## Natural Gas Dehydration by Absorption Process:

# A comparative simulation study towards high effective natural gas dehydration using TEG technology

by

Muhammad Aimen Bin Isa

Dissertation submitted in partial fulfilment of the requirements for the

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(Chemical Engineering)

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### CERTIFICATION OF APPROVAL

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By

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A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the Bachelor of Engineering (Hons) (Chemical Engineering)

Approved by,

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Universiti Teknologi PETRONAS

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MAY 2011

### **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Muhammad Aimen Bin Isa

#### ABSTRACT

Natural gas dehydration by absorption using triethylene glycol (TEG) is one of the most effective techniques with high efficiency. There are many processes using this approach but any of them is able to combine the high performance and the economic energy consumption. In this study water hydrocarbon phase behavior was determined for different gas dehydration unit. The effects of the operating conditions of the gas dehydration unit in determining the outlet gas dew point and water content remaining in dry gas were studied by means of simulation run using ASPEN HYSYS software. DRIZO process showed the most significant change of water dew point curve followed by conventional stripping gas dehydration process and then the typical gas dehydration process. At the other hand, study was done on improving the absorption capacity of TEG as the water absorbent by adding additives to the absorbent. Lastly, comparisons between theoretical and simulation results are justified to determine whether it shows a good validation of the results to meet the requirements of current industry practices.

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#### **CHAPTER 1: INTRODUCTION**

#### **1.1 Project Background**

Natural gas is a mixture of naturally occurring hydrocarbon and nonhydrocarbon gases found in porous geologic formations beneath the earth's surface. Raw natural gas comes from three types of wells: oil wells, gas wells and condensate wells. It may associated with oil known as associated gases (wet gas) or it may come alone to be known as non-associated gases (dry gas) (Kermit E. Woodcock)<sup>[1]</sup>. Basically, natural gas that comes out from oil wells is known as 'associated gas' while natural gas that comes out from gas and condensate wells, in which there is little or no crude oil is known as 'non-associated gas' (Kh. Mohamadbeigy, 2008)<sup>[2]</sup>.

The main constituent of natural gas is methane and the minor compositions are ethane, propane, butane, and pentane. Non-hydrocarbon gases such as carbon dioxide, nitrogen, hydrogen sulfide, various mercaptans, and water vapour along with trace amounts of other inorganic and organic compounds can also be present. Once brought from underground, natural gas is refined through gas processing to remove other impurities such as water vapour, volatile organic component (VOC) gases, sand and other compounds as well (H.K.Abdel-Aal et al., 2003) <sup>[3]</sup>.Natural gas that needs to be transported by pipelines must meet certain specifications. Among them is water content that is probably the most common undesirable component found in untreated natural gas. This is due to the reason that the water vapour contains in natural gas will condense into liquid water under low temperature and/or high pressure conditions that later can affect long-distance transmission of natural gas by pipelines <sup>[4]</sup>.

The condensation of water vapour into liquid water in the pipelines during the transmission process need to be avoided since it can cause corrosion on transmission pipelines. This is due to the reason that initially natural gas that contains carbon dioxide and/or hydrogen sulfide is corrosive when liquid water is present that later will cause corrosion to the pipelines itself. Moreover, condensation of water vapour into liquid water can form hydrates that may plug the pipeline and other equipments as well that will caused slugging flow conditions resulting in lower flow efficiency of the pipelines (Luká Polák, 2009)<sup>[5]</sup>.

Thus, in order to meet these requirements for transmission of natural gas through the pipelines and also for further downstream processes, the gas must go through several stages of processing including the removal of entrained liquids from the gas followed by drying to reduce water contents (Myron Gottlib, 2003) <sup>[6]</sup>. The process of removal the water content in the gas is known as the dehydration process and it is important in order to lower the dew point of the gas so that later it will decreased the tendency of the water vapour to be condensed. This process usually involves one of two processes either by absorption or adsorption process.

The dehydration method by absorption is the most commonly used method to removes water vapour from raw natural gas. Absorption dehydration involves the use of liquid desiccant to remove water vapour from the gas. By far, the most common process for dehydrating natural gas is to contact the gas with a hygroscopic liquid such as one the glycols. The glycols are particularly ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T4EG). Water and the glycols show complete mutual solubility in the liquid phase due to hydrogenoxygen bonds, and their water vapor pressures are very low (Kh. Mohamadbeigy, 2007)<sup>[7]</sup>. The most common frequently used glycol for dehydration is triethylene glycol (TEG).

#### **1.2 Problem Statement**

Removing the water from the gas offshore is essential because it decreases the problems associated with water in the gas. This makes the dehydration process an essential part of the offshore gas treatment (Luká Polák, 2009)<sup>[5]</sup>. Upon natural gas dehydration process, the dew point of the wet gas decreases with the degree of lowering the water content of the gas. The acceptable limit of water content as well as the dehydration method depends on the intended use of the gas. In a gas transmission line a water content of 6-10 lb/mmscf (96-160 kg /mmm3) giving a gas dew point of  $-2^{\circ}$ C to  $-9^{\circ}$ C is needed (Reza Salamat, 2009)<sup>[9]</sup>. However nowadays, very low natural gas dew points are required for gas transmission by pipelines and other downstream gas processing, corresponding to a lower reduction of water content (Naif A. Darwish a et al., 2007) <sup>[10]</sup>. In order to attain these restrictions specifications, TEG regeneration step is crucial part of the dehydration process.

If the water-rich TEG exiting the absorption column is regenerated at atmospheric pressure, TEG can only be regenerated to levels about 98.9-98.9% by weight (I.M.T Arubi et al., 2008) <sup>[11]</sup>. This is due to the reason that the re-boiler operating temperature which cannot be fixed above 204°C. In fact, this temperature must be regarded as an upper limit for TEG processing, because of the thermal degradation at higher values (Steele et al., 1996) <sup>[12]</sup>. Thus, in order to attain higher regeneration levels without exceeding the upper limit temperature for TEG processing, several alternative processes need to be proposed, requiring a clear representative relationship between TEG concentration and the water content and its dew point as well.

#### 1.3 Objective and Scope of Study

The objectives of this study are:

- To study on current technologies of natural gas dehydration process
- To study the effect of operating conditions on the efficiency of the process.
- To compare between current technologies for natural gas dehydration in terms of its efficiency in removing water contents and reducing the water dew point temperature using mathematical correlation and simulation results data.
- To investigate the possibility of absorbent modifications.

The major scope of this study is to come out with the best solution of natural gas dehydration process by using the existence technology of absoprtion process. All related data are collected from several trusted resources that relate with the scope of study. These data are used as the main input for the purpose of simulation studies using Aspen HYSYS software.

#### **1.4 Significance of Study**

Nowadays very low natural gas dew points are required for gas transmission by pipelines, corresponding to a reduction of water contents, on average, down to 70 -120 mg/Nm<sup>3</sup> (Huffmaster, 2004). This was due to the transmission process that may cause problems if water contents exceeded the limit that later will formed hydrates. In the past years, glycol dehydration plants have been designed using rule of thumb procedure (Hernandez-Valencia et al., 1992) <sup>[13]</sup>. While still sufficient for many applications, today more efficient designs are often required especially that involved with absorption process since it is more preferable of its economical value to the gas dehydration process. This relates with the scope of study of this project whereby a comparative simulation study towards high effective natural gas dehydration using TEG technology

#### 1.5 Feasibility of Study

Throughout this study there are several phases that will be done throughout completing the project:

- I. Research based on literature review on Natural Gas dehydration process from multiple types of references and sources. This phase involved doing researches within the limit of scopes of the project in order to built strong foundation on the theoretical part before proceeding with the next phases of the project.
- II. Identifying related data used for the simulation process. This phase involved collecting all the required data needed before proceed with the simulation process of the respective natural gas dehydration process. These collected data will involved all the related parameters including the process flow diagram of the respective processes and the raw data to be used for the purpose of simulation using Aspen HYSYS software.

- III. Testing, Comparing and Modifying of all collected data. This data that are previously collected from various trusted sources and references will be tested in terms of their feasibility and later to be used as input data in executing the simulation process in determining the best possible methods that can be used. Based on these data, certain criteria will be modified in order to optimise and to increase the effectiveness on the process. The outcome results from simulation are to be compared with calculations from theoretical part using specific equations for the purpose of validation of the results.
- IV. Determining the most optimize process parameters. Based on the results of testing and analyzing of each data collected, the best process parameters will be determined. Then the best modified process best on the existence process will be proposed as the final outcome of this project.

#### **CHAPTER 2: LITERATURE REVIEW**

#### 2.1 Natural Gas Dehydration

Water is almost accompanied with hydrocarbon and there will be a requirement for a gas or liquid hydrocarbon to reduce the water content to acceptable limit to avoid water separation from the gas. Natural gas dehydration is the process of removing water vapour from the gas stream to lower the dew point of that gas. Water is the most common contaminant of hydrocarbons. It is always present in the gas-oil mixtures produced from wells. Basically, there are three reasons of having this natural gas dehydration (H.K.Abdel-Aal et al, 2003)<sup>[20]</sup>:

- I. To prevent hydrate prevention: hydrates are solids formed by the physical combination of water and other small molecules of hydrocarbons. They are icy hydrocarbon compounds of about 10% hydrocarbons and 90% water. Hydrates grow as crystals and can build up in orifice plates, valves, and other areas not subjected to full flow. Thus, hydrates can plug lines and retard the flow of gaseous hydrocarbon streams. Among the factors that contributing in the formation of these hydrates are the low temperature of the gas and high pressure of the surrounding.
- II. To avoid from any corrosion to occurred: the water vapour will dissolve in hydrogen sulphide in the natural gas to form an acidic solution. This acidic solution will reacts with carbon steel in the pipeline to caused corrosion.
- III. Downstream process requirements: in most commercial hydrocarbon processes, the presence of water may cause side reactions, foaming, or catalyst deactivation. Consequently, purchasers typically require that gas and liquid petroleum gas (LPG) feedstocks meet certain specifications for maximum water content.

The amount of water to be removed from the gas depends on the lowest temperature at which the gas will be exposed in the pipeline. This is due to the reason that as the gas temperature reducing, the water vapour contained in it tends to condense into liquid that later will increase the tendency of hydrate formation in the pipelines. The point where water vapour starts to condensed known as dew point. This dew point acts as an indicative of the quantity of water vapour present in the gas stream.

#### 2.2 Gas Hydrates

Gas hydrates are crystalline molecular complexes formed from mixtures of water and suitably sized gas molecules (B.Tohidi et al.,1990)<sup>[27]</sup>. Based on hydrogen bonding, water molecules form unstable lattice structures with several interstitial cavities. The gas molecules mostly methane can occupy the lattice cavities and, when a minimum number of cavities are occupied, the crystalline structure becomes stable and solid gas hydrates are formed, even at temperatures well above the ice point as what shown in figure 2.30 (Sloan, 1997)<sup>[28]</sup>. Only molecules having a certain range of diameters can form inclusions. This is because the diameter of the molecule must be smaller than that of the cavity or close to it for the molecule to enter the cavity, and sufficiently large for the crystal lattice to be stable (Sloan, 1997; Rojey et al., 1994)<sup>[28]</sup>. The main concern of hydrates is that they can form in the pipelines with large amounts of it can be in the gas simultaneously. This can create plugs or blockage in the pipelines that later will retard the flow of the gas itself. Moreover, this blockage can arise in the pipelines within minutes without any prior of warnings.



Figure 2.20: Natural gas hydrate structure for type-I gas hydrates

The formation of hydrates depends on the operating pressure and temperature whereby it increases with increasing pressure and can form at temperature as high as at  $25-30^{\circ}$ C (77-86°F)(James G. Speight, Dr.,2006)<sup>[30]</sup>. This is further depicted in figure 2.31 from typical pressure-temperature diagram for the formation of natural gas hydrates.



Figure 2.21: Pressure-temperature graph for a typical natural gas hydrate<sup>[30]</sup>.

At present, the known gas hydrate structures are structure-I, structure-II, and the recently discovered structure-H (Ripmkester et al., 1987)<sup>[29]</sup>. Different types of hydrates will be stabilized by different sizes of gas molecules. Structure I can be formed when the natural gas is mostly contains of smaller gas molecules such as methane and contains almost no C3–C4 hydrocarbon components. Structure II is the most common gas hydrate structure encountered in the field since it is stable whenever a natural gas mixture contains some propane or butanes besides methane. As for Structure H, it is very rarely encountered in the oil industry. It is stabilized by methane in small cages and fairly large hydrocarbons such as methylcyclopentane or benzene in large cages. Different types of hydrates are differs in terms of their ratio between small and large type cavities that they have as shown in figure 2.32.



Figure 2.22: Different types of gas hydrates

#### 2.3 Glycol Selection as the Absorbent Medium

Glycol used in this process is a thermodynamic inhibitor type or called as 'hydrate antifreeze' whereby it works by changing the thermodynamic properties of the fluid system, thereby shifting the equilibrium conditions for gas hydrate formation to lower temperatures or higher pressures(James G. Speight, Dr., 2006)<sup>[30]</sup>. This glycol selection for natural gas dehydration may be based on a number of factors including dehydration capability, glycol losses in the contactor and regenarator and absorption of VOCs (I.M.T Arubi et al., 2008)<sup>[11]</sup>. The liquid desiccants most commonly used at present are certain glycols: ethylene glycol, diethylene glycol (DEG) and triethylene glycol (TEG), although other compounds have been utilized for special circumstances, such as methanol or glycerol. The basic principle of the absorption capability of glycol and other absorbent such as methanol in removing water vapour from gas lies in its chemical structure. Each of these molecules of the absorbents contains hydroxyl groups (OH) whereby they will form hydrogen-bonds with the water molecules (M. A. Huffmaster, 2004)<sup>[15]</sup>. Thus, water vapour molecules contain in wet gas will be easily attracted to the absorbent once a direct contact occurred between them. From figure 2.1, glycol having two hydroxyl groups bonds even more strongly and acts as better absorbent compared to methanol.

| Name                           | Formula                                                                               |                         |
|--------------------------------|---------------------------------------------------------------------------------------|-------------------------|
| Ethylene<br>glycol (EG)        | HO-(CH <sub>2</sub> ) <sub>2</sub> OH                                                 | $\mathrm{C_2H_6O_2}$    |
| Diethylene glycol<br>(DEG)     | HO((CH <sub>2</sub> ) <sub>2</sub> O)(CH <sub>2</sub> ) <sub>2</sub> OH               | $\mathrm{C_4H_{10}O_3}$ |
| Triethylene glycol<br>(TEG)    | HO((CH <sub>2</sub> ) <sub>2</sub> O) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> OH | $\mathrm{C_6H_{14}O_4}$ |
| Tetraethylene glycol<br>(TREG) | HO((CH <sub>2</sub> ) <sub>2</sub> O) <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH | $\mathrm{C_8H_{18}O_5}$ |
| Propylene glycol               | HO-(CH <sub>2</sub> ) <sub>3</sub> -OH                                                | $\mathrm{C_3H_8O_2}$    |

Figure 2.30: Chemical Structure Glycols used in Natural Gas Dehydration<sup>[28]</sup>

The most commonly used glycol in the industry of natural gas dehydration process is triethylene glycol (TEG), diethylene glycol (DEG) and ethylene glycol (EG) may also be used in dehydration applications however, DEG and EG are often not considered due to dry gas water requirements. By using DEG and EG instead of TEG, it is an environment concern since it can greatly reduced BTEX emissions, thus reduce emissions from the glycol still vent (Braek et al., 2001) <sup>[16]</sup>. TEG offers the best cost beneficial compromise, and is the most widely used (Manning and Wood, 1993)<sup>[26]</sup>. Even though it is marginally more expensive than DEG, but it brings much less losses due to lower vapour pressure. It also has higher affinity towards water but lesser than tetraethylene glycol (TREG). However it is less viscous compared to TREG which translates into lower pumping costs. Moreover, TREG is more costly compared to the other glycols. At the other hand, TEG is easily regenerated since it has a higher decomposition temperature of 204°C and is not too viscous as the temperature is above 4°C (Manning and Thompson, 1991)<sup>[27]</sup>. Thus it is suitable to be used with broad range of temperatures for the process.

#### 2.4 Enhanced Natural Gas Dehydration

Instead of choosing the right absorbents in the gas dehydration process, enhanced regeneration is another focus topic of many researches since it can greatly improves the capability process of glycol dehydration. Enhanced regeneration can be defined as any system that improves glycol regeneration to achieve a leaner or more concentrated glycol solution once it has been recycled. It could be achieved either by injection of stripping gas into the re-boiler, azeotropic regeneration or other proprietary processes (Ebeling et al., 2008) <sup>[17]</sup>. Typically, rich TEG is regenerated under low pressure and high temperature in a regeneration process. Among them are:

- I. Vacuum: where a TEG concentration of 99.2 to 99.9% giving a possible water dew point depression of 100-105°F (38-66°C) to be achieved. The disadvantage of this method is the difficulty holding the required vacuum in the process.
- II. Coldfinger: 99.9wt% TEG is regenerated giving a dew point depression of 100-150°F (38-66°C).
- III. Drizo: TEG concentration in excess of 99.99wt% is obtained with the adherent dew point depression of 180-220°F (82-104°C). This is used when super dryness is required for further gas processes. This process used azeotropic distillation method to achieve leaner regenerated TEG thus to have higher dew point depressions of the wet gas.

The dehydration rate using the typical gas dehydration process shown in figure 2.40 has a little significant impact on the efficiency of the gas dehydration process since the concentration of the regenerated TEG is directly proportional to the amount of water being absorbed in the absorption column. This due to further increase of re-boiler temperature will not be so effective to remove more water vapour from TEG since excessive increase of reboiler temperature will caused the decomposition of TEG itself. The maximum recommended reboiler temperature for TEG is 350 F and 400F and equivalent to TEG concentration of 97-98% wt. for the respective typical gas dehydration process (M. A. Huffmaster, 2004)<sup>[10].</sup>



Figure 2.40: Typical natural gas dehydration<sup>[25]</sup>

#### 2.41 Stahl Columns and Stripping Gas

One of the alternative methods in order to increase the rate of regeneration for TEG is by reducing the partial water vapour pressure in the regenerator column by introducing the use of stripping gas and additional Stahl column or by lowering operating pressure of the regenerator column to be below atmospheric pressure (vacuum). In this case, uses of stripping gas is more preferable since reducing the regenerator column to pressure below atmospheric pressure would be a lot more complicated and costly as well. A Stahl column gives an extra stage of regeneration by taking the solvent from reboiler and contacting it with a flow of dry stripping gas.

By reducing the total pressure in the regenerator, the boiling point of water could be reduced since it is directly proportional to the regenerator column pressure, thus at constant temperature more water will be extracted from TEG in the form of water vapour that comes out as the top product of regenerator column. This process is further depicted in figure 2.41.



Figure 2.41: Natural gas dehydration with Stahl column and stripping gas <sup>[25]</sup>

#### 2.42 DRIZO Process

For downstream processes that require natural gas with the least amount of water vapour, the gas dehydration process should be at its most optimum condition while maintaining the highest achievable concentration of regenerated TEG. This could be achieved by further enhancing TEG regeneration process using the DRIZO process. DRIZO technology regenerates the glycol by solvent stripping instead of the conventional gas stripping that uses the flash gases. This solvent stripping allows obtaining higher TEG purities than gas stripping up to 99.998% wt and consequently to get much large water dew point depressions ( up to 100 °C) <sup>[22]</sup>. As illustrated in figure 2.42, the principle is that the effluent gas from the regeneration column is recovered as liquid after the regeneration column (top product of regeneration column).

These liquids are the condensed hydrocarbon solvent (e.g, aromatics gas) separated from condensed water and light gas in three phase separator or it can be introduced externally (e.g, n-heptane, benzene, etc.) together with these condensed aromatics gases. These condensed aromatics gases are superheated to form stripping gas introduced at the bottom of the stripping column (Stahl column).

Aromatics gases introduced act as entrainer in TEG-Water system in the regeneration column in order to conduct homogeneous azeotropic distillation between benzene and water that will later form homogeneous azeotrope and rise as the top products of the regeneration column in vapour form. This helps to increase the concentration of regenerated TEG so that more water vapour will be absorbed from wet natural gas by TEG hence leaving only very small amounts of water vapour remained that is up to 1 lbm/MMscf of dry gas.



Figure 2.42: DRIZO natural gas dehydration<sup>[26]</sup>

#### 2.5 Water Content with Respect to Hydrate Region

Hydrate formation is a time dependent process. The rate at which hydrate crystals form depends upon several factors including gas compositions, presence of crystal nucleation sites in the liquid phase, degree of agitation and etc.(Dr. Mahmood Moshfeghian, 2010)<sup>[18]</sup>. For water saturated gases, the water dew point temperature line is either above or at the hydrate formation temperature line.

However, if the gas is water under-saturated, the hydrate formation temperature line will be higher than water dew point line. Shown in figure 2.50, is an example of gas condition whereby its water dew point line is illustrated with a dashed line while hydrate formation line is illustrated with a solid line. From the figure, it shows that when the gas is saturated with water vapour; water dew point line will be located above the hydrate temperature line since its water content is high.



Figure 2.50: Water content of 94.69 mole % methane and 5.31 mole % propane – gas in equilibrium with hydrate at 1000 Psia (6,897 kPa)<sup>[18]</sup>

Further explanation pertaining to the water content with respect to hydrate region can be seen by hydrocarbon phase envelope illustrated in figure 2.51. Notice that up to pressure 414 psia, the water dew point curve is slightly to the left of the hydrate formation curve. This indicates that the gas is under-saturated with water at pressure below this point. This condition known as 'meta-stable' water condition and indicates that the gas is thermodynamically unstable and will not form a free aqueous phase. As for the point where the pressure is above 414 psia, it shows that the water dew point curve locates to the right of the hydrate curve. Under this condition free water forms and the hydrates may form if conditions are right (Ebeling et al, 1998) <sup>[19]</sup>. At this condition, as the temperature keeps on declining, the condensed water phase will transform into solid hydrate even its temperature higher than freezing point of water. Once the hydrate formed, the 'meta-stable' water condition is now known as 'meta-stable' equilibrium.



Figure2.51: Phase envelope, hydrate formation and water dew point curves of a natural gas<sup>[19]</sup>.

It could be seen from the figure itself that the relative location of the water dew point and hydrate curves with respect to each other is a strong function of water content, It is shown that for the cases where water content is above saturation point, the water dew point curve locates to the right of the hydrate curve while for undersaturated gas, the water dew point will locates to the left of the hydrate curve.

#### 2.6 Addition of Salts to Improve Absorption Capacity of TEG

Further modifications of TEG as the absorbent in the process are needed in order to improving the rate of absorption of TEG towards water vapour from the wet natural gas. This is possible since by addition of salts, it could increase the absorption capacity and the hygroscopicity of TEG towards water vapour contains in the wet natural gas. This is done by mixing the glycols used in the natural gas dehydration process with salts preferably selected from the group consisting of potassium formate and potassium acetate. Potassium formate aqueous solution has known with its ability to absorb water vapour from wet natural gas and currently it is used in the concentration from 40% to 80%, preferably from 65% to 77% and most preferably from 70% to 75% weight percent (GilbStephen Atkinson, 1994)<sup>[31]</sup>. Furthermore, the salt to be mix with TEG is relatively non-toxic and non-corrosive towards metals (GilbStephen Atkinson, 1994)<sup>[31]</sup>.

This is proven from corrosion test using 65% of weight percentage of the aqueous potassium formate solution that showed measurement readings at a rate equivalent to less than 1.0 mm/year (GilbStephen Atkinson, 1994)[31]. In addition, in dilute solution of aqueous potassium formate, it is biodegradable, environmentally responsible (low ecotoxicity), and has a low level of toxicity. However, potassium formate is useful at concentrations up to its limit of solubility only and it may be used in conjunction with other known absorbents. In the range 40% to 70% of weight percentage in the aqueous solution, potassium formate has many physical and chemical properties that make it useful to be used as an absorbent or an additive to the absorbent itself such as it has low crystallization temperature whereby crystallization takes place at temperatures below  $-36^{\circ}$ C.and demonstrate an unusually low viscosity that cam lowered the pumping cost of the process as well (John H. Hallman, 2001)<sup>[32]</sup>.

Through addition of aqueous potassium formate solution in TEG, it will helps to increase the amount of water vapour being absorbed from the wet natural gas that is up to three times or more depending upon the amounts of salt added to the mixture itself (Gilbert Gavlin et al., 1996)<sup>[33]</sup>. Basically, the maximum amounts of the salt to be added with TEG used in the process rely on the solubility of the salt itself in the TEG as what shown in tables 2.60 below, that is the solubility of potassium formate and potassium acetate in the TEG solution. From the data it could be seen that potassium formate is substantially more soluble in TEG rather than potassium acetate. Thus, potassium formate is the preferred dissolved salt to be mix as an additive in the anhydrous TEG solution.

| Salt              | Solution                                       | Solubility (wt%) |
|-------------------|------------------------------------------------|------------------|
| Potassium Acetate | tassium Acetate anhydrous ethylene glycol (EG) |                  |
|                   | anhydrous diethylene glycol (DEG)              | 35               |
|                   | anhydrous triethylene glycol (TEG)             | 4                |
| Potassium Formate | anhydrous ethylene glycol (EG)                 | 40               |
|                   | anhydrous diethylene glycol (DEG)              | 25               |
|                   | anhydrous triethylene glycol (TEG)             | 21               |

Table 2.60: Potassium formate and potassium acetate solubility in glycol solutions.<sup>[33]</sup>

Moreover, the ability of potassium formate to absorb water vapour is shown in table 2.61 below whereby aqueous potassium formate solution in the concentration of 70 weight percent alone without mixing with any other solutions is compared with 100 weight percent of TEG. From the table, it shows that at the same initial weight percent of water content in the solution, potassium formate solution showed better results in terms of amount of the water vapour being absorbed from the gas itself compared to the TEG with respect to time. Thus, it is proven that aqueous potassium formate solution itself have high affinity towards water vapour hence it is suitable to be used with TEG in the gas dehydration process.

|          | Original wt.% | 24 hours | 48 hours | 72 hours | 96 hours |
|----------|---------------|----------|----------|----------|----------|
|          | in solution   |          |          |          |          |
| KCOOH    | 20.27         | 50       | 71       | 87       |          |
| 70wt.%   | 43.44         | 16       | 28       |          |          |
|          | 35.88         | 25       | 32       | 59       | 61       |
|          | 43.65         | 22       | 33       | 49       | 56       |
|          | 63.22         | 13       | 22       | 31       |          |
| TEG      | 21.06         | 36       | 46       | 56       |          |
| 100 wt.% | 37.44         | 19       | 26       | 32       |          |
|          | 44.37         | 17       | 23       | 30       |          |

Table 2.61: Percent of water vapour absorbed by weight<sup>[32]</sup>

#### 2.7 Equilibrium Correlations for Predicting Water Dew Point

Evaluation of TEG system involves first establishing the minimum concentration of TEG concentration required to meet the outlet gas water dew point specification (Bahadori e. al, 2008)<sup>[12]</sup>. Several equilibrium correlations for predicting water dew point of natural gas in equilibrium with TEG dehydration system have been presented since 1950 (Akireza Bahadiro et al., 2009)<sup>[21]</sup>. It is important to have an easy-to-use correlation to predict accurately the equilibrium between water dew point of natural gas with respect to TEG concentration in the dehydration system. This is further depicted by the correlations in figure 2.70 that relates between the water dew point (Td) of natural gas stream with respect to the concentration of TEG.

| $T_{d} = a + bT + cT^{2} + dT^{3}(1)$                                                                                                                   |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                                                                                                                         |
| Where:                                                                                                                                                  |
| $a = A_1 + B_1 W + C_1 W^2 + D_1 W^3. $ (2)                                                                                                             |
| $b = A_2 + B_2 W + C_2 W^2 + D_2 W^3 $ (3)                                                                                                              |
| $c = A_3 + B_3 W + C_3 W^2 + D_3 W^3 \dots (4)$                                                                                                         |
| $d = A_4 + B_4 W + C_4 W^2 + D_4 W^3 \dots \dots$ |

Figure 2.70: Equilibrium correlations between water dew point(Td) of dry gas with respect to concentration of regenerated TEG(W)<sup>[21]</sup>

By using the correlations, rapid estimation for water dew point (Td) of the natural gas stream in equilibrium with concentration of regenerated TEG solution at various contactor temperatures (T) could be done. The equation used contains several relevant coefficients as what shown in equations (2)-(5) and they are related with their tuned coefficients reported in table 2.60. These coefficients are applicable for contactor temperature between 10-80°C and regenerated TEG purity of 90-99.999 weight percent. These equilibrium coefficients are important since they could be used as the point of reference to validate the results generated through simulation with respect to the results from the theoretical part.

Table 2.70: Tuned coefficients used in Equations (2)-(5)<sup>[21]</sup>

| Coefficient | 90% <teg<99%< th=""><th>99%<teg<99.9%< th=""><th>99.9%<teg<99.999%< th=""></teg<99.999%<></th></teg<99.9%<></th></teg<99%<> | 99% <teg<99.9%< th=""><th>99.9%<teg<99.999%< th=""></teg<99.999%<></th></teg<99.9%<> | 99.9% <teg<99.999%< th=""></teg<99.999%<> |
|-------------|-----------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------------------------------------------|
| A1          | 2.727934205E+07                                                                                                             | 5.948778272E+09                                                                      | -1.434042060E+13                          |
| B1          | -8.631372857E+05                                                                                                            | -1.790765204E+08                                                                     | 4.304293620E+11                           |
| C1          | 9.095756908E+03                                                                                                             | 1.796891322E+06                                                                      | -4.306461745E+09                          |
| D1          | -3.192394177E+01                                                                                                            | -6.010038602E+03                                                                     | 1.436210186E+07                           |
| A2          | -2.653646110E+05                                                                                                            | -6.033812029E+07                                                                     | 1.377170114E+11                           |
| B2          | 8.394220905E+03                                                                                                             | 1.816573930E+06                                                                      | -4.133592993E+09                          |
| C2          | -8.843532185E+01                                                                                                            | -1.823001079E+04                                                                     | 4.135676304E+07                           |
| D2          | 3.103038903E-01                                                                                                             | 6.098082811E+01                                                                      | -1.379253425E+05                          |
| A3          | 8.616616028E+02                                                                                                             | 2.040747181E+05                                                                      | -4.362719887E+08                          |
| B3          | -2.725023220E+01                                                                                                            | -6.144735183E+03                                                                     | 1.309475458E+07                           |
| C3          | 2.870185527E-01                                                                                                             | 6.167227567E+01                                                                      | -1.310135159E+05                          |
| D3          | -1.006847138E-03                                                                                                            | -2.063239321E-01                                                                     | 4.369316891E+02                           |
| A4          | -9.319294190E-01                                                                                                            | -2.273886760E+02                                                                     | 4.616804880E+05                           |
| B4          | 2.946481646E-02                                                                                                             | 6.847347278E+00                                                                      | -1.385739729E+04                          |
| C4          | -3.102601747E-04                                                                                                            | -6.873040245E-02                                                                     | 1.386438215E+02                           |
| D4          | 1.088073589E-06                                                                                                             | 2.299579468E-04                                                                      | -4.623789735E-01                          |

#### **CHAPTER 3: METHODOLOGY**

Throughout completing the project, it will follow the project's flow as follows:



Figure 3.1: Complete Project's Flow

#### **3.1 Literature Review**

During the first phase of the project, a literature research is conducted from several trusted sources (book, journals, thesis, website, etc.). Then, these data are summarised and documented into a complete literature review format. Preparing literature review is vital at the very early phase of the project since it can create a good foundation and improves understanding towards completing the project.

#### **3.2 Simulation Run**

All required data are collected from several sources during the early phase of the project. These data are documented and used as the inputs for the simulation run of the project using Aspen HYSYS software. Initially, simulation run was done based on the typical model of natural gas dehydration plant. Property package used in running the simulation is carefully determined in order to increase the efficiency of the output data collected. Raw data for natural gas components and several operating conditions involved in the process need to be determined first before initial run can be done using HYSYS simulation tool. These data are adjusted accordingly until the process simulation is fully converged. Data are then stored and tabulated to be compared with the theoretical one.

#### **3.3 Data Analysis of Simulation Run**

Outputs gained from the simulation run are analysed and compared to those output data presented in several sources collected before from the previous phase of the project. Types of output data from simulation that need to be collected are determined and properly showed in table and figure diagram.

Comparisons were done on the water content of the natural gas based on the pre and post of the natural gas dehydration unit. Later, the input data that is the parameters that involved in the process simulation are modified accordingly with respect to the objective of the project that is to study the effect of operating conditions on the efficiency of the process by means of simulation approach that is by using this HYSYS software. Heat utilizations of the re-boiler for the regeneration column was set as the constant parameter while comparisons are done in terms of changes of other operation conditions parameters towards the output data of the simulation process. Variations between these data from simulation run and the theoretical data are to be justified accordingly for the purpose of validation of the results gained.

#### 3.4 Enhanced Model Simulation Run

The similar raw data used for the previous step in 3.2 of the process are used to develop a new and enhanced flowsheet for the next simulation run. Together with several other data collected from several sources that relate with the enhance natural gas dehydration by absorption, they are used as the inputs in developing a new enhanced simulation model. Different enhanced simulation models will have different principle of working in the way they regenerate the absorbents to be used and to be recycled in the process. Each data are determined carefully so that the output data will have high degree of efficiency in terms of water dew point depressions and the water content remained in the dry gas after it passed through the gas dehydration unit.

#### 3.5 Data Analysis of Overall Simulation Run

The overall outcomes of simulation run for different types of flowsheet (typical and enhanced model) are to be compared between each other. These data are compared in terms of their ability in dehydrating the wet gas at the most minimum level of water contents remained in the dry gas after it leaves the dehydration facility at constant amount of energy input. This was done with respect to the objective of the project that is to compare between current technologies for natural gas dehydration in terms of its efficiency in removing water contents and reducing the water dew point temperature of the natural gas.

The most significant comparison was done using the P-T diagram (phase envelope diagram) in order to compare the water dew point of the natural gas after it passed through different types of enhanced gas dehydration unit. Output data are also compared in terms of the absorbent modifications toward improving the dehydrating capability of the absorbent. This was done by mixing the absorbent with additives in the gas dehydration unit. Overall analysis were justified and documented accordingly.

#### **3.6 Conclusion and Report Writing**

Last but not least, a conclusion is justified based on the overall output data collected from the simulation runs. Based on the conclusion the author decides whether the objectives of the project are achieved or not. All these data and analysis involved throughout the completions of the project are summarised into a complete documentation of final report thesis writing.

#### **CHAPTER 4: RESULTS AND DISCUSSIONS**

In nature, water and glycol will mix and create a single water/glycol phase, due to the polar attraction between the components. This mixture is complicated to simulate because of the polar interaction between water and glycol (Dan Laudal Christensen, 2009)<sup>[25]</sup>. Thus proper thermodynamic equations are needed to simulate the water/glycol mixture correctly in order to model the gas dehydration process accurately. Models based on a cubic equation of state generally guarantee good phase equilibrium predictions over a wide range of temperature and pressure. This is important in view of modelling the multi-component system in the natural gas dehydration units, where it is necessary to account for the presence of gases and for the high operating pressure of the absorption column (Peng, D., Y., Robinson, 1976)<sup>[23]</sup>.

For the purpose of this simulation, that is both for the typical gas dehydration unit and the enhanced gas dehydration unit, several thermodynamic packages have been used. The main simulation platform used for this simulation is the Aspen HYSYS software and it is used for the simulation of this gas dehydration process. Peng-Robinson and Twu-Sim-Tassone (Glycol) is chosen as the thermodynamic packages in running the simulation. Two thermodynamic packages are required due to the reason that Peng-Robinson alone cannot calculates accurately the TEG-water system for the regeneration part of the gas dehydration unit since it calculates significant amounts of TEG as the top product of the column (Lars Erik Øi et al., 2002)<sup>[19]</sup>.

This is against with the real case since vapour pressure of TEG is really low thus reduced its tendency to vaporize and to be collected as the product of the regeneration column. In the meantime, Twu-Sim-Tassone (Glycol) thermodynamic package is good in determining accurately the activity coefficients of the TEG-water system and it is also applicable for broader range of pressure and temperature (Chorng H. Twu ,2005)<sup>[34]</sup>. Thus it is suitable to be used in the regeneration part of the gas dehydration unit since TEG regeneration process involved at high temperature.

The inlet data used in the simulation are based on the conditions resemble one of the onshore oil and gas-processing facilities in the UAE (Naif A. Darwish a et al., 2002)<sup>[24]</sup> as shown in Table 4.0 is the summary of operating conditions of the base case employed in the simulation while in Table 4.1 is the composition of wet gas with respect to its mass fraction in the appendix.

### 4.1 Effects of Operating Conditions on the Efficiency of the Gas Dehydration by Absorption Process

Analyses are done on the effects of the operating conditions toward the efficiency of the gas dehydration process by simulation run of the typical natural gas dehydration unit model using Aspen HYSYS software. Typical gas dehydration units are typically represented by a contactor, a flash tank, and a regenerator as shown in figure 2.40 in chapter 2 of the report. The outcome data from simulation that is in terms of the water content remaining in the gas after it passed through the gas dehydration unit is being manipulated by several parameters. These parameters are stages of absorption column, volume flow rate of TEG, re-boiler temperature of the regeneration column, and volume flow rate of the stripping gas used in the stripping column. The following result shows a parametric study of a typical gas dehydration unit in optimizing the dehydration process itself.

#### 4.11 Effect of Number Equilibrium Stages in the Contactor

Figure 4.11(a) illustrates the effect of number of equilibrium stages on residual water content of the dry gas exiting the dehydration facility using a 202°C re-boiler temperature to regenerate the TEG. It can be seen that increase in number of stages of the contactor will allows more water vapour to be absorbed from the wet gas thus reducing the residual water content of the dry gas. Lower circulation of TEG with higher number of stages of the contactor is needed to produce certain amount of residual water content of the dry gas compared to those with lower number of stages. This is due to the reason that increase in number of stages allows the gas to approach equilibrium with the lean glycol at lower circulation rate of TEG (I.M.T Arubi et al., 2008)<sup>[11]</sup>.



Figure 4.11(a): Effect of number of equilibrium stages on residual water content

#### 4.12 Effect of Volume Flow Rate of TEG in the Contactor

Lower amount of residual water content in the dry gas will affects the overall water dew point depression. Lower water dew point of the gas is needed for pipelines transmissions and other downstream gas processes. The relations between dew point depression and number of stages with respect to TEG volume flow rate is further depicted in Figure 4.12. It can be seen that higher TEG volume flow rate will cause higher water dew point depressions since higher degree of contact between the gas and TEG. Thus enables more TEG to be hydrogen-bonded with water molecules hence to absorb them from the raw natural gas and to reduce the dry gas water dew point as well.



Figure 4.12: Effect of volume flow rate of TEG to dew point depressions

#### 4.13 Effect of Re-boiler Temperature

One of the disadvantages of the gas dehydration process by absorption process using TEG is that by increasing the re-boiler temperature of the regeneration column to a temperature higher than 204°C, it will leads to thermal decomposition of TEG. Figure 4.12 in appendix illustrates the residual water content of the dry gas from the contactor outlet with respect to the re-boiler temperature of the regenerator used to regenerate the rich TEG. The reboiler temperature influences the overhead water content by changing the purity of the TEG thus improve its absorbent capacity as well. Higher reboiler temperature will produced higher purity of regenerated TEG to absorb more water vapour from the wet gas (Alireza Bahadori et al., 2009)<sup>[21]</sup>.



Figure 4.13: Effect of re-boiler temperature to the residual water content in TEG

#### 4.14 Effect of Stripping Gas

Applications requiring high dew point depression will virtually always utilize stripping gas in the regenerator. Low water dew point cannot simply be achieved by typical natural gas dehydration facilities. Further enhancing of the existence gas dehydration facilities are needed such as the use of stripping gas in the dehydration process. Figure 4.13 illustrates the effect of stripping gas on the residual water content of the dry gas. Increasing the stripping gas volume flow rate will have much greater effect than increasing re-boiler temperature. By reducing the total pressure in the regenerator using the stripping gas, it will increase the tendency of water molecules in TEG to be vaporized hence reduced its boiling point as well.

At constant re-boiler temperature, more water will be extracted from TEG in the form of water vapour that comes out as the top product at the regeneration column with increasing stripping gas volume flow rate. Hence, the concentration of regenerated TEG will increase as well.



Figure 4.14: Effect of stripping gas on the residual water content

# 4.2 Simulation of Typical Gas dehydration Unit, Stripping Gas and Stahl Column Gas Dehydration Unit and DRIZO Gas Dehydration Unit

By using Aspen HYSYS software, several gas dehydration units (GDU) are simulated using the real data plant resemble one of the onshore oil and gas-processing facilities in the UAE (Naif A. Darwish a et al., 2002)<sup>[24]</sup>. These gas dehydration units are the typical gas dehydration unit and the enhanced gas dehydration units such as the Striping gas Stahl column GDU and the DRIZO GDU.

The performance for each of these gas dehydration units (GDUs) are investigated in terms of the water dew point and water content remaining in the dry gas after it passed through the GDU with respect to concentration of regenerated TEG. These data are further depicted in figure 4.22 to figure 4.25. From figure 4.22, it shows the P-T diagram (phase envelope diagram) of the wet gas before it enters the gas dehydration unit for the gas dehydration process. It could be seen from the P-T diagram of the wet gas itself that it is saturated with water vapour since the water dew point curve located at the right side of the hydrate curve as what mentioned previously in the literature review part of the report. Under this condition free water
forms and the hydrates may form if conditions are right (Ebeling et al, 1998). Once the hydrates are formed, the 'meta-stable' water condition is known as 'meta-stable' equilibrium.



Figure 4.22: P-T diagram of wet natural gas

As for figure 4.23, it shows the P-T diagram for the dry gas after it passed through Stripping gas and Stahl column GDU while for figure 4.24, it is for the dry gas after it passed through the DRIZO GDU. Due to the removal of water vapour from the wet natural gas absorbed by TEG in the column, the water dew point curve has been shifted to the left side of the phase envelope. At this condition, the water content of natural gas has been reduced significantly while reducing the water dew point temperature as well. Thus, dry gas from the absorption column can operates at lower temperature since the water dew point has been shifted to lower temperature. This is due to the reason that at temperature higher than water dew point temperature, the gas is under-saturated with water and will not form free aqueous phase. Under this condition water vapour will not evolve into free water that later will not promote the formation of gas hydrates. DRIZO GDU showed the most significant changes of water dew point curve followed by conventional Stripping gas and Stahl column GDU and last but not least the typical gas GDU. Water vapour extracted the most from wet natural gas in DRIZO GDU since concentration of regenerated TEG there is the highest compared to the other two gas dehydration units.



Figure 4.23: P-T diagram of dry natural gas from typical GDU



Figure 4.24: P-T diagram of dry natural gas from stripping gas and stahl column GDU



Figure 4.25: P-T diagram of dry natural gas from DRIZO GDU

\*HYSYS simulation diagram for all three gas dehydration units are available in appendix in figures (4.28)-(4.30)

As what shown in figure 4.25, the water dew point curve of the dry gas has been shifted to the most left side of hydrocarbon dew point resulted in large amount of water dew point depressions. Thus it is proven from the literature review that largest water dew point depressions are gained from DRIZO GDU compared to the other two gas dehydration units. The effect of having these BTEX gases that act as the entrainer in the DRIZO GDU in the azeotropic distillation between TEG and water is shown in figure 4.26.

In figure 4.26, benzene is used as one of the components in the residual curve map to represent the other BTEX gases since it is the major components of the BTEX gases. Thus considerations are only taken on plotting between TEG, water and benzene onto the residual curve map using Aspen PLUS software. From the figure itself, it showed that benzene will form homogeneous azeotrope with water that will later come out as the top products in the regeneration column. This is further clarified from figure 4.26 at appendix, using ASPEN Plus software that water and benzene will tend to form homogeneous azeotrope in the TEG-water system.



Figure 4.26: Residue curve map for TEG-water-benzene

In figure 4.27, a material balance line illustrated onto the residue curve map showed a 'bow-tie region' of both the distillate and bottom products region. A feasible product composition region can be found for each of the distillation region. Data used for the illustrated region in figure 4.27 are based on the maximum amount of Benzene needed to produce the least amount of water vapour remain in the dry gas in implementing the process of the azeotropic distillation between TEG and water in DRIZO GDU. It can be seen that comparisons between data from simulation using HYSYS are comparable with the data on the residue curve map of TEG-water system since mol fraction of products calculated for bottom and distillate product of the column using HYSYS are available in the distillation region illustrated in the figure itself.

|                                         | mol flow rate (kmol/h) | mol fraction |
|-----------------------------------------|------------------------|--------------|
| Benzene entrainer into reboiler         | 3.7967                 | 0.2408       |
| TEG-water feed into regeneration column | 15.7672                | 0.7592       |
| Bottom product (from HYSYS)             |                        |              |
| TEG                                     | 15.7637                | 0.9999779573 |
| Water                                   | 0.0003                 | 0.0000220427 |
| Top Product (from HYSYS)                |                        |              |
| Benzene                                 | 2.5513                 | 0.38423784   |
| Water                                   | 1.5920                 | 0.61576216   |

Table 4.20: Material balance line data for TEG-water-benzene map from HYSYS



TEG: 0.99998

Figure 4.27: Residue curve map for TEG-water-benzene with material balance line

Meanwhile, from previous the P-T diagrams, it is showed that there are only small variations of the hydrate formation curve and the hydrocarbon curve in the phase envelope between these three gas dehydration units (GDU) since the hydrate formation curve is mostly controlled by lighter components and the major components of natural gas is methane that are not removed in the dehydration process while as for the hydrocarbon curve it is controlled by heavier components of the hydrocarbons. These heavy components of the hydrocarbon are still remaining in the dry gas even after they passed through the gas dehydration unit (GDU). This showed that TEG used in gas dehydration process meets the criteria needed to be as the liquid desiccants as it has high affinity towards water and low affinity towards other components in the wet natural gas.

## 4.3 TEG modifications by addition of additive to improve absorption capacity

Addition of salts preferably potassium formate (KOOCH) aqueous solution as an additive to the anhydrous TEG solution showed an increasing amount of water vapour being absorbed from wet natural gas. This is studied by simulation approach using HYSYS software and the results obtained in the form of water vapour left in the dry gas after it passed through the typical gas dehydration unit are tabulated in table 4.30.

| Mass flow rate | Water vapour content |             |             |               |          | BTEX         |
|----------------|----------------------|-------------|-------------|---------------|----------|--------------|
| KOOCH (kg/h)   | in dry gas (ppm)     | Benzene     | Toluene     | Ethyl Benzene | Xylene   | gases (kg/h) |
| 0              | 173                  | 3.048324091 | 1.967549653 | 0.149216374   | 1.64E-02 | 5.181528116  |
| 131.1085192    | 158                  | 3.646447657 | 2.897248274 | 0.307333583   | 3.35E-02 | 6.884530003  |
| 363.2804273    | 136                  | 5.149598273 | 4.511127238 | 0.67594906    | 7.28E-02 | 10.40943406  |
| * 588.2928376  | 112                  | 6.341296112 | 5.392103997 | 0.738210938   | 8.41E-02 | 12.55575491  |
| 879.004936     | 73                   | 7.514682964 | 5.263781546 | 0.463786527   | 5.76E-02 | 13.29985188  |
| 980.3050149    | 62                   | 7.66403     | 4.916261853 | 0.339194076   | 4.40E-02 | 12.9635226   |
| 1086.675765    | 51                   | 7.335825957 | 4.219333599 | 0.210654224   | 2.87E-02 | 11.79454891  |

Table 4.30: Water vapour left in dry gas and BTEX gas absorbed by TEG with<br/>addition of potassium formate (KOOCH) at typical GDU

\*The limit amounts of KOOCH to be mix with TEG since its maximum solubility in TEG is at 21wt.%

From the table, it is proven as what mentioned previously in literature section of the report whereby by addition of potassium formate (KOOCH) it will increase the absorption capacity of TEG by 2-3 times. This is further shown in the table as the water vapour content in dry gas is reducing from 173 ppm to 112 ppm once KOOCH solution is added to the TEG. However, this is still insufficient since the maximum amount of water vapour content in the raw natural gas allowed before it could be transported through the gas pipelines is around 6-8ppm. Apart from that, it could be seen that the amounts of BTEX gases absorbed by TEG are increased with mass flow rate of potassium formate (KOOCH) that later will increase the amount of them being released to atmosphere. Thus it is not applicable to be used in the typical natural gas dehydration unit since it could cause pollutions to the environment.

On the contrary, addition of aqueous potassium formate (KOOCH) is applicable to DRIZO GDU since it uses solvent stripping method instead of gas stripping method by utilizing the effluent gas from the regeneration column whereby BTEX gases are the major components there. Instead of being released to the atmosphere, these BTEX gases are condensed into liquids form to be introduced into the re-boiler of the regeneration column as an entrainer in the azeotropic distillation between TEG and water.

By addition of aqueous solution of potassium formate (KOOCH) to TEG, the rate absorption of TEG towards BTEX gases will increased as well as it could increase the absorption capacity of TEG towards water vapour in the process. This could reduced the amounts of external solvents (eg. Benzene solvent) to be used as the entrainer in the azeotropic distillation at the regeneration column that later will save costs in terms of amounts of make-up solvents to be used as the entrainer in the system since some of it may loss to the atmosphere through the flash tank due to its high value in vapour pressure. From table 4.31 it can be seen that by addition of potassium formate (KOOCH) into DRIZO gas dehydration unit, it showed a reduced amount of Benzene to be used as an external solvent for the entrainer in the process. In addition, aqeous solution of KOOCH has low vapour pressure even at high temperature that is suitable to be used in the regeration process of TEG since only

minimum amount of it will vaporized and lost the atmosphere. This will reduced amounts of makeup KOOCH aqueous solutions to replace the lost one.

Table 4.31: Comparison in the make-up amount of Benzene used in DRIZO gas dehydration unit between the process with addition of potassium formate (KOOCH) and without addition of potassium formate (KOOCH)

| Mass flowrate of      | Mass flow rate | Water vapour content | KOOCH loss as   | BTEX gases  |
|-----------------------|----------------|----------------------|-----------------|-------------|
| makeup Benzene (kg/h) | KOOCH (kg/h)   | in dry gas (ppm)     | flash gas(kg/h) | (kg/h)      |
| 0                     | 0.00000        | 45                   | 0.00000         | 13.69166551 |
| 0                     | 162.20762      | 38                   | 0.00001         | 17.64755415 |
| 0                     | 282.77188      | 32                   | 0.00001         | 22.24018272 |
| 0                     | 378.87853      | 30                   | 0.00001         | 28.68016662 |
| * 0                   | 518.48628      | 28                   | 0.00001         | 57.36530767 |
| 0                     | 771.73911      | 25                   | 0.00002         | 101.2966691 |
|                       |                |                      |                 |             |
| Makeup->Benzene       |                |                      |                 |             |
| 2                     | 518.486279     | 18                   |                 |             |
| 4                     | 518.486279     | 11                   |                 |             |
| 6                     | 518.486279     | 6                    |                 |             |
| 8                     | 518.486279     | 3                    |                 |             |
| 9                     | 518.486279     | 1                    |                 |             |
|                       |                |                      |                 |             |
|                       |                |                      |                 |             |
|                       |                |                      |                 |             |

With addition of KOOCH:

\*The limit amounts of KOOCH to be mix with TEG since its maximum solubility in TEG is at 21wt.%

## Without addition of KOOCH:

| Mass flow rate        | Water vapour content | Top product flash |
|-----------------------|----------------------|-------------------|
| makeup Benzene (kg/h) | in dry gas (ppm)     | tank (kg/h)       |
| 0                     | 45                   | 0.00000           |
| 2                     | 40                   | 0.35087           |
| 4                     | 32                   | 0.35381           |
| 6                     | 25                   | 0.35381           |
| 8                     | 19                   | 0.35796           |
| 9                     | 19                   | 0.35792           |
| 10                    | 14                   | 0.36155           |
| 12                    | 8                    | 0.36446           |
| 14                    | 5                    | 0.36344           |
| 16                    | 3                    | 0.36673           |
| 18                    | 1                    | 0.36793           |

It could be seen that without addition of potassium formate (KOOCH) solution, higher value of mass flow rate needed to obtain desired amount of water vapour content left in the dry gas. At the same mass flow rate of 8 kg/h of benzene into the re-boiler of the regeneration column, only certain amount of water vapour being absorbed thus leaving 19ppm of water vapour content remained in the dry gas as compared to if KOOCH is added, lower value is achieved that is at 3 ppm water vapour of the dry gas. This is because, KOOCH added to TEG solution helps to increase its absorption capacity towards water vapour and BTEX gases from the wet gas. Hence, the increase amount BTEX gases being absorbed from the wet gas will reduce the amounts of external solvents to be used as the entrainer in the azeotropic distillation in the regeneration column of DRIZO GDU.

## 4.4 Equilibrium correlations for predicting water dew point

Comparisons between the theoretical data and simulation data for each of the water dew point temperature with respect to its regenerated TEG are done for several other TEG concentrations as what showed in tables (4.40)-(4.43). Figures (4.40)-(4.42) depicted the difference between the theoretical and simulation data in the form of polynomial graph.

The outcome results from simulation are compared with the theoretical data calculated using the equation and coefficients given that relate between the water dew point of the dry gas with respect to concentration of regenerated TEG. It is noted that these data are comparable within each other since the deviations between the simulation and theoretical data are satisfying since the percentage difference between these two data are mostly not exceeding 10% difference and it is considered acceptable for industry practices.

Table 4.40: Comparisons water dew point (Td) from simulation and theoretical for concentration 90 wt.% - 99 wt.%

| TEG Concentration (wt%) | T.dew Theory (°C) | T.dew Simulation (°C) | Temp. Diff (°C) |
|-------------------------|-------------------|-----------------------|-----------------|
| 99.997                  | -56.32            | -49.74                | 6.58            |
| 99.995                  | -48.35            | -44.11                | 4.24            |
| 99.992                  | -48.35            | -45.21                | 3.14            |
| 99.985                  | -40.29            | -41.19                | -0.9            |
| 99.981                  | -36.77            | -41.19                | -4.42           |
| 99.976                  | -33.39            | -34.47                | -1.08           |
| 99.92                   | -28.5             | -31.42                | -2.92           |
|                         |                   |                       |                 |

Table 4.41: Comparisons water dew point (Td) from simulation and theoretical for concentration 99 wt.% - 99.9 wt.%

| TEG Concentration (wt%) | T.dew Theory (°C) | T.dew Simulation (°C) | Temp. Diff (°C) |
|-------------------------|-------------------|-----------------------|-----------------|
| 99.891                  | -26.46            | -26.58                | -0.12           |
| 99.87                   | -24.34            | -22.84                | 1.5             |
| 99.85                   | -22.95            | -20.76                | 2.19            |
| 99.724                  | -13.52            | -12.62                | 0.9             |
| 99.68                   | -9.78             | -8.91                 | 0.87            |

Table 4.42: Comparisons water dew point (Td) from simulation and theoretical forconcentration 99.9 wt.% - 99.999 wt.%

| TEG Concentration (wt%) | T.dew Theory (°C) | T.dew Simulation ( <sup>o</sup> C) | Temp. Diff (°C) |
|-------------------------|-------------------|------------------------------------|-----------------|
| 98.95                   | 8.09              | 6.88                               | -1.21           |
| 98.642                  | 11.23             | 11.53                              | 0.3             |
| 98.533                  | 12.11             | 11                                 | -1.11           |
| 98.14                   | 15.93             | 14.95                              | -0.98           |
| 97.653                  | 19.93             | 19.17                              | -0.76           |
| 96.917                  | 25.01             | 23.78                              | -1.23           |
| 95.778                  | 30.94             | 28.52                              | -2.42           |
| 94.025                  | 36.61             | 33.73                              | -2.88           |



Figure 4.40: Comparisons water dew point (Td) from simulation and theoretical for concentration 90 wt.% - 99 wt.%



Figure 4.41: Comparisons water dew point (Td) from simulation and theoretical for concentration 99 wt.% - 99.9 wt.%



Figure 4.42: Comparisons water dew point (Td) from simulation and theoretical for concentration 99.9 wt.% - 99.999 wt.%

#### **CHAPTER 5: CONCLUSION AND RECOMMENDATIONS**

As for further developments of the project, experimental approach needed especially in terms of the addition of salts into TEG solution. This is important in order to set a reference point between results gained from simulations and results gained from experiment. Certain chemical properties of KOOCH solution are unknown and are estimated by the software. Thus better results are possible if real data could be gained from experimental approach instead of solely depends on the estimated data from the software.

As for conclusion, overall objectives of the project are achieved. It is discovered that in order to achieve the most optimum conditions of gas dehydration process several factors need to be met. In the gas dehydration process, water content of natural gas has been reduced significantly by the gas dehydration process while reducing the water dew point temperature as well. By simulation run using HYSYS software, DRIZO GDU showed the most significant change of water dew point curve followed by conventional stripping gas dehydration process and the typical gas dehydration process. Water vapour extracted the most from wet natural gas in DRIZO GDU since concentration of regenerated TEG there is the highest compared to the other two given processes that enables it to absorb more water vapour from the wet gas. By implementing the concept of azeotropic distillation, it allows more water vapour to be separated from TEG in the regeneration column and resulted in higher concentration of the regenerated TEG to be recycled in the process.

Addition of potassium formate (KOOCH) together with TEG into the process gave good results whereby it helps to increase the absorption capacity of TEG thus reduces the amount of water vapour remaining in the dry natural gas. However it will also increased the amount of BTEX gases being absorbed by TEG which increases their emission to the atmosphere as well. Therefore, it is not recommended to be used in typical GDU but instead to be used in DRIZO GDU Justifications between overall simulation results with respect to theoretical results calculated from given correlations shown a satisfactory results whereby the difference between these two data are mostly not exceeding 10% difference and it is considered acceptable for industry practices.

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# APPENDIX

| Table 4.0: Summary of operating conditions of the base case employed in the |  |
|-----------------------------------------------------------------------------|--|
| simulation.                                                                 |  |

| Stream        | Operating conditions          |
|---------------|-------------------------------|
| (1) Wet gas   | Temperature = $56 \text{ C}$  |
|               | Pressure = 4261  kPa          |
|               | Volume flow = 11 MMSCFD       |
| (2) Lean TEG  | Temperature = $60 \text{ C}$  |
|               | Pressure = 4261  kPa          |
| (3) Absorber  | Number of stages $= 3$        |
|               | Pressure = 4261  kPa          |
|               | simulator input: no reboiler  |
|               | (QN=0),                       |
|               | no condenser (Ql=0)           |
| (4)           |                               |
| Regenaration  | Pressuse = 101.3 kPa          |
| column        | Temperature = $202 \text{ C}$ |
| (5) Stripping | Number of stages $= 5$        |
| column        | Pressure = 101.3  kPa         |
| (Stahl        | simulator input: no reboiler  |
| column)       | (QN=0),                       |
|               | no condenser (Ql=0)           |

| Species              | Mass fraction |
|----------------------|---------------|
| H20                  | 0.002         |
| CO2                  | 0.084         |
| N2                   | 0.005         |
| C1                   | 0.386         |
| C2                   | 0.129         |
| C3                   | 0.158         |
| n-C4                 | 0.097         |
| i-C4 (isobutane)     | 0.052         |
| n-C5                 | 0.032         |
| i-C5                 | 0.033         |
| n-C6                 | 0.006         |
| c-C6(cyclo hexane)   | 0.002         |
| i-C6                 | 0.006         |
| n-C7                 | 0.001         |
| i-C7                 | 0.001         |
| c-C7                 | 0.002         |
| i-C8                 | 432PPM        |
| c-C8                 | 807PPM        |
| C6H6(benzene)        | 857PPM        |
| C7H8(toluene)        | 697PPM        |
| C8H10(xylene)        | 402PPM        |
| C8H10(ethyl benzene) | 40PPM         |

Table 4.1: Composition of wet gas with respect to its mass fraction

\_\_\_\_\_

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| DEL SR RR R III                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | File Edit View Data Tools Run Library Window Help   Image: Second performance Image: | Simulation 1 - Aspen Plus 2006      | i - as | nenONE - [A | zeotrone Analysis | -1          |           |          |        |          |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|--------|-------------|-------------------|-------------|-----------|----------|--------|----------|
| □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □ □                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                     |        |             |                   |             |           |          |        |          |
| Image: Comparison of the second se | Control   <                                                                                                                                                                                                                                                                                                                                                                                                        |                                     |        |             |                   |             |           |          |        |          |
| Input   Temp (C)   Classification   Type   No. Comp.   TRIET-01   WATER   BENZE-01     V Pure Components   1   100.56   Stable node   Homogeneous   1   1.0000   0.0000   0.0000     V Azeotropes   2   100.02   Saddle   Homogeneous   1   0.0000   1.0000   0.0000     W Report   80.13   Saddle   Homogeneous   1   0.0000   1.0000                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | Input   Temp (C)   Classification   Type   No. Comp.   TRIET-01   WATER   BENZE-01     Ø Dutput   1   100.56   Stable node   Homogeneous   1   1.0000   0.0000   0.0000     Ø Azeotropes   2   100.02   Saddle   Homogeneous   1   0.0000   1.0000   0.0000   0.0000   0.0000   0.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   0                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                     |        |             |                   |             |           |          |        |          |
| Output   Temp (C)   Classification   Type   No. Comp.   TRIET-01   WATER   BENZE-01     Ø Pure Components   1   100.56   Stable node   Homogeneous   1   1.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Image: Construction   Temp (C)   Classification   Type   No. Comp.   TRIET-01   WATER   BENZE-01     V Pure Components   1   100.56   Stable node   Homogeneous   1   1.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000   1.0000   0.0000 <t< td=""><td colspan="5">🖻 😋 Azeotrope Analysis 🗈 🖓 🗸 Mole 🗸</td></t<>                                                                                                                                                                                                                                                                                                                                                                    | 🖻 😋 Azeotrope Analysis 🗈 🖓 🗸 Mole 🗸 |        |             |                   |             |           |          |        |          |
| Ø Azeotropes   2   100.02   Saddle   Homogeneous   1   0.0000   1.0000   0.0000     Ø Singular Points   80.13   Saddle   Homogeneous   1   0.0000   0.0000   1.0000   0.0000   1.0000                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Ø   Azeotropes   2   100.02   Saddle   Homogeneous   1   0.0000   1.0000   0.0000     Ø   Singular Points   3   80.13   Saddle   Homogeneous   1   0.0000   0.0000   1.0000                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                     |        | Temp (C)    | Classification    | Туре        | No. Comp. | TRIET-01 | WATER  | BENZE-01 |
| Vision   Vision<                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Ø Singular Points   2   Hoto2/3 stable   Hotogeneous   1   0.0000   0.0000   1.0000     Ø Report   3   80.13   Saddle   Homogeneous   1   0.0000   0.0000   1.0000                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                     | 1      | 100.56      | Stable node       | Homogeneous | 1         | 1.0000   | 0.0000 | 0.0000   |
| Report 3 80.13 Sadale Homogeneous I 0.0000 0.0000 1.0000                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Report 3 80.13 Sadale Homogeneous I 0.0000 0.0000 1.0000                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                     | 2      | 100.02      | Saddle            | Homogeneous | 1         | 0.0000   | 1.0000 | 0.0000   |
| 4 57.25 Unstable Node Homogeneous 2 0.0000 0.4253 0.5747                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 4 57.25 Unstable Node Homogeneous 2 0.0000 0.4253 0.5747                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                     | 3      | 80.13       | Saddle            | Homogeneous | 1         | 0.0000   | 0.0000 | 1.0000   |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                     | 4      | 57.25       | Unstable Node     | Homogeneous | 2         | 0.0000   | 0.4253 | 0.5747   |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                     |        |             |                   |             |           |          |        |          |
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Figure 4.29: HYSYS simulation diagram for typical gas dehydration unit (GDU)



Figure 4.29: HYSYS simulation diagram for Stripping gas and Stahl column gas dehydration unit (GDU)



Figure 4.30: HYSYS simulation diagram for DRIZO gas dehydration unit (GDU)