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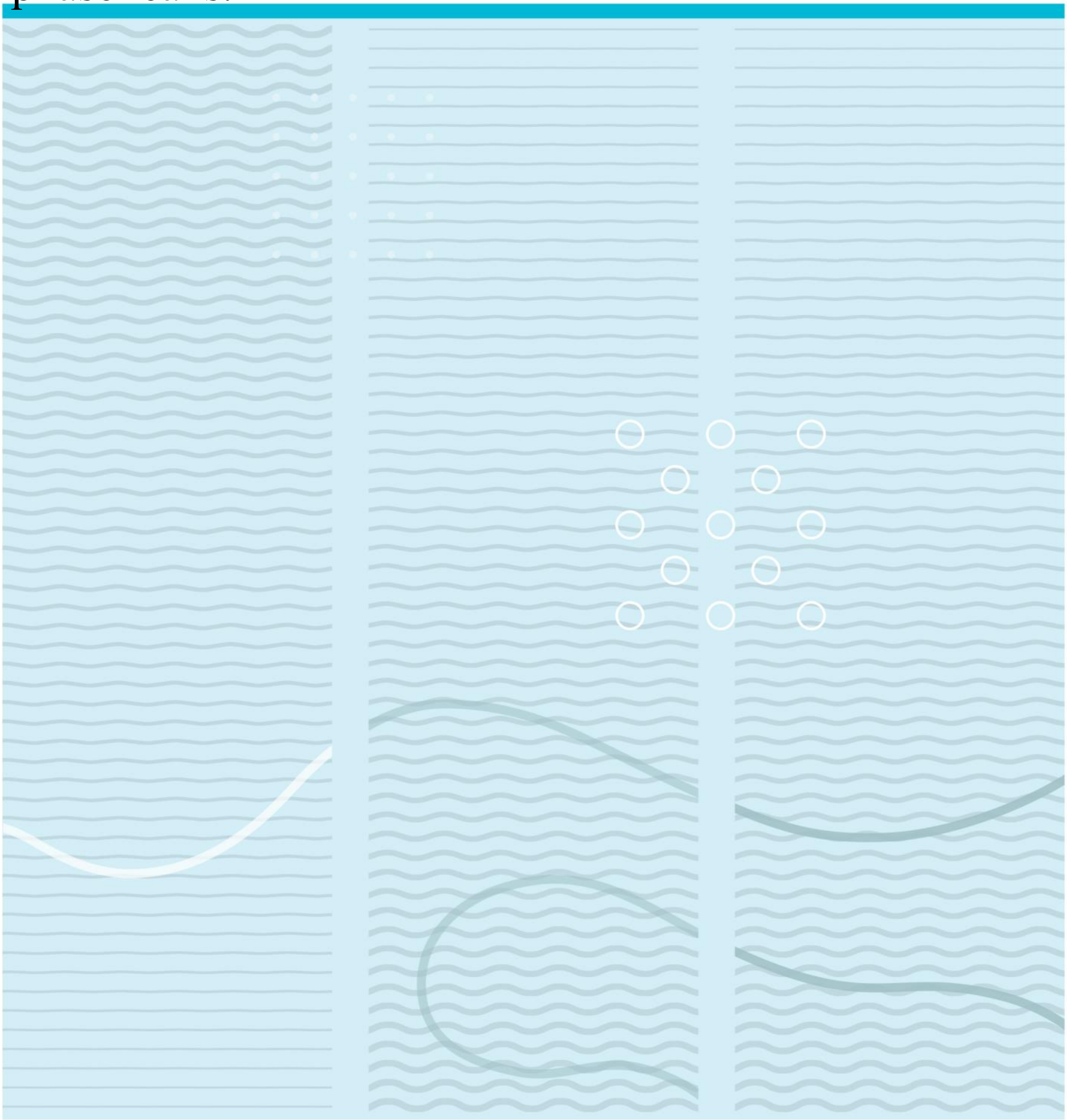

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Abstract:

Solutions incorporating the thermodynamic behavior between gas and liquid phases can help in the model development and accurate prediction of transient hydrocarbon leaks.

The system used in this report is a separator. In the industry, safety critical elements like process vessels can trigger large scale hazards if there is a failure in its process containment barrier as a result of leakages in either the gaseous or liquid phases. Thus, there is need to establish and maintain proactively, technical integrity of process vessels so as to prevent the release or mitigate the impact of major accident hazards (MAH) that can harm people, environment, or asset value.

An in-depth literature review of thermodynamics models has been performed in order to compute the model for estimation of hydrocarbon leak rate and depressurization rate of the segment.

A computational leak model was developed and with its coding, the stability and convergence of the model can be assured.

This paper demonstrates that a rigorous dynamic model simulation using a UV flash approach can predict accurately hydrocarbon leak rate.

Contents

Foreword

The entire project work was carried out in University College of Southeast Norway (HSN), Porsgrunn Campus.

For one to gain an insight on what happens inside the 2 phase process vessel used, Chapter 1, 2 and 3 gives an analytical theoretical background on the thesis topic based on scientific equations and publications. Chapter 4 covers the thermodynamic behavior and leak models algorithm computation.

My special acknowledgement goes to my Supervisor, Amaranath S. Kumara and Lars Andre Tokheim for their technical assistance and guidance throughout the course of this thesis.

My Final gratitude goes to my families and friends for their kind support and without whom, I couldn’t have reached this stage.

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Kenneth Ikechukwu Okoli

1 Introduction

Many accidents are involved in multi-component two-phase flashing releases of flammable or toxic chemicals to the atmosphere. A typical hazard analysis of hydrocarbon leaks in offshore chemical process installations involves several hazardous materials/streams. Rigorous thermodynamics is a standard feature of models used in process plant design and process simulation. In modelling thermodynamics of two-phase leaks, the actual compositions and properties of the two phases can be different. This changes in compositions and properties affects the accuracy of hydrocarbon release and its calculations (Henk, 2006). Modelling of the behaviour of the multicomponent mixture requires calculation of mixture thermodynamic properties such as density, enthalpy, fugacity and phase equilibrium conditions.

This report presents in detail, implementation of UV Flash in the modelling of thermodynamics of two-phase leaks.

1.1 Literature Review

For UV Flash model algorithms development, there are almost little or no references that explains the thermodynamic behavior between gas and oil phases in hydrocarbon leak calculations. Most of the algorithms developed in this report are based mainly on related thermodynamics textbooks and a few related publications.

(Flatby, 1994) demonstrates the use of UV Flash approach in the dynamic simulation of distillation columns. They presented a Flash calculation algorithm and a simplified thermodynamic model using Virial and Cubic Equations of state which helps to reduce significantly simulation time when compared to a simple nested loop solution. The steps (Flatby, 1994) applied in its flash calculations are highlighted below;

- Step 0: Initial guess of T, P, f, x_j and y_j .
- Step 1: Calculate u_L, u_V, v_V, v_L and K_j .
- Step 2: Calculate x_j and y_j from $x_j = \frac{z_j}{1+f(K_j-1)}$; $y_j = K_j x_j$
- Step 3: Their report equations (13), (14) and (16) are written in the form $g_x = 0$ with $g = (g_u, g_v,\ g_r)^T$ and $x = (T, P, f)^T$. Newton-Raphson iteration was used to update T, P and f .

- Step 4: Steps 1-3 were repeated until convergence for all variables $(T, P, f,\ x_j)$ and y_j was reached.

Thus, their paper concluded that it is necessary to use UV flash in dynamic simulation.

(Saha, 1997) used UV Flash (Isoenergetic – Isochoric) method to simulate the dynamic filling of a process vessel. To ensure convergence of their flash calculations, they used partial newton iterations to a set of nonlinear equations. They applied stability analysis in their initial Isobaric-Isothermal (PT) Flash before using UV flash. (Saha, 1997) used 1st order Taylor series approximation method with a relaxation parameter to calculate ΔT and ΔP . Their Flowchart for temperature and pressure initialization was applied in the problem solving and they concluded that stability analysis can be used as a valuable tool for other flash calculations rather than only for TP flash.

(Rachford, 1952) applied the use of electronic digital computers in calculating flash vaporization hydrocarbon equilibrium ratio, K_i . Their method is well suited to sequence-controlled computing equipment. They derived a simple objective function assuming a constant K values to calculate phase compositions for two equilibrium phases. They used an iterative bisection method where the phase molar fraction, either liquid or vapour, is constrained to lie in the range from 0.0 to 1.0. Equilibrium phase compositions are then calculated by mass balance from the converged phase molar fraction and the overall compositions. Their method works well for the overall composition that lies inside the two-phase region. However, their objective function has many poles and roots and is often very nonlinear. Moreover, when the overall composition lies outside the two-phase zone, the correct root is not between 0.0 and 1.0.

(Henk, 2006) modelled the consequence of hazardous multicomponent two-phase releases to the atmosphere in a chemical process unit using Equations of state (EOS). This was implemented in their hazard assessment package and risk analysis package. The two models they used are the discharge and dispersion models as stated in (Crowl & Louvar, 2011).

(Yinghui Li., 2012) developed a rapid and robust alternative method to (Rachford, 1952) in determining equilibrium compositions from constant equilibrium ratios (K –values). Their general procedure are outlined below;

- Step 1: Perform a stability analysis
- Step 2: Make an initial guess of the K- values, where $K_i = {}^{y_i}/_{x_i}$

- Step 3: calculate x_i and y_i using the Rachford-Rice procedure.
- Step 4: calculate the cubic EOS parameters, applying the Mixing rules.
- Step 5: solve the cubic EOS for the phase molar volume.
- Step 6: calculate the component fugacities of each component in each phase
- Step 7: check to see if equilibrium has been reached.
- Step 8: Update the K - values if the criteria of step 7 have not been reached.

(Yinghui Li., 2012) concluded that their method is significantly faster than (Rachford, 1952) because of improved linearity and that it is robust even when overall compositions are zero or negative. From the works of (D'Alessandro, 2015), a mathematical model, VBsim, for blowdown simulation based on a system of mass and energy balances equations was applied. They concluded that VBsim produces reasonably accurate results requiring a very limited CPU time.

According to (Honeywell, 2008), Equations of state models have proven to be reliable in predicting properties of most hydrocarbon- based fluids over a large range of operating conditions and in estimating thermodynamic properties for both liquid and vapour phases. Thus, its usage in this report.

1.2 Well Stream Separation

In this report, the system used in modelling of thermodynamics of two-phase leaks is a separator (Figure 1-1). An understanding of the changes within the system will help in developing the leak models algorithms.

Figure 1-1 Offshore 1st Stage separator

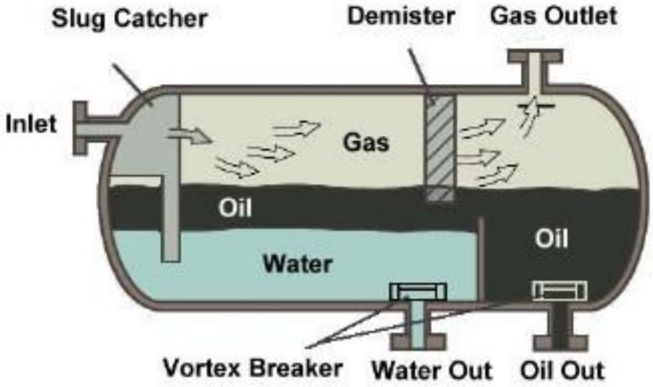


Figure 1-2 Three-phase separator (Devold, 2013).

The well stream into the system may consist of crude oil, gas, condensates, water and various contaminants. Separator is a cylindrical or spherical vessel used to separate oil, gas and water from the total fluid stream produced by a well. Separators can be either horizontal or vertical. It can also be classified into two-phase and three-phase separators (Figure 1-2). The two-phase type deals only with oil and gas, while the three-phase type handles oil, water and gas (Arnold & Stewart, 2008). Additionally, separators can be categorized according to their operating pressure; low-pressure (LP), medium-pressure and high-pressure (HP) separator.

Gravity segregation is the main force that accomplishes the separation, which means the heaviest fluid settles to the bottom and the lightest fluid rises to the top. Additionally, inside the vessel, the degree of separation between gas and liquid will depend on the separator operating pressure, the residence time (retention period) of the fluid mixture - typically 5 minutes (Devold, 2013) and the type of flow of the fluid. Turbulent flow allows more bubbles to escape than laminar flow. A sudden pressure reduction might allow flash vaporization leading to instability and safety hazards (Devold, 2013). Blowdown valve (BDV) are normally initiated to depressurize the system.

1.2.1 Test Separator

Test separators are used to separate the well flow from one or more wells for analysis and detailed flow measurement. In this way, the behaviour of each well under different pressure flow conditions can be defined.

1.2.2 Production Separator

Production separator are divided into 1st stage, 2nd stage and 3rd stage separators. These main separators are gravity types. The production choke reduces well pressure to the HP manifold and 1st stage separator to about 3-5 MPa (30 – 50 times atmospheric pressure). Inlet temperature is often in the range of 100 – 150^{O}C.

In 2nd stage separator, the pressure is reduced to around 1Mpa (10 bar).

The Final 3rd stage separator is a two-phase separator, also called a flash drum. At this stage, the pressure is now reduced to around 100kPa so that the last heavy gas components can boil out.

In some processes where the initial temperature is low, it might be necessary to heat the liquid again in a heat exchanger before the flash drum so as to achieve good separation of the heavy components (Devold, 2013).

2 Phase Equilibrium

Petroleum reservoir fluids are complex mixtures containing many hydrocarbon components that ranges in size from light gases such as methane (C_1) and ethane (C_2) to very large hydrocarbon molecules containing 40 or more carbon atoms. Non-hydrocarbon components also may be present such as nitrogen, H_2S, or CO_2.

Production of reservoir fluids is often accompanied with variations in;

- Composition
- Pressure
- Temperature.

This leads not only to changes in fluid properties, but also to formation of new phases, or elimination of some of the existing phases. As changes within the reservoir are often quite slow, it is reasonable to assume that all co-existing phases, at any point in the reservoir are in equilibrium (Danesh, 1998).

Hence the problem basically reduces to the determination of the equilibrium conditions for a multicomponent system. From (Danesh, 1998; Smith, 2005), 1st law of thermodynamics states that the total energy change of a closed system equals the net energy transferred to or from it as heat and work.

$$\Delta E = Q + W \tag{2-1}$$

$$\Delta E = \Delta U + \Delta E_P + \Delta E_K = dQ + dW \tag{2-2}$$

$$dW = -PdV\ ;\ \ dQ = TdS \tag{2-3}$$

Since there is no change in kinetic and potential energy at uniform pressure and temperature, combining together the three equations above results to,

$$\Delta U = TdS - PdV \tag{2-4}$$

Where;

U = Internal Energy

S = Entropy

V = Volume.

All of the primary thermodynamic properties, P, V, T, U, S are included in Equation 2-4.

Gibbs Energy, G is defined as

$$G = H - TS \tag{2-5}$$

The enthalpy of the system is defined as,

$$H = U + PV \tag{2-6}$$

2.1 Fugacity

The chemical potential, μ_i, provides the fundamental criterion for phase equilibria. Since it exhibits characteristics which discourage its usage, a property, fugacity, f_i, which does not exhibit less desirable characteristics takes its place.

For ideal gas, the fugacity of each component is equal to its partial pressure,

$$f_i = P \tag{2-7}$$

For multicomponent system,

$$\phi_i = \frac{f_i}{P} \tag{2-8}$$

Where;

$\boldsymbol{\phi}_i$ = fugacity coefficient of component i .

f_i = fugacity of component i.

Since all systems behave as ideal gases at very low pressure, $\boldsymbol{\phi}_i \rightarrow 1$ when P→0.

2.2 Vapour-Liquid Equilibrium Correlations

One of the criterion for Vapour-Liquid equilibrium (VLE) states that the fugacity of component i in the vapour phase is equal to the fugacity of component i at the liquid phase (Danesh, 1998; Perry, Green, & Maloney, 1997; Smith, 2005).

$$f_i^l = f_i^v \qquad ; v = G = vapour\ phase \tag{2-9}$$

According to (Danesh, 1998; Perry et al., 1997; Poling, O'Connell, & Prausnitz, 2001), the fugacity coefficient of species i in the liquid phase is given by,

$$f_i^L = \phi_i^L x_i P \tag{2-10}$$

While the vapour-phase is given by

$$f_i^G = \phi_i^G y_i P \tag{2-11}$$

The fugacity of component i in the liquid phase is generally calculated by one of two approaches: the equation of state approach or the activity coefficient approach. In the former, the liquid-phase fugacity coefficient, is introduced by

$$\phi_i^L = \frac{f_i^L}{x_i P} \tag{2-12}$$

Also, based on activity coefficient, γ_i , derived from excess Gibbs energy, the fugacity of species i can be given as, (Perry et al., 1997),

$$f_i^L = \gamma_i x_i P \tag{2-13}$$

A measure of how a given chemical species distributes itself between liquid and vapour phases is the equilibrium ratio, K_i , (Perry et al., 1997; Poling et al., 2001; Smith, 2005).

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^G} \tag{2-14}$$

According to Raoult's Law (Danesh, 1998; Smith, 2005),

$$y_i P = x_i P_i^{sat} \quad \text{, thus} \quad K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} \tag{2-15}$$

Wilson (Danesh, 1998) proposed equation for solving K_i , to be,

$$K_i = \left(\frac{P_{c_i}}{P}\right) exp\left[5.37(1+\omega_i)\left(1-\frac{T_{c_i}}{T}\right)\right] \tag{2-16}$$

Where,

P_c and T_c = Absolute critical pressure and temperature respectively.

2.3 Equations of State (EOS)

An equation of state (EOS) is a thermodynamic equation describing the state of matter under a given set of physical conditions. It provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or internal energy. Thus equation of state is a simplified mathematical model that calculates thermodynamic properties and the equilibrium state. To develop the EOS, we need equations that relate thermodynamic quantities in terms of pressure, molar volume, and temperature data (PVT data), and we want to eliminate any path dependence by eliminating all properties that are not state functions (Prausnitz, Lichtenthaler, & Azevedo, 1999). Equations of state are basically developed for pure components, but applied to multicomponent systems by employing some mixing rules to determine their parameters for mixtures.

It is useful in describing the properties of fluids, mixtures of fluids and solids.

In practice, vapor/liquid reservoir phase behavior is calculated by an equation of state.

2.3.1 Multicomponent mixture Mixing Rules

The parameters of EOS represent the attractive and repulsive forces between molecules. The mixing rules are applied in describing this prevailing forces between molecules of different substances forming the mixtures. The simplest realistic expression are a linear mixing rule for parameter, *b* and a quadratic mixing rule for parameter, *a* , (Danesh, 1998; Prausnitz et al., 1999; Smith, 2005; Solorzano-Zavala, Barragan-Aroche, & Bazua, 1996).

Linear mixing Rule;

$$b = \sum_i x_i b_i \; = \; \sum_i y_i b_i \tag{2-17}$$

Quadratic mixing rule;

$$a = \sum_i \sum_j x_i x_j a_{ij} \; = \; \sum_i \sum_j y_i y_j a_{ij} \tag{2-18}$$

with $a_{ij} = a_{ji}$.

Also from (Perry et al., 1997), the quadratic mixing rules can be expressed as,

$$b = \sum_{i=1}^{N} \sum_{i=1}^{N} x_i x_j b_{ij}$$

According to (Danesh, 1998; Prausnitz et al., 1999; Smith, 2005), the attractive force between molecules i and j, i.e. $i \neq j$, represented in EOS by parameter a_{ij} , which is of an energy nature, can be expressed in a simple geometric average form as,

$$a_{ij} = \left(a_i a_j\right)^{1/2} \tag{2-19}$$

The repulsive force between molecules i and j , represented in EOS by parameter b_{ij} , which has the characteristic of volume, can be determined by arithmetic average,

$$b_{ij} = \left(b_i + b_j\right)/2 \tag{2-20}$$

Equations (2-19) and (2-20) describes the interaction between a pair of different molecules.

2.3.2 Virial equations of state

The virial equation is based on theories of statistical mechanics and can be expressed as an infinite series of either molar volume (molar density) or pressure,

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots \tag{2-21}$$

Molar density, ρ_M , is equal to $1/V$, (Danesh, 1998; Prausnitz et al., 1999), thus compressibility factor, Z can be expressed as,

$$Z = 1 + B\rho_M + C{\rho^2}_M + D{\rho^3}_M \tag{2-22}$$

Writing Z as a power series in the pressure gives,

$$Z = B'P + C'P^2 + D'P^3 \tag{2-23}$$

Where;

Z = Compressibility factor

ρ_M = Molar density

P = Pressure

V = Molar volume

The parameters, B', C', D' and B, C, D are called virial coefficients.

The virial coefficients are functions of temperature only. $B'B$, $C'C$, $D'D$, are 2nd, 3rd and 4th virial coefficients respectively and accounts for interaction between 2, 3 and 4 molecules.

$$B' = \frac{B}{RT} \qquad (2\text{-}24)$$

$$C' = \frac{C-B^2}{(RT)^2} \qquad (2\text{-}25)$$

$$D' = \frac{D-3BC+2B^3}{(RT)^3} \qquad (2\text{-}26)$$

The parameters B, C, D , are defined in Van der Waals Cubic equation of state.

For ideal gas equation, when P →0, $Z = 1.$

2.3.3 Cubic equations of state

Cubic equations of state are a convenient form of calculating vapour-liquid equilibria, VLE, and may be used for pure substances and mixtures.

The two most common and favoured Cubic Equation of State in the industry, that have been used for oil-recovery solvent-injection processes are the Peng-Robinson EOS and the Soave-Redlich-Kwong (SRK) EOS.

Peng-Robinson EOS (Elliott & Lira, 1999; Henk, 2006; Housam Binous., 2009; Prausnitz et al., 1999; Solorzano-Zavala et al., 1996; valderrama, 2002):

$$P = \frac{RT}{V-b} - \frac{a(\alpha)}{V(V+b)+b(V-b)} \qquad (2\text{-}27)$$

$$a = 0.45723553 \, \frac{(RT_c)^2}{P_c} \qquad (2\text{-}28)$$

$$b = 0.07779607 \frac{RT_c}{P_c} \qquad (2\text{-}29)$$

Soave-Redlich-Kwong (Danesh, 1998; Housam Binous., 2007):

$$P = \frac{RT}{V-b} - \frac{a(\alpha)}{V(V+b)} \qquad (2\text{-}30)$$

$$a = 0.42747 \, \frac{(RT_c)^2}{P_c} \qquad (2\text{-}31)$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{2-32}$$

Where;

P is the pressure, V is the molar volume, R is the universal gas constant, T is the temperature.

The parameter α is defined in Table (2-1) as gotten from Table 3.1 (Smith, 2005) and also in (Elliott & Lira, 1999).

Table 2-1 Parameter Assignments for Equations of State (Smith, 2005)

Equations of State	$\boldsymbol{\alpha(T_r)}$	$\boldsymbol{\sigma}$	$\boldsymbol{\epsilon}$	$\boldsymbol{\Omega}$	$\boldsymbol{\Psi}$	$\boldsymbol{Z_c}$
Van der Waals (1873)	1	0	0	1/8	27/64	3/8
Redlich-kwong (1949)	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
Soave-Redlich-Kwong (1972)	$\alpha_{SRK}(T_r;\omega)$	1	0	0.08664	0.42748	1/3
Peng Robinson (1976)	$\alpha_{PR}(T_r;\omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724	0.30740
$\alpha_{SRK}(T_r;\omega) = \left[1+(0.480+1.574\omega-0.176\omega^2)\left(1-T_r^{1/2}\right)\right]^2$						
$\alpha_{PR}(T_r;\omega) = \left[1+(0.37464+1.54226\omega-0.26992\omega^2)\left(1-T_r^{1/2}\right)\right]^2$						
$PR = Peng\ Robinson\ ; SRK = Soave - Redlich - Kwong$						

2.3.4 Residual Properties by Cubic EOS

In thermodynamics a residual property is defined as the difference between a real gas property and an ideal gas property, both considered at the same pressure, temperature, and composition.

For instance, if M is the actual value of a thermodynamic property for a non-ideal gas, and M^{ig} is the value the property will have if the gas was ideal at the same Temperature & Pressure, then the residual property M^R, is defined as,

$$M^R \equiv M - M^{ig} \tag{2-33}$$

$$G^R \equiv G - G^{ig} \tag{2-34}$$

From the thermodynamic relations (Elliott & Lira, 1999; Smith, 2005),

$$H = U + PV \tag{2-35}$$

$$dH = C_p dT \tag{2-36}$$

The residual enthalpy is defined as,

$$H^R \equiv H - H^{ig} \tag{2-37}$$

$$\frac{H^R}{RT} = -T \int_0^P \left(\frac{\partial z}{\partial T}\right)_P * \frac{\partial P}{P} \tag{2-38}$$

$$\frac{G^R}{RT} = \int_0^P (Z-1) * \frac{\partial P}{P} \tag{2-39}$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} \tag{2-40}$$

From Virial equation of state,

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots \tag{2-41}$$

$$Z = 1 + \frac{BP}{PT} \tag{2-42}$$

$$Z - 1 = \frac{BP}{PT} \tag{2-43}$$

Substituting the compressibility factor, Z , into Equation (2-39) and solving equation (2-38), residual enthalpy for mixture can be gotten (M. J. Moran & Shapiro, 2006; Smith, 2005).

3 Leak Models Analysis

Several industrial disasters involves accidental releases of hazardous, toxic, flammable and explosive chemicals from leaking vessels. Such releases may cause major damages to people, properties, environment and damage to company reputation.

(Richardson, 1992) stipulated that heat transfer in a vessel is by:

- Forced/natural convection in the top zone.
- Nucleate/film boiling in the middle zone
- Natural convection in the bottom zone
- Transient conduction through the wall

To assess the potential hazards of such release caused by leakages within the three distinct zones, it is important to estimate the flow rate and properties of the discharged fluid and its change with time during the leaking process. Thus, the following models are proposed.

3.1 Source Model

Accidents begin with an incident, which usually result in loss of containment of material from the process. Typical incidents might include a hole in a vessel or pipe, rupture or break of a pipeline, runaway reaction or fire external to the vessel.

Once the incident is known, source models are selected to describe how materials are discharged from the process, (Crowl & Louvar, 2011).

This source models provides a description of the rate of discharge, the total quantity discharged (or total time of discharge) and the state of the discharge (that is solid, liquid, vapour or a combination). Release mechanisms are classified as wide and limited aperture releases, Figure (3-1).

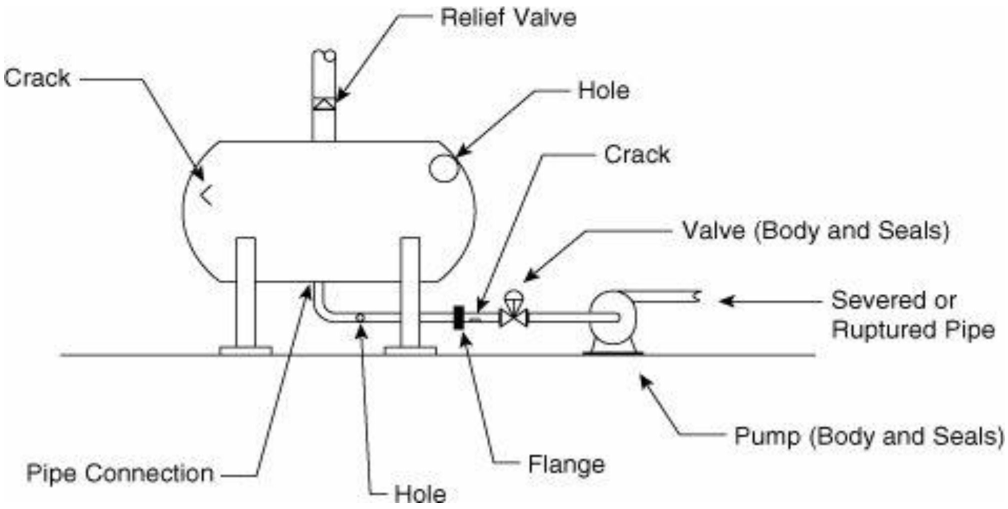


Figure 3-1 various types of limited aperture releases (Crowl & Louvar, 2011)

Seven leak source models are discussed in (Crowl & Louvar, 2011), but for the purpose of this report, only two are presented as sketched in Figure (3-2) below.

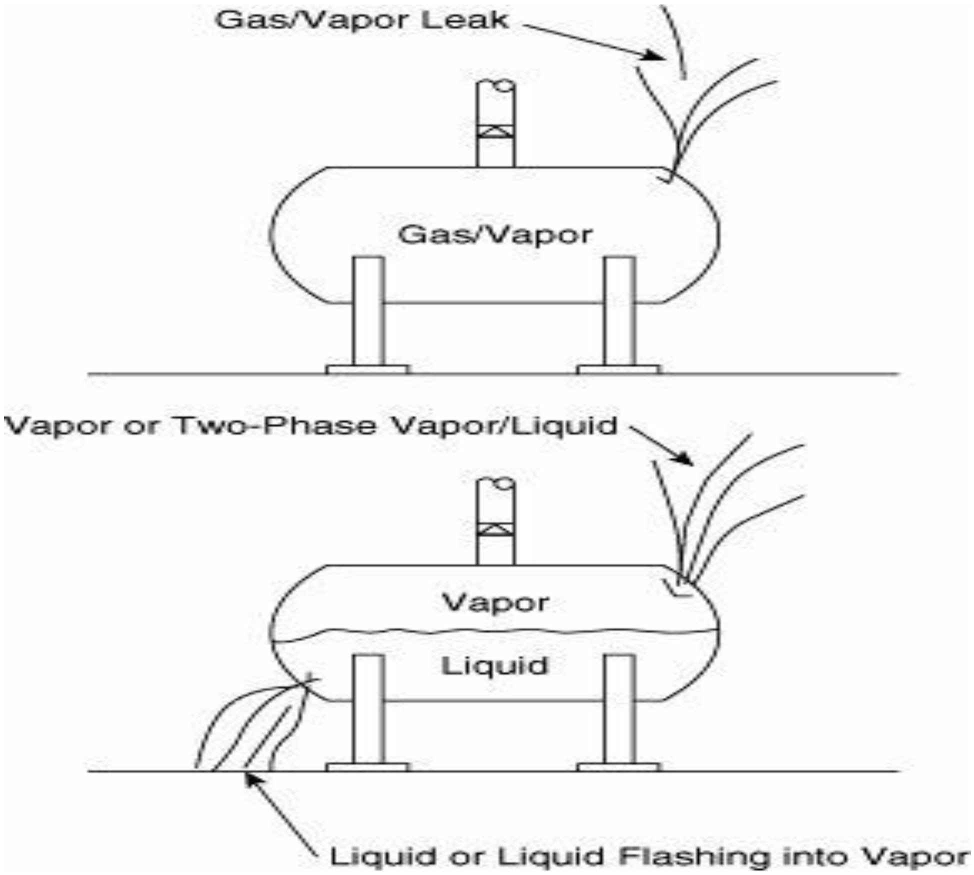


Figure 3-2 Ejection of vapour and liquid from process units in either single or two-phase states (Crowl & Louvar, 2011).

3.1.1 Flow of liquid through a hole

A mechanical energy balance describes the various energy forms associated with flowing fluids:

$$\int \frac{dP}{\rho} + \Delta\left(\frac{\bar{u}^2}{2\alpha g_c}\right) + \frac{g}{g_c}\Delta z + F = -\frac{W_s}{\dot{m}} \qquad (3\text{-}1)$$

Where;

P = pressure

ρ = fluid density,

$\bar{u}$ = average instantaneous velocity of the fluid

z = height above datum, g_c = gravitational constant,

α = unitless velocity profile correction factor

F = net frictional loss term

W_s = Shaft work

$\dot{m}$ = mass flow rate

For incompressible liquids, the density is constant, and

$$\int \frac{dP}{\rho} = \frac{\Delta P}{\rho} \qquad (3\text{-}2)$$

Considering a process unit with small hole as shown in Figure (3-3),

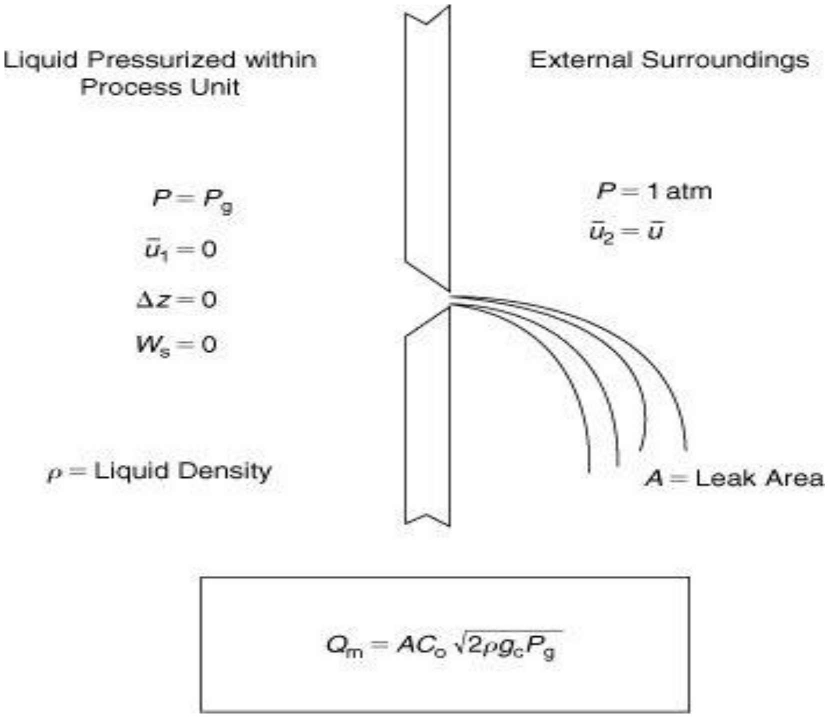


Figure 3-3 Liquid escaping through a hole in a process unit (Crowl & Louvar, 2011).

The pressure of the liquid contained within the process unit is converted to kinetic energy as the fluid escapes through the leak.

For this limited aperture, we assume a constant gauge pressure, Pg ,within the process unit. Thus,

$$\Delta P = Pg \quad , \qquad W_s = 0 \quad , \qquad \bar{u}_1 \; and \;\; \Delta z = 0 \; (assumed \; neglible)$$

Frictional forces in the leak are approximated by a discharge coefficient, C_1 ,

$$-\frac{\Delta P}{\rho} - F = C_1^2\left(-\frac{\Delta P}{\rho}\right) \tag{3-3}$$

Substituting equation (3-3) into equation (3-1) gives,

$$\frac{\Delta P}{\rho} + \Delta\left(\frac{\bar{u}^2}{2\alpha g_c}\right) + \frac{g}{g_c}\Delta z + F = -\frac{W_s}{\dot{m}} \tag{3-4}$$

$$\bar{u}^2 = -\frac{\Delta P}{\rho} - F(2\alpha g_c) \tag{3-5}$$

$$\bar{u}^2 = C_1^2\alpha\left(-P_g * \frac{2g_c}{\rho}\right) \tag{3-6}$$

$$\bar{u} = C_1\sqrt{\alpha}\sqrt{\frac{2g_cP_g}{\rho}} \tag{3-7}$$

A new discharge coefficient, C_0 , is defined as

$$C_0 = C_1\sqrt{\alpha} \tag{3-8}$$

$$\bar{u} = C_0\sqrt{\frac{2g_cP_g}{\rho}} \tag{3-9}$$

Thus, the mass flow rate resulting from a hole of area, , is given by

$$Q_m = \rho\bar{u}A \tag{3-10}$$

$$Q_m = AC_o\sqrt{2\rho g_cP_g} \; = \; AC_o\sqrt{(P - P_\infty)2\rho g_c} \tag{3-11}$$

$P_{Atm} = P_\infty \quad and \;\; \Delta P = P_g = P - P_\infty$, Leak Area, $A = \frac{\pi d^2}{4}$

Discharge coefficient is a function of the Reynolds number of the fluid escaping through the leak and the diameter of the hole.

(Lees & Mannan, 2005) suggested the following guidelines for discharge coefficient, C_0 , table (3-1). More details could be found in (Perry et al., 1997).

Table 3-1 certain values of discharge coefficient, C_o or C_d, for flow of liquid or vapour through holes

$\boldsymbol{C_o}$ value	Condition for its Usage
0.61	For sharp-edged orifices and for Reynolds numbers greater than 30,000
1.00	For a well-rounded nozzle
0.81	For short sections of pipe attached to a vessel
1.00	When the discharge coefficient is unknown or uncertain

3.1.2 Flow of vapour through holes

For flowing gases or vapours, energy contained within the gas or vapour is converted into kinetic energy as a result of its pressure as the gas or vapour escapes and expands through the hole. Gas and vapour discharges are classified into throttling and free expansion releases. The assumption of isentropic behaviour is usually valid in free expansion releases. Throttling release are not considered here because it requires detailed information on the structure of the leak.

The density, pressure and temperature changes as the gas or vapour exits through the leak.

For Isentropic expansion analysis starting from mechanical energy balance, the mass flow rate using continuity equation is,

$$Q_m = \rho \bar{u} A \tag{3-12}$$

For mass flow at any point during the isentropic expansion, Q_m , becomes;

$$Q_m = C_o A P_o \sqrt{\frac{2 g_c M}{R_g T_o} \frac{\gamma}{\gamma - 1} \left[\left(\frac{P}{P_o} \right)^{2/\gamma} - \left(\frac{P}{P_o} \right)^{(\gamma+1)/\gamma} \right]} \tag{3-13}$$

For maximum Flow;

$$(Q_m)_{choked} = C_{oA} A P_o \sqrt{\frac{\gamma g_c M}{R_g T_o} \left(\frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)}} \tag{3-14}$$

Equation (3-14) and Figure (3-4) is for a type of flow called choked, critical or sonic flow. For pressure ratio resulting in this maximum flow,

$$\frac{P_{choked}}{P_o} = \left(\frac{2}{\gamma+1}\right)^{\gamma/(\gamma-1)} \tag{3-15}$$

Where,

M= Molecular weight of the escaping vapour or gas

T_o= Temperature of the source process unit

R_g= Ideal gas constant

P = Pressure within the process unit or system.

P_o= Initial process unit pressure where the velocity is zero

$P_{choked} = P_\infty$ = Maximum downstream pressure resulting in maximum flow through the hole.

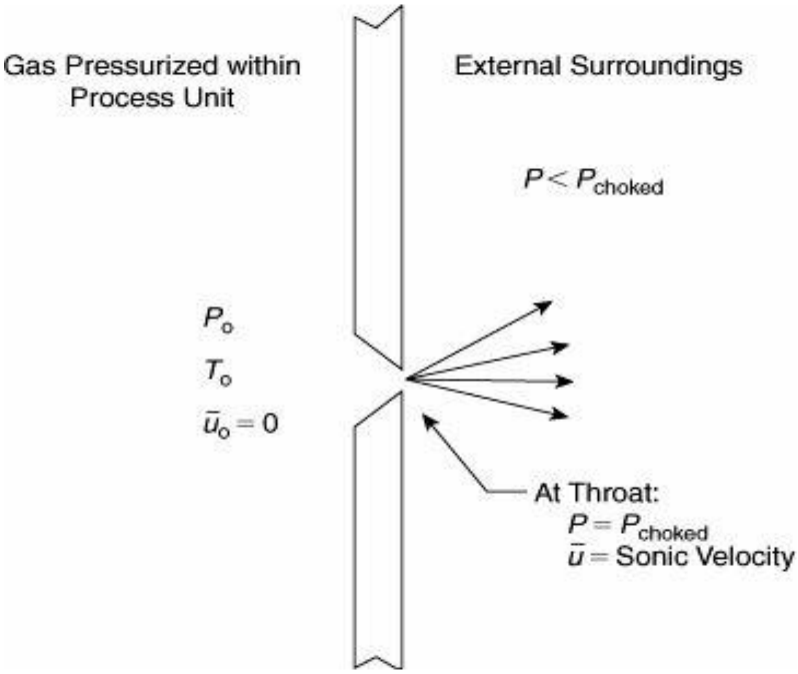


Figure 3-4 Choked flow of gas through a hole (Crowl & Louvar, 2011).

3.2 Thermodynamic leak models of the system

According to (Consulting, 2013), A time-dependent model is used for the representation of process leakages.

The mass of gas in time step, , can be expressed as,

$$m_{g,t+dt} = m_{g,t} - \left(Q_{leak} + Q_{flare} - Q_{in}\right) * dt \quad ; \quad \text{if} \quad \left(Q_{leak} + Q_{flare}\right) > Q_{in} \qquad (3\text{-}16)$$

3.2.1 Gaseous leaks

The critical or sonic flow for gaseous leak is determined by Equation (3-17);

$$Q_{Critical} = AC_d\sqrt{P\rho Z} * \sqrt{\gamma * \left(\frac{2}{\gamma+1}\right)^{\gamma+1/_{\gamma-1}}} \qquad (3\text{-}17)$$

The condition for critical flow is if,

$$\frac{P_a}{P} \leq \left(\frac{2}{\gamma+1}\right)^{\gamma/_{\gamma-1}} \qquad (3\text{-}18)$$

For sub-critical or sub-sonic flow, the leak rate or flare rate is determined as stated below;

$$Q_{sub-critical} = AC_d\sqrt{2\rho P} * \sqrt{\frac{\gamma}{\gamma+1}} * \sqrt{\left(\frac{P_a}{P}\right)^{2/_{\gamma}} - \left(\frac{P_a}{P}\right)^{\gamma+1/_{\gamma-1}}} \qquad (3\text{-}19)$$

Where,

P = System or segment pressure

P_a = Atmospheric pressure

$\gamma = \frac{C_p}{C_v}$ = ratio of heat capacities

C_d = Coefficient of discharge

ρ = Gas density

3.2.2 Liquid leaks

The model used for liquid leaks is a separator model (Consulting, 2013).

Liquid is released first, thereafter gaseous phase.

For liquid side, $Q_{flare} = 0$, thus the time step in equation (3-16) reduces to,

$$m_{g,t+dt} = m_{g,t}(Q_{leak} - Q_{in})dt \tag{3-20}$$

Liquid leak rate is determined according to Bernoulli's equation,

$$Q_{L,t} = AC_d\rho_L\sqrt{2 * \frac{P_t - P_a}{\rho_L} + 2\Delta z_t g} \tag{3-21}$$

For pressure segment in the liquid rate,

$$P_t = P_{t,i}\frac{\varepsilon V_{tot}}{\varepsilon V_{tot} + \Delta V_{L,t}} \tag{3-22}$$

$\Delta V_{L,t}$ = the volume of liquid released at time, t.

4 Phase Behaviour and UV Flash Calculations

A phase is the portion of a system that is homogeneous, is bounded by a surface, and is physically separable from other phases (Prausnitz et al., 1999). Equilibrium phase diagrams offer convenient representations of the ranges of temperature, pressure, and composition within which various combinations of phases coexist. Phase behaviour plays an important role in a variety of reservoir engineering applications, ranging from pressure maintenance to separator design, to enhanced oil recovery (EOR) processes.

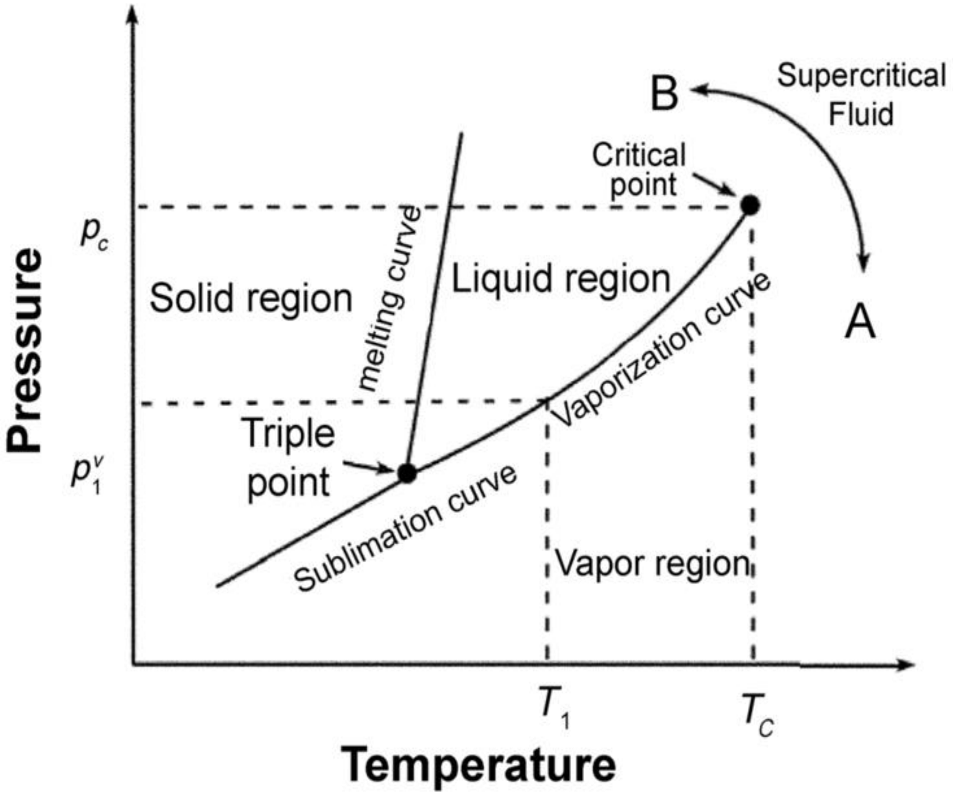


Figure 4-1 Phase behaviour of a pure component (M. J. Moran & Shapiro, 2006; Smith, 2005)

Figure 4-1 summarizes the phase behaviour of a single component. The saturation curves indicate the temperatures and pressures at which phase changes occur. At temperatures below the triple point, the component forms a vapour phase if the pressure is below that indicated by the sublimation curve and forms a solid phase at pressures above the curve. At pressures and temperatures lying on the sublimation curve, solid and vapour can coexist. At pressures and temperatures on the melting curve, solid and liquid are in equilibrium. At higher temperatures, liquid and vapour can coexist along the vaporization or vapour-pressure curve. If the pressure is greater than the vapour pressure, a liquid forms; if the pressure is lower than the vapour pressure, a vapour forms. The vapour-pressure curve terminates at the critical point. At temperatures above the critical temperature, Tc, a single phase forms over the entire range of pressures. For a single component, the critical temperature is the maximum temperature at which two phases can exist. Critical temperatures of hydrocarbons vary widely. Small hydrocarbon molecules have low critical temperatures, while large hydrocarbon molecules have much higher critical temperatures.

According to data presented in chapters 13-10 to 13-26 of (Perry et al., 1997) and in some thermodynamics textbooks, (M. J. Moran & Shapiro, 2006; Prausnitz et al., 1999; Smith, 2005); the phase-equilibrium calculations of a multicomponent stream produces results for vapour composition, liquid composition, pressure, temperature, enthalpy, entropy, density, etc. The property system allows the following types of flash calculations: isothermal, isentropic, isenthalpic, constant energy, constant vapour fraction, etc.

In this chapter, more emphasis is made on VLE calculations and UV Flash calculations.

4.1 Vapour – Liquid Equilibrium (VLE) Calculations

Assuming one mole of mixture is flashed at pressure, P and temperature, T into n^L moles of liquid and n^G moles of vapour.

The material balance for the system, (Danesh, 1998), is,

$$n^L + n^G = 1 \tag{4-1}$$

Material balance for each component, i is

$$z_i = x_i n^L + y_i n^G \quad ; \quad i = 1,2, \ldots\ldots N \tag{4-2}$$

Where;

z_i = mole fractions of the component, i , in the mixture.

x_i = mole fractions of the component, i , in the liquid phase.

y_i = mole fractions of the component, i , in the vapour phase.

N = total number of components in the system.

$$\sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i = 1 \tag{4-3}$$

The material balance equations and the vapour-Liquid Equilibrium Correlations equations, chapter 2-2, provide the required $2N + 2$ independent equations to determine the $2N + 2$ unknowns of x_i, y_i, n^L, n^G .

From, $n^L + n^G = 1 \quad \Rightarrow \quad n^L = 1 - n^G$ and using

$K_i = \frac{y_i}{x_i}$; $y_i = K_i x_i$; $x_i = \frac{y_i}{K_i}$, Z_i becomes,

$$Z_i = x_i(1 - n^G) + K_i x_i n^G = x_i[1 - n^G + K_i n^G] \tag{4-4}$$

$$Z_i = x_i[1 + (K_i - 1)n^G] \tag{4-5}$$

$$x_i = \frac{Z_i}{1 + (K_i - 1)n^G} \tag{4-6}$$

$$y_i = \frac{K_i Z_i}{1 + (K_i - 1)n^G} \tag{4-7}$$

4.2 UV Flash Calculations of the System

If pressure is reduced on any system in which a liquid is in equilibrium with its vapour at its boiling temperature, it will cause the liquid to boil without the need for an externally supplied heat. This process is described as flashing (Vic Marshall. & Ruhemann, 2001).

The fraction of the liquid which vaporizes under any given circumstances is a function of the initial and final pressures, and of the geometry of the release.

For flashing to be a hazardous process, the initial pressure of the liquid in equilibrium with its vapour must be above atmospheric. If there is then a loss of containment, the pressure of the system will eventually fall to atmospheric and a fraction of the liquid will vaporize.

In a hydrocarbon leak scenario, mass of the mixture flows out of the system. Thus, the system will be changing as a result of mass loss, which then leads to changes in temperature and pressure.

The following calculation analysis is for implementation into a UV Flash (Smith, 2005)

The definition of a UV Flash is: Given the internal energy, U, volume V and the component fractions, z_i , do a flash calculation to find the vapour fraction of the mixture, ϑ , composition in the vapour phase, y_i and the liquid phase, x_i, the pressure, P and the temperature, T , (Flatby, 1994; Saha, 1997).

4.2.1 Dynamic Model for hydrocarbon Leak

UV- Flash:

Consider a Separator,

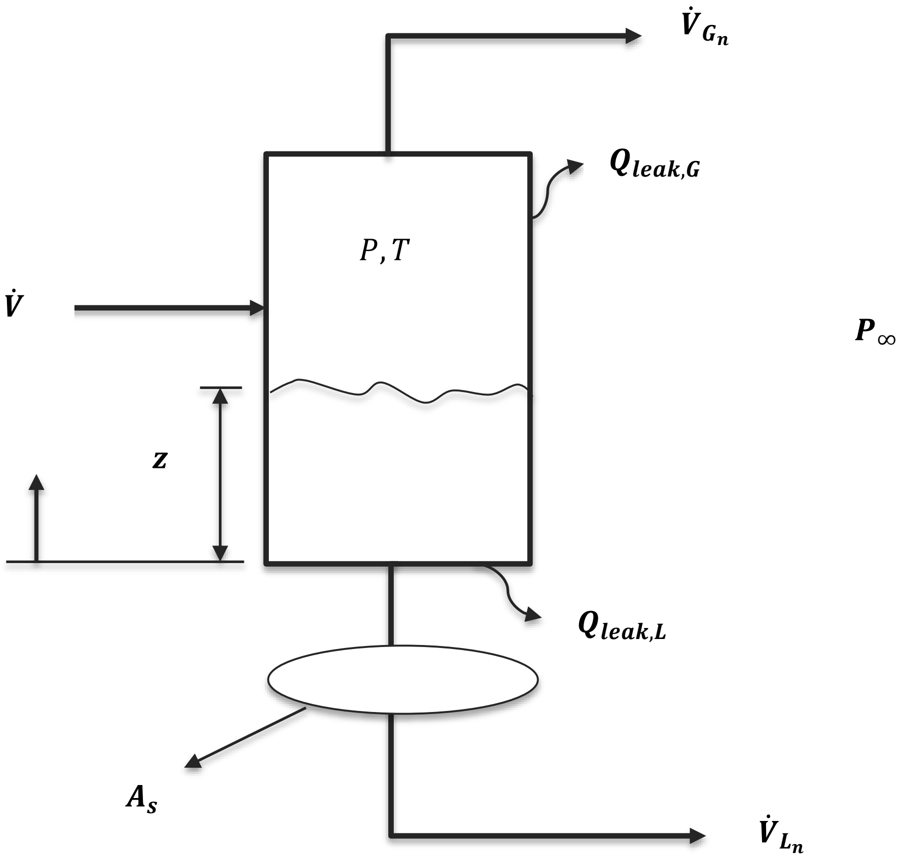


Figure 4-2 Separator with a feed containing multicomponent mixture

Where;

$\dot{V}$ = Volumetric flow of the feed

$\dot{V}_{G_n}$ = Volumetric flow in gas phase

$\dot{V}_{L_n}$ = Volumetric flow in liquid phase

$Q_{leak,G}$ = Leak volume flowrate in gas phase

$Q_{leak,L}$ = Leak volume flowrate in Liquid phase

P_∞ = Atmospheric pressure

A_s = Area of the system

z = height of the liquid.

Specified parameters:

Specific Internal energy: $u = {}^{U}\!/_{n}$

Specific Volume: $v = {}^{V}\!/_{n}$

Component total molar fraction: $z_i = {}^{n_i}\!/_{n}$

Where $n = \sum n_i$ = total number of moles

U = total internal energy of the mixture.

Mole Balance: for finding $\boldsymbol{n_i}$

$$\frac{dn_i}{dt} = \left(\dot{V}_L x_i + \dot{V}_G y_i\right)_{in} - \left(\dot{V}_{L_n} x_i + \dot{V}_{G_n} y_i\right)_{out} - \left(Q_{leak,L} x_i + Q_{leak,G} y_i\right) \tag{4-8}$$

Assuming steady state feed;

$$\dot{V} = \dot{V}_L + \dot{V}_G \tag{4-9}$$

$$\dot{V}_G = \vartheta \dot{V} \quad ; \quad \dot{V}_L = (1-\vartheta)\dot{V} \tag{4-10}$$

Thus, equation (4-8) becomes,

$$\frac{dn_i}{dt} = \left[(1-\vartheta)\dot{V} x_i + \vartheta \dot{V} y_i\right]_{in} - \left[(1-\vartheta)\dot{V} x_i + \vartheta \dot{V} y_i\right]_{out}$$

$$\frac{dn_i}{dt} = [(1-\vartheta) x_i + \vartheta y_i]_{in}\dot{V} - [(1-\vartheta) x_i + \vartheta y_i]_{out}\dot{V} \tag{4-11}$$

Where; ϑ = vapour fraction of the mixture.

$$\dot{V}_L = \dot{V}_{L_n} + Q_{leak,L} \tag{4-12}$$

$$\dot{V}_G = \dot{V}_{G_n} + Q_{leak,G} \tag{4-13}$$

Energy Balance: for finding $\boldsymbol{U}$

Assuming no heat transfer and work across the boundary;

$$\frac{dU}{dt} = \left(\dot{V}_L h_L + \dot{V}_G h_G\right)_{in} - \left(\dot{V}_L h_L + \dot{V}_G h_G\right)_{out}$$

$$\frac{dU}{dt} = [(1-\vartheta) h_L + \vartheta h_G]_{in}\dot{V} - [(1-\vartheta) h_L + \vartheta h_G]_{out}\dot{V} \tag{4-14}$$

According to (Crowl & Louvar, 2011);

$$Q_{leak,L} = A_{LL} C_d \sqrt{2\rho_L (P - P_\infty) + 2\rho_L z g} \quad ; \quad \rho_L = \frac{\sum x_i M_{w_i}}{V_L} \tag{4-15}$$

$$Q_{leak,G} = A_{LG} C_d P \sqrt{\frac{\gamma g M_{w,G}}{RT} \left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(\gamma-1)}} \quad ; \quad \frac{P_\infty}{P} \leq \left(\frac{2}{\gamma+1}\right)^{\gamma/\gamma-1}$$

else;

$$= A_{LG} C_d P \sqrt{\frac{2 g M_{w,G}}{RT} \left(\frac{\gamma}{\gamma-1}\right) \left[\left(\frac{P}{P_\infty}\right)^{2/\gamma} - \left(\frac{P}{P_\infty}\right)^{(\gamma+1)/\gamma}\right]} \tag{4-16}$$

$$\gamma = \frac{C_P}{C_V} \tag{4-17}$$

Where;

γ = heat capacities ratio

C_d = Coefficient of discharge

M_w = Molecular weight

A_{LL}= Leak area, Liquid

A_{LG} = Leak Area, Gas or vapour

Finding the volume/height of liquid:

From $V = Az$

$$z = \frac{V_L}{A_S} \tag{4-18}$$

$$V_L = \frac{m_L}{\rho_L} \tag{4-19}$$

$$m_L = (1 - \vartheta)nM_{w,L}$$

Where z = Height of the liquid in the separator (4-20)

As can be seen, the leak rate and liquid level depend on $x_i, y_i, \vartheta, P, T$. This takes us to flashing model.

4.2.2 UV Flash Model

Component material balance:

$$z_i = (1 - \vartheta)x_i + \vartheta y_i \tag{4-21}$$

Summation of mole fractions (Danesh, 1998; Elliott & Lira, 1999):

$$\sum(x_i - y_i) = 0 \tag{4-22}$$

This leads to

$$\sum \frac{z_i(K_i - 1)}{1 + \vartheta(K_i - 1)} = 0 \tag{4-23}$$

Where, $K_i = \frac{y_i}{x_i}$ (4-24)

$$x_i = \frac{z_i}{1 + \vartheta(K_i - 1)} \quad \text{and} \quad y_i = \frac{z_i K_i}{1 + \vartheta(K_i - 1)} \tag{4-25}$$

The equilibrium condition for flashing:

Balancing the liquid and vapour fugacity (Smith, 2005);

$$f_i^G - f_i^L = 0 \tag{4-26}$$

Giving that,

$$K_i = \frac{\varphi_i P_i^{sat}}{\emptyset_i P} \tag{4-27}$$

And $\emptyset_i$ is defined by, $\emptyset_i = \frac{\widehat{\emptyset}_i}{\emptyset_i^{sat}}$

Using the Antoine Equation (Smith, 2005), or by the Shortcut method, P_i^{sat} can be calculated from Equation (4-28);

$$P_i^{sat} = exp\left(A - \frac{B}{T+C}\right) \quad , \text{ Shortcut: } Log_{10} P_R^{sat} \approx \frac{7}{3}(\omega + 1)\left(1 - \frac{1}{T_R}\right) \tag{4-28}$$

Where,

$P_i^{sat} = P_R^{sat} * P_c$; $T_R = \frac{T}{T_c}$ and $P_R = \frac{P}{P_c}$

A, B, C = Antoine Equation constants

φ = activity coefficient.

$\emptyset$ = fugacity coefficient

Finding the temperature and pressure:

Using Equations for the mixture;

$$u = (1-\vartheta)u_L + \vartheta u_G \quad \Rightarrow u - [(1-\vartheta)u_L + \vartheta u_G] = 0 \tag{4-29}$$

$$v = (1-\vartheta)v_L + \vartheta v_G \tag{4-30}$$

From $Pv = ZRT \quad \Rightarrow \quad v = \frac{ZRT}{P}$, (4-31)

Substituting $v = \frac{ZRT}{P}$ into Equation (4-30), we have

$$v = (1-\vartheta)\frac{Z_L RT}{P} + \frac{\vartheta Z_G RT}{P}$$

$$P = [(1-\vartheta)Z_L + \vartheta Z_G]\frac{RT}{v} \tag{4-32}$$

From $u = h - Pv$

$$u_L = h_L - Pv_L \tag{4-33}$$

$$u_G = h_G - Pv_G \tag{4-34}$$

Where,

$$v_L = \frac{P}{Z_L RT} \quad ; \quad v_G = \frac{P}{Z_G RT} \tag{4-35}$$

$$u - u^* \leq error \tag{4-36}$$

Where,

$$u^* = [(1-\vartheta)u_L + \vartheta u_G] \tag{4-37}$$

u^* = calculated internal energy

u = Reference internal energy obtained from $u = {}^{U}/_{n}$

For updating temperature;

$$T = T^* + \Upsilon \Delta T \tag{4-38}$$

Where,

ΔT = change in temperature

T^* = calculated temperature

Υ = relaxation parameter. It is used to ensure convergence of iterations.

Supposing, $\left(\frac{\partial U}{\partial T}\right)_v \approx \frac{u-u^*}{\Delta T}$ (4-39)

Since the system is of constant volume (Smith, 2005),

$$\left(\frac{\partial U}{\partial T}\right)_v \approx \bar{C}_P - R \tag{4-40}$$

Substituting Equation (4-40) into Equation (4-39), we have

$$\Delta T = \frac{u-u^*}{\left({}^{\partial U}/_{\partial T}\right)_v} = \frac{u-u^*}{\bar{C}_P - R} \tag{4-41}$$

Where,

$$\bar{C}_P = \sum Z_i \bar{C}_{P,i} \tag{4-42}$$

According to (Saha, 1997)

$$\Upsilon = 1 - \frac{|\Delta T|}{T^*} \tag{4-43}$$

Mixture Equations:

Compressibility factor: Based on cubic equations of state, the compressibility factors for both liquid and gas phase can be obtained as described below (Smith, 2005).

Liquid: $Z_L = \beta_L + (Z_L + \epsilon\beta_L)(Z_L + \sigma\beta_L)\left(\frac{1+\beta_L - Z_L}{q_L\beta_L}\right)$ (4-44)

Vapour: $Z_G = 1 + \beta_G - q_G\beta_G\left[\frac{Z_G - \beta_G}{(Z_G + \epsilon\beta_G)(Z_G + \sigma\beta_G)}\right]$ (4-45)

$$\beta_p = \frac{b_p P}{RT} \quad ; \quad q_p = \frac{a_p}{b_p RT} \quad ; \quad (p = L, G) \tag{4-46}$$

$$b = \sum w_i b_i \quad ; \quad a = \sum_i \sum_j w_i w_j a_{ij} \quad ; \quad (w = x, y) \tag{4-47}$$

$$a_{ij} = \left(a_i a_j\right)^{1/2} \tag{4-48}$$

$$a_i = \frac{\Psi \alpha_i R^2 T_{c,i}^2}{P_{c,i}} \tag{4-49}$$

$$b_i = \frac{\Omega\, R T_{c,i}}{P_{c,i}} \tag{4-50}$$

Using Peng Robinson EOS, Table (2-1) above;

σ = 2.414, ϵ = - 0.414 , Ω = 0.07780 , Ψ = 0.45724

$$\alpha_i = \left[1 + \left(0.37464 + 1.54226\omega_i - 0.2699\omega_i^2\left(1 - T_{r,i}^{1/2}\right)\right)\right]^2 \tag{4-51}$$

$$T_{r,i} = \frac{T}{T_{c,i}} \tag{4-52}$$

Fugacity:

According to (Smith, 2005),

$$ln\phi_{p,i} = Z_{p,i} - 1 - ln\left(Z_{p,i} - \beta_i\right) - q_i I_{p,i} \qquad ; \qquad (p = L, G) \tag{4-53}$$

Where,

$$I_{p,i} = \frac{1}{\sigma - \epsilon}\, ln\left(\frac{Z_{p,i} + \sigma\beta_i}{Z_{p,i} + \epsilon\beta_i}\right) \tag{4-54}$$

This is subject to the equilibrium condition, that,

$$ln\phi_{L,i} = ln\phi_{G,i} \tag{4-55}$$

Error limit: $\sum\left(\frac{\phi_{G,i}}{\phi_{L,i}} - 1\right)^2 \le 10^{-12}$ (4-56)

Activity coefficient:

Based on Wilson equation (UNIQUAC) (Poling et al., 2001; Prausnitz et al., 1999; Smith, 2005) ;

$$ln\varphi_i = 1 - ln\left(\sum_j x_i \Lambda_{ij}\right) - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \tag{4-57}$$

$$\Lambda_{ij} = \frac{V_{L,j}}{V_{L,i}} \exp\left(\frac{-a_{ij}}{RT}\right) \qquad ; \qquad (i \ne j) \tag{4-58}$$

Where v_L = molar volume of species i & j in liquid phase at the temperature T .

a_{ij} = a constant, independent of composition and temperature.

Enthalpy:

$$h = h^{ig} + h^R \tag{4-59}$$

$$h^{ig} = \bar{c}_p^{ig}\left(T - T_{ref}\right) + h_{ref}^{ig} \tag{4-60}$$

Where the reference state conditions, $T_{ref} = 298K$; $h_{ref}^{ig} = 0$, (Poling et al., 2001; Smith, 2005).

$\bar{c}_p^{ig}$ = Mean heat capacity of ideal gas.

(Smith, 2005) defined mean heat capacity as,

$$\bar{c}_p^{ig} = R\left[A + \frac{B}{2}T_{ref}(\tau + 1) + \frac{C}{3}T_{ref}^2(\tau^2 + \tau + 1) + \frac{D}{\tau\, T_{ref}^2}\right] \tag{4-61}$$

$$\tau = \frac{T}{T_{ref}} \tag{4-62}$$

τ = Temperature ratio.

Based on cubic EOS, the reduced enthalpy can be written as, (Smith, 2005),

$$\frac{h^R}{RT} = Z - 1 + \left[\frac{dln\alpha(T_r)}{dln(T_r)} - 1\right] qI \tag{4-63}$$

Using Peng Robinson EOS,

$$h^R = RT\left[Z - 1 + \left(-\zeta\left(\frac{T_r}{\alpha}\right)^{0.5} - 1\right) qI\right] \tag{4-64}$$

Where $\zeta = 0.37464 + 1.54226\omega - 0.26992\omega^2$ (see Table 2-1).

$$h_L = \sum x_i h_{L,i} \tag{4-65}$$

$$h_G = \sum y_i h_{G,i} \tag{4-66}$$

4.3 Computation Algorithm

This section covers the iterative algorithm for Bubble point pressure, UV flash and the overall computation of hydrocarbon leak. The general procedure for the computation of the leak model are described in section 4.3.1 below.

4.3.1 General Procedure for Leak Model computation

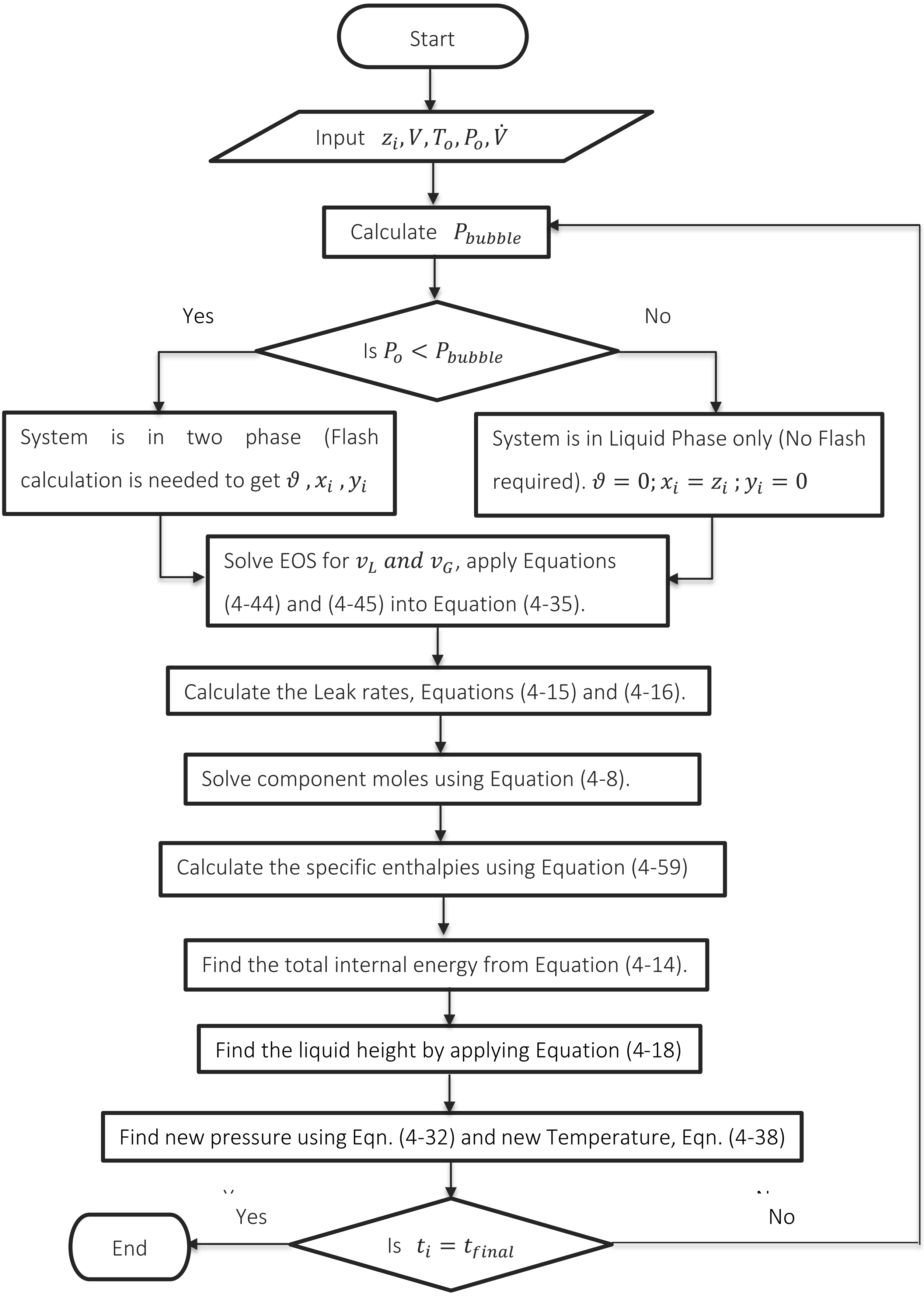


Figure 4-3 Flow chart for leak model computation

This general procedure, Figure (4-3), considers the iteration of the algorithm for a particular time step. For the next time step, the deviation of the system properties from those of old time step is due to leaks.

Due to leaks, the total internal energy loss can be estimated from,

$$U' = \left(\frac{Q^L_{leak_k}}{M_L} + \frac{Q^G_{leak_k}}{M_G}\right) u_k \Delta t \tag{4-67}$$

Where;

Δt = time step indicating the duration of leaks within a computation time interval.

Thus the drop in the temperature of the system is given by,

$$\Delta T' = \frac{u_k - u'}{n_k (C_P - R)} \tag{4-68}$$

Where;

n_k = total number of moles at time, k.

$$C_P = (1 - \vartheta)_k C_{P_L} + \vartheta_k C_{P_G} \tag{4-69}$$

Where;

$$C_{P_L} = \sum x_i C_{P_i} \quad ; \quad C_{P_G} = \sum y_i C_{P_i}$$

The guess temperature and pressure for the start of next time step are thus calculated from,

$$T^*_{k+1} = T_k - \Delta T' \tag{4-70}$$

$$P^*_{k+1} = \frac{Z^L_k \, R T^*_{k+1}}{V^L_k} \tag{4-71}$$

4.3.2 Procedure for Bubble-Point pressure Computation

The bubble pressure at a given temperature is the pressure at which the first bubble of vapour is formed. The procedure for the estimation of the bubble pressure at a given temperature, based on the Peng-Robinson EOS, are outlined in Figure (4-4) below,

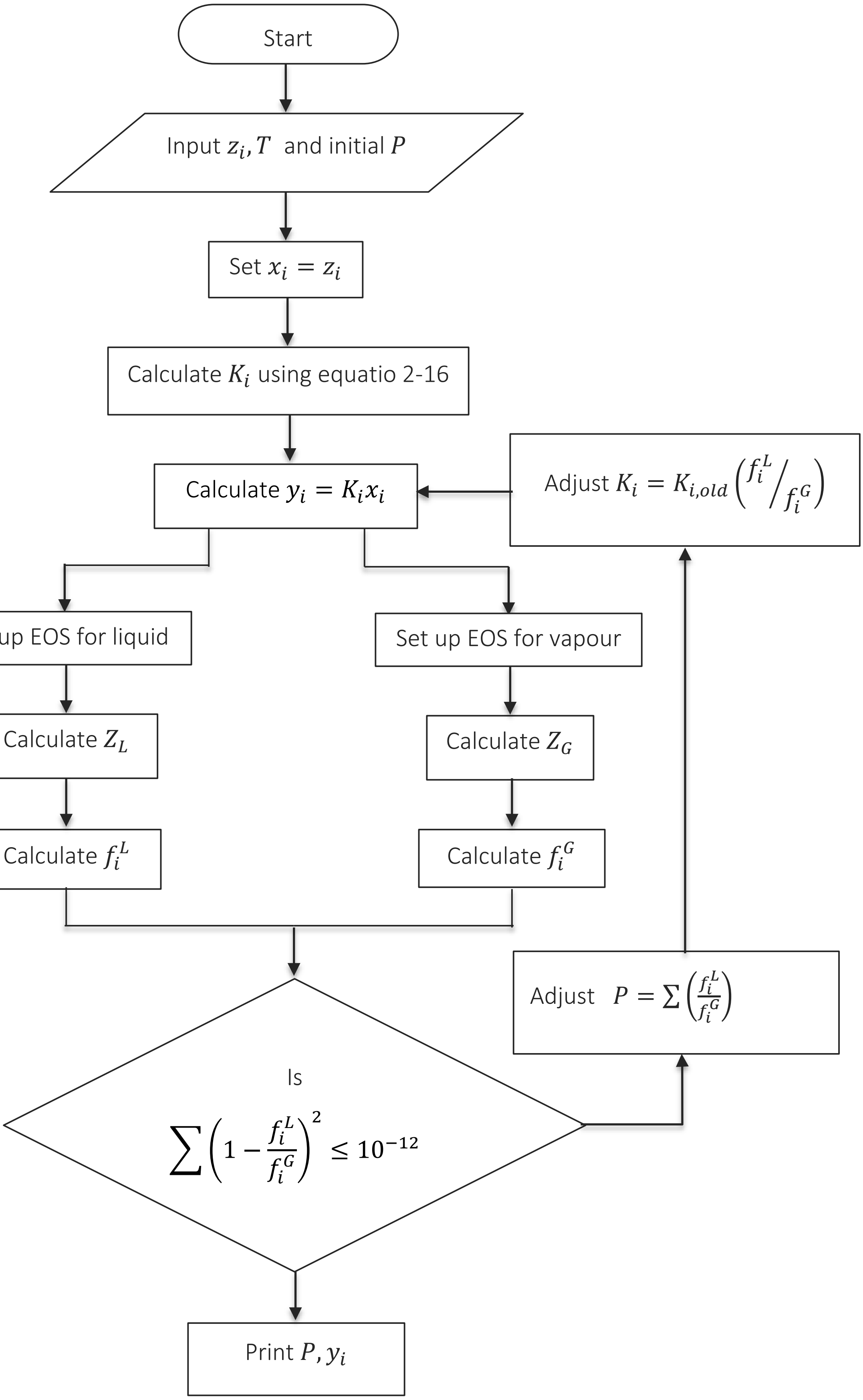
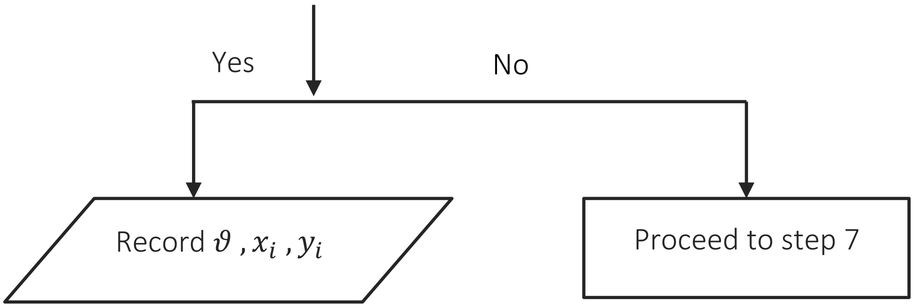


Figure 4-4 Flow chart for the calculation of Bubble Pressure

4.3.3 Detailed algorithm for Leak Model Computation

1. Guess (Given) T^* and P^*
2. Guess $K_i = \left(\frac{P_{c,i}}{P}\right) exp\left[5.37(1+\omega_i)\left(1-\frac{T_{c,i}}{T}\right)\right]$
3. Solve for ϑ from Equation (4-23)
4. Solve for x_i and y_i from (4-25)
5. Solve for $\phi_{L,i}$ and $\phi_{G,i}$
6. Check if $\sum\left(\frac{\phi_{G,i}}{\phi_{L,i}}-1\right)^2 \leq 10^{-12}$

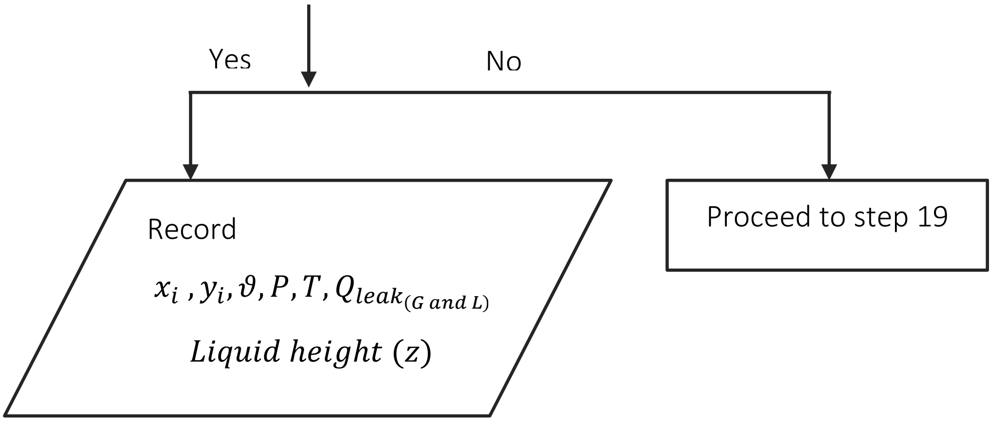


7. Solve for K_i from equation (4-27)
8. Repeat from step 3

Temperature/Pressure update

9. Solve for Z_L and Z_G from equations(4-44) and (4-45)
10. Solve for $\frac{V_L}{\rho_L}$ and $\frac{V_G}{\rho_G}$ from equation (4-35)
11. Solve for n_i using equation (4-11)
12. Solve for h_G and h_L from equation (4-59)
13. Solve for U from equation (4-14)
14. Solve for z (liquid height) from equation (4-18)
15. Solve for P from equation ((4-32)
16. Solve for T from equation (4-38)
17. Solve for Q_{leak} (vapour/liquid) from Equations (4-15) and (4-16)

18. Check if $u - u^{*} \leq error$



19. Repeat from step 3 using new computed values of T and P

Next time step due to leaks

20. Find the drop in total internal energy using equation (4-67)

21. Find new guess temperature, and pressure from equation (4-70) and (4-71)

22. Repeat from step 1

4.4 Parameters for UV Flash Calculations

The multicomponent mixture comprises of Methane, Ethane, Propane, Iso-butane, Butane, Iso-pentane, Pentane, and Decane while their respective component fractions are 0.0524, 0.0596, 0.1542, 0.0381, 0.0830, 0.0322, 0.0393 and 0.5412 (Najar, 2015). The parameters that will be used in UV flash algorithm for each of the 8 components are as stated in Table (4-1) and (4-2) below;

Table 4-1 Properties of pure hydrocarbon species (Elliott & Lira, 1999; M. J. Moran, Shapiro, H.N, 2010; Perry et al., 1997; Smith, 2005)

Chemical Species	Chemical Formula	Molar Mass g/mol	Density $\rho\left(\frac{k_g}{m^3}\right)$	Critical Temp. $T_c(K)$	Critical Pressure $P_c(P_a) * 1E-06$	Z_c	Acentric factor ω
Methane	CH_4	16.043	0.656	190.6	4.59	0.286	0.012
Ethane	C_2H_6	30.070	1.36	305.3	4.85	0.279	0.100
Propane	C_3H_8	44.097	2.01	369.8	4.21	0.276	0.152
Isobutane (Methylpropane)	C_4H_{10}	58.123	2.51	408.1	3.65	0.282	0.181
Butane	C_4H_{10}	58.123	2.48	425.1	3.77	0.274	0.200
Isopentane (2-Methyl butane)	C_5H_{12}	72.150	616	460.4	3.37	0.268	0.226
Pentane	C_5H_{12}	72.150	626	469.7	3.36	0.270	0.252
Decane	$C_{10}H_{22}$	142.285	730	617.7	2.09	0.247	0.492

Table 4-2 gives a detailed information on the eight components in the mixture while Table 4-2 is to be applied in solving the specific and residual enthalpy equations.

Table 4-2 Heat capacities and enthalpies of gases in Ideal Gas state (Elliott & Lira, 1999; Smith, 2005)

${C_P^{ig}}/{R} = A + BT + CT^2 + DT^{-2} \quad ; \quad T(K) from\ 298\ to\ T_{max}(1500)$					
Species	$\Delta H_{f,298}\left({KJ}/{mol}\right)$	$C_{P_{298}}^{ig}/R$	A	$10^3 B$	$10^6 C$
Methane	-74.89	4.217	1.702	9.081	-2.164
Ethane	-83.82	6.369	1.131	19.225	-5.561
Propane	-104.68	9.011	1.213	28.785	-8.824
Isobutane	-134.99	11.901	1.677	37.853	-11.945
Butane	-125.79	11.928	1.935	36.915	-11.402
Isopentane	–	14.279	–	–	–
Pentane	-146.76	14.731	2.464	45.351	-14.111
Decane	-249.46	28.217	–	–	–

5 Results and Discussion of Results

5.1 Results

5.1.1 Results stability and relevance analysis

5.2 Discussion of Results

6 Conclusion and Recommendations

Appendix 1: Nomenclature

a	Attractive term parameter of equation of state
a_{ij}	Attractive force between molecules i and j in mixing rules EOS
A_{leak}	Leak cross-sectional area
A_{LL}	Leak area, liquid
A_{LG}	Leak area, gas or vapour
A_s	Area of the system
A, B, C	Antoine coefficients
b	Repulsive term parameter of equation of state
b_{ij}	Repulsive force between molecules i and j in mixing rules EOS
$B'B$	**Defines** 2nd Virial coefficients for context used in
$C_o \ or \ C_d$	Discharge coefficient
C_P	Specific heat capacity
$\bar{c}_p^{ig}$	Mean heat capacity of ideal gas.
$C'C$	Defines 3rd Virial coefficients for context used in
EOS	Equation of state
ΔE	Change in total energy of the system
ΔE_K	Change in kinetic energy
ΔE_P	Change in potential energy
f	Fugacity
F	Net frictional loss term
g_c	Gravitational constant,
G	Gibbs energy
h_L, h_G	Enthalpy in the liquid and gas phase
H	Total enthalpy
H^R	Residual enthalpy
K	Equilibrium ratio
M_w	Molecular weight
$\dot{m}$	Mass flow rate
n^L, n^G	Moles of liquid and vapour respectively
P	Pressure within the process unit or system

P_c	Critical pressure
P_{choked}	Maximum downstream pressure resulting in maximum flow through a leak hole
Pg	Gauge pressure
P_i^{sat}	Saturated vapour pressure of component i
P_∞ or P_{Atm}	Atmospheric pressure
Q	Volumetric flow rate
R	Universal gas constant
S	Entropy
T	Temperature
T_c	Critical temperature
T^*	Calculated temperature
Δt	Time step indicates the duration of leaks within a computation time interval.
$\Delta T'$	Drop in the temperature of the system
U	Total internal energy of the mixture.
U'	Total internal energy loss
u	Specific Internal energy
u^*	Calculated internal energy
$\bar{u}$	Average instantaneous velocity of the fluid
V	Molar volume
$\dot{V}$	Volumetric flow of the feed
v	Specific Volume
W_s	Shaft work
x_i	Liquid-phase mole fraction of component i
y_i	Vapour-phase mole fraction of component i
Z	Compressibility factor
z	Height of the liquid
z_i	Component total molar fraction

Greek Letters

μ	Chemical potential
$\boldsymbol{\phi}_i$	fugacity coefficient of component i .

ρ	Fluid density
ρ_M	Molar density
$\boldsymbol{\alpha(T_r)}$	Temperature dependency coefficient of attractive term
α	Unitless velocity profile correction factor
γ_i	Activity coefficient of species i
$\gamma = \frac{C_p}{C_v}$	Defines ratio of heat capacities
ω	Acentric factor
β	Parameter, cubic equations of state
σ	Constant, cubic equations of state
ϵ	Constant, cubic equations of state
Ψ	Constant, cubic equations of state
Ω	Constant parameter, cubic equations of state
Υ	Relaxation parameter
τ	Temperature ratio $\equiv \frac{T}{T_{ref}}$
Δ	Difference operator

Subscripts/Superscripts

c	Denotes critical property
i or j	Species or component
ig	Denotes value for an ideal gas
l	Liquid phase
v or $_G$	denotes vapour or gas phase
$_R$	Denotes residual thermodynamic property
ref	reference condition
∞	Denotes a value at infinite dilution
o	Denotes an initial value at source

Appendix 2: List of tables and figures

Annexes

Annex 1: Project Task Description

Annex 2: Matlab /Python Leak Model codes

Annex 3: VBA / Multiflash codes

Annex 1: Project Task description

FMH606 Master's Thesis

Title: Transient hydrocarbon leak calculations in offshore installations – Modelling of thermodynamics of two-phase leaks

TUC supervisor: Associate Professor Amaranath S. Kumara

External partner: Lloyd’s Register Consulting - Senior Consultant Knut Erik Giljarhus

Task description:

- Perform in-depth literature study on thermodynamic models and evaluate their implementation in TLT model.
- Implementation of simple thermodynamic model in TLT. This will be based on the implementation of UV flash routine using VBA (Visual Basic Applications) or MATLAB.
- Validation of model predictions based on VESSFIRE simulations and experimental data

Task background:
The accuracy of transient hydrocarbon leak predictions is extremely important for the Quantitative Risk Assessments (QRA). It has a direct influence on the design and operational specifications of offshore installations with respect to fire and explosion risk.
Transient Leak Tool (TLT) is extensively used as a screening software for both QRA and probabilistic fire and explosion studies. TLT is a non-commercial in-house computer tool developed by Lloyd's Register Consulting. It is based on Visual Basic Applications (VBA). TLT predicts transient leak behaviour of gas and liquid leaks from process segments based on the inventory, initial pressure and hole size. TLT accounts for the transient nature of process leaks by considering the provision of safety systems, such as gas detection, emergency shutdown, time to isolation, blowdown, etc.

Student category:
PT and EET

Practical arrangements:
All the practical issues will be arranged at the kick-off meeting.
Software: Lloyd's Register Consulting will have exclusive rights for software for three years.

Signatures:

Student (date and signature):

Supervisor (date and signature):

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