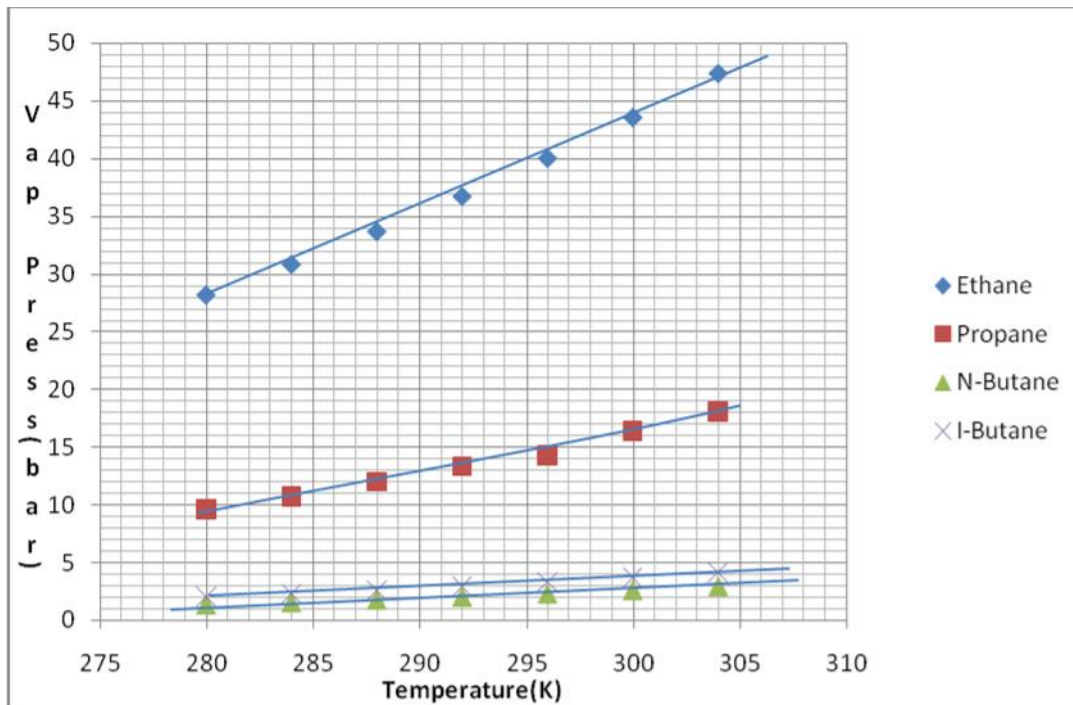
$$l_i = x_i \times \left(1 - \frac{V}{F}\right) \quad (2.38)$$

3 RESULTS AND DISCUSSION

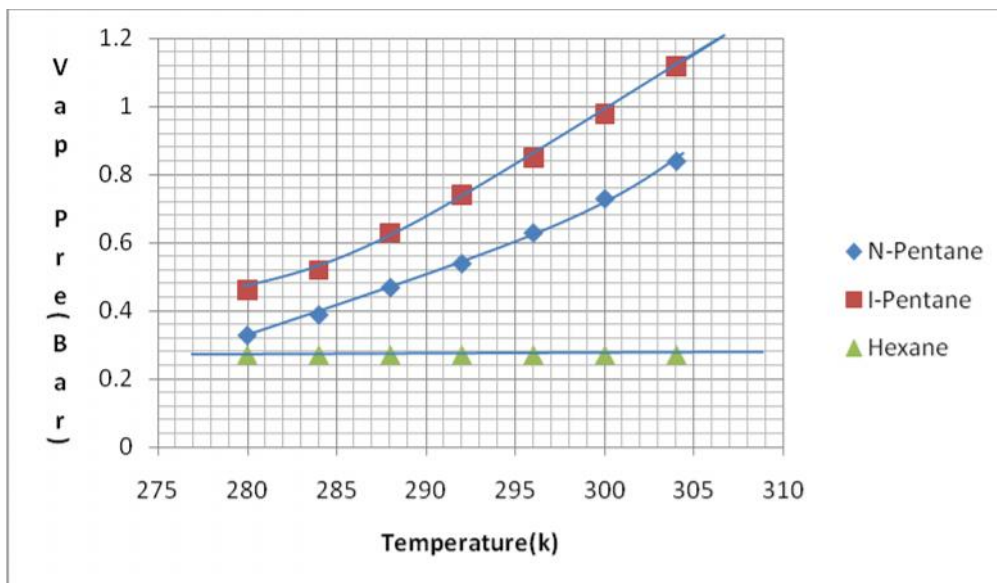
The results of these theories applied for natural gas liquid (a mixture of hydrocarbon compounds) shows that a natural gas liquid subjected to a temperature of 411.07k forms a two phase vapor-liquid equilibrium system at a temperature of 304k and pressure of 3.8bar to give 72.8% of the feed in the vapor phase with average feed molar heat capacity of 103.56j/mol k and corresponding 11089.09J as the enthalpy of vapor.

The interface (form) for the computer implementation of the calculations involved

The vapor pressures-temperatures relationships are shown in Figures 3.1 and 3.2.



Figures 3.1: Vapor pressures- temperatures relationship



Figures 3.2: Vapor pressures- temperatures relationship

It has been found that equilibrium pressure is inversely proportional to the vapor split (as depicted in Figure 3.3)

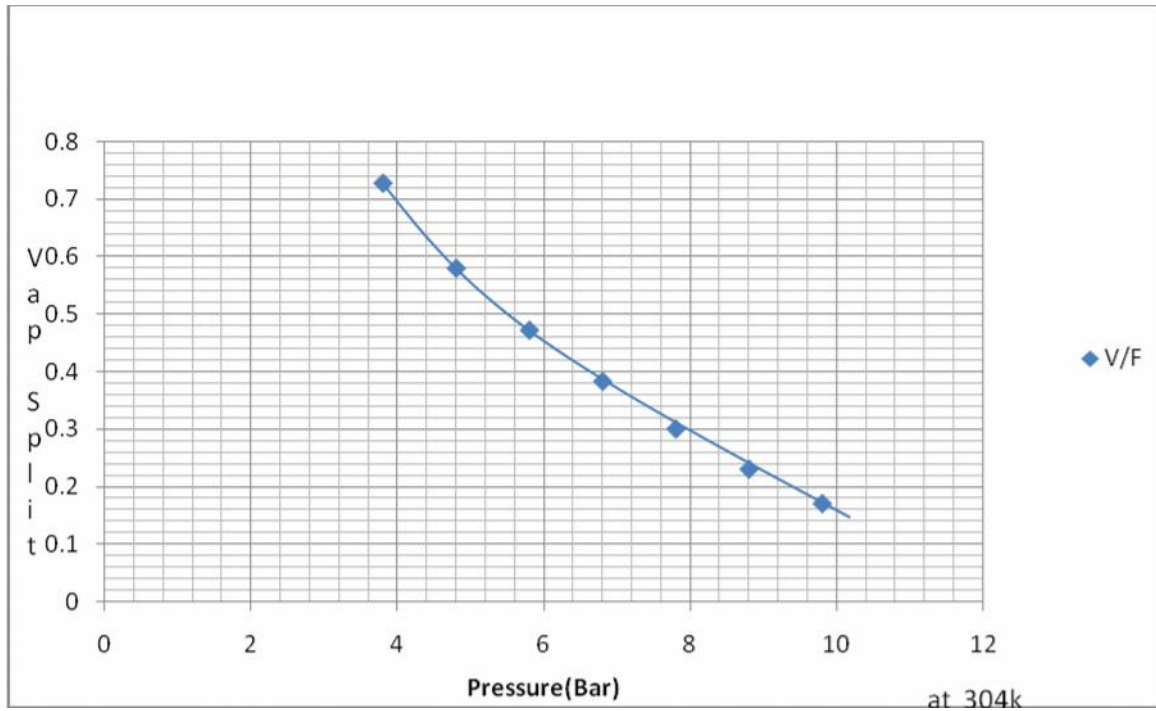


Figure 3.3: Variation of vapor splits with pressures at constant temperature

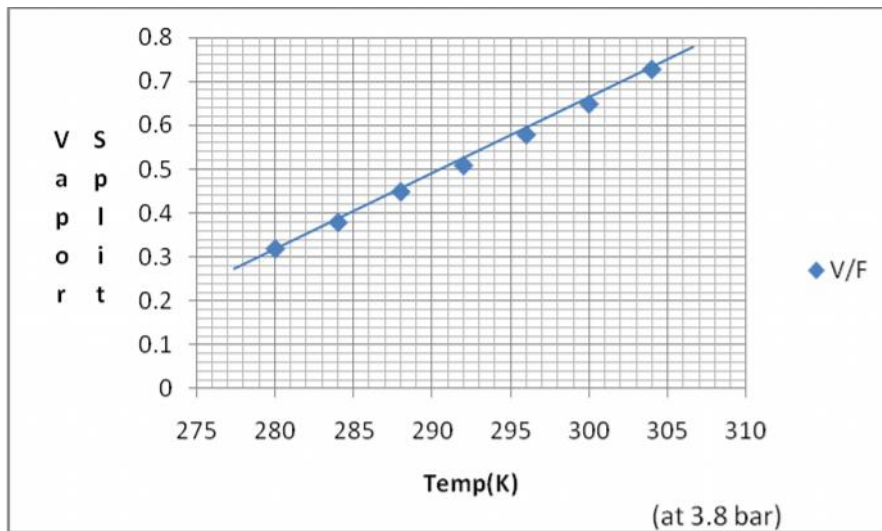


Figure 3.4: Variation of vapor split with temperature at constant pressure

The results of the vapor and liquid compositions and their respective molar flow rates are presented in Table 3.1.

Table 3.1: Results of the Liquid Phase compositions (x_i), Vapor Phase Compositions (y_i), Vapor Molar Flow Rates (V_i) and Liquid Molar Flow Rates (L_i)

Feed's Component	Z	K_i	x_i	y_i	V_i	L_i
Ethane	0.14	12.47	0.015	0.1867	0.1359	0.00408
Propane	0.25	4.77	0.0668	0.3185	0.2317	0.0182
N-Butane	0.05	0.77	0.0601	0.0462	0.0336	0.0163
I-Butane	0.30	1.09	0.2816	0.3069	0.2234	0.0766

N-Pentane	0.13	0.22	0.3008	0.0662	0.0482	0.0818
I-Pentane	0.12	0.30	0.2447	0.0734	0.0534	0.0666
Hexane	0.01	0.07	0.031	0.0022	0.0016	0.0084
			$\sum x_i=1$	$\sum y_i=1$		

For the estimation of the preheat temperature, the results of reduced temperature (T_r), heat of vaporization (H_v) and average heat capacity ($\bar{C}_{pi}$) for each component of the feed with the values of the acentric factors(w) are shown in Table 3.2.

Table 3.2: The Results of the Reduced Temperature (T_r), Heat of Vaporization (H_{vi}) and Average Heat Capacity ($\bar{C}_{pi}$) for each Component of the Feed with the Values of the Acentric Factors(w)

Feed's Component	Acentric factor(w)	T_r	$H_{vi}(J)$	$\bar{C}_{pi}$ (J/kmol)
Ethane	0.099	0.9956	2854.19	58.81
Propane	0.152	0.8220	14149.08	83.65
N-butane	0.200	0.7149	20423.89	111.52
I-butane	0.186	0.7448	18522.02	110.25
N-pentane	0.252	0.6471	25831.00	136.03
I-pentane	0.229	0.6603	24362.89	137.04
Hexane	0.300	0.5985	30793.66	163.86

4 CONCLUSION

The procedures put forward in this work are appropriate for any mixture of hydrocarbon compounds (with their isomers) and other molecules of relatively uncomplicated molecular force field. The condition of low pressure will favor more components in the vapor phase. Thus, this condition is most suitable when each component of the mixture is needed to be treated or separated; although, as already explained, the conditions of the process (both temperature and pressure), for example equilibrium pressure at a specific equilibrium temperature or equilibrium temperature at a specific equilibrium pressure, can be varied to regulate or determine the quantity of the resulted vapor split. Also, since most of the extraction processes designed for separating natural gas liquid are targeted towards obtaining certain component of the mixture, the method put forward here will be highly essential for processing all of the components of the natural gas liquid, even as the demand for them increases. This work can further be extended to estimate the cost and be applied to aid plant's fabrication of any two-phase vapor liquid equilibrium process.

In estimating the pre-heat temperature as put forward in this work, the range of temperature predicted for estimating the heat capacity of the feed's components can be reduced in other to save time and especially for texts use. This can only increase the accuracy of the result.

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