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# Evaluation of potassium formate as a potential modifier of TEG for high performance natural gas dehydration process

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## ABSTRACT

Triethylene glycol (TEG) is one of the most effective sorbents for natural gas dehydration. There are many processes using this approach but none of them can combine high performance and economical energy consumption. In this study hydrocarbon–water phase behavior was investigated for different TEG concentrations in different natural gas dehydration processes. The equilibrium correlations were investigated for predicting water dew point as a function of TEG concentration. The effect of TEG concentration on the outlet gas dew point was also determined using phase envelope diagrams. The results showed that the (DRIZO) process achieved the most significantly reduces water dew point followed by conventional stripping gas dehydration process. Moreover, TEG was modified using potassium formate as additive. The results showed that the absorption capacity of the modified TEG was improved, that is almost duplicated. This modification augments the performance of the proposed mixture which can be potentially applied to a real scale process.

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**Keywords:** Glycols; Dehydration; Natural gas; Dew point; Hydrate; Potassium formate

## 1. Introduction

Inhabitation of hydrate formation is the main purpose of natural gas dehydration processes, which definitely helps to avoid of blockage of pipelines or process equipments (Ripmeester et al., 1987; Tohidi et al., 1990). Glycol compounds are well known as the best candidates for gaseous phase dehydration (Gilbert and Boris, 1996; Gottlib, 2003). The glycol selection is based on a number of factors which include: dehydration capability, glycol losses in the contactor or the regenerator and absorption of volatile organic matters (VOC's) (Herskowitz and Gottlib, 1984). The advantage of using triethylene glycol (TEG) is that, it can greatly reduce the emission of benzene, toluene, ethyl benzene and xylene (BTEX) (Braek et al., 2001; Ebeling, 1998). TEG offers the best cost beneficial solution and it is the most widely used for gas dehydration (Woodcock, 2004). TEG is marginally more expensive than DEG, but it can achieve much lower losses due to lower vapor pressure (Kelland, 2009). Due to the association between water and TEG, water mixes with the glycol and creates a single liquid phase (Sloan, 1990).

However, this mixture is difficult to be simulated due to the association between water and the glycol (Christensen, 2009). Thus, proper thermodynamic equations are needed to accurately simulate the water/glycol mixture in simulating a gas dehydration process. Some models based on cubic equations of state (EOS) guarantee a good phase equilibrium prediction over wide ranges of temperature and pressure. This is important in view of modeling natural gas multicomponent systems in dehydration units, where it is necessary to account for the presence of gases and the high operating pressure of the absorption column (Peng and Robinson, 1976). The main platform used for this study was the simulation software: Aspen HYSYS. Peng and Robinson (1976) and Twu et al. (2005) glycol thermodynamic packages were employed in this study. The two thermodynamic packages were required due to the fact that Peng–Robinson thermodynamic package alone cannot calculate accurately the TEG–water system for the regeneration part of the gas dehydration unit. Further, Peng–Robinson package calculates significant amounts of TEG as the bottom product of the regeneration column (Bahadori et al., 2008). In

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the real case, the vapor pressure of TEG is very low which reduces its tendency to vaporize and to exist as a top product of the regeneration column. Twu-Sim-Tassone (Glycol) thermodynamic package is accurate in determining the activity coefficients of the TEG-water system and it is also applicable to broader ranges of pressure and temperature (Twu et al., 2005). This makes it suitable to be used in the regeneration part of the gas dehydration unit since the TEG regeneration process involves a high temperature. The inlet stream data used in the simulation are based on the real data of a gas processing facility in the United Arab Emirates (UAE) (Naif et al., 2004). In the dehydration process, the lean (water-free glycol), with purity above 99% is fed to the top of an absorber (also known as a contactor) where TEG is contacted with the wet natural gas stream. Glycol absorbers can either be tray columns or packed columns. The glycol removes water from the natural gas by physical absorption and carries it to the bottom of the column. Upon exiting at the absorber, the glycol stream is often referred to as rich glycol (Huffmaster, 2004). The dry natural gas leaves the top of the absorption column and is fed either to a pipeline system or to a gas plant (Rosman, 1973; Salamat, 2009). After leaving the absorber, the rich glycol is fed to a flash vessel where hydrocarbon vapors are removed and any liquid hydrocarbons are skimmed from the glycol (Speight, 2006; Vincente et al., 1992). This step is necessary to reduce the solution pressure before the regeneration step, as the absorber operates at high pressure. Additionally, a vapor phase having high hydrocarbon content is formed when the pressure is reduced. After leaving the flash vessel, the rich glycol is heated in a cross-exchanger and fed to the stripper which is also known as regenerator. The glycol stripper regenerator consists of a column, an overhead condenser and a reboiler. The glycol is thermally regenerated to remove water and achieve high purity glycol. The hot stream of lean glycol is cooled by cross-exchange heat with the cool rich glycol stream entering the stripper. It is then fed to a lean pump where its pressure is elevated to the pressure level of the glycol absorber. The lean solvent is cooled again with a trim cooler before being fed back into the absorber. This trim cooler can either be a cross-exchanger with the dry gas leaving the absorber or an aerial type cooler. Several methods are used to enhance the stripping of the glycol to higher purities which are required for minimizing the moisture content of the gas out of the absorber. The reboiler temperature is limited to 400 °F or less to prevent thermal degradation of the glycol. Furthermore, almost all of the enhanced systems focus on lowering the partial pressure of water in the system to increase stripping efficiency. The common enhanced methods include the use of stripping gas, the use of a vacuum system (lowering the entire stripper pressure), the (DRIZO) process, which is similar to the use of stripping gas but uses a recoverable hydrocarbon solvent and the cold finger process where the vapors in the reboiler are partially condensed and drawn out separately from the bulk vapor. In this study the performance of different dehydration processes were compared. The results show that the DRIZO process has a great potential to greatly lower water dew points. In this study, the results showed that the DRIZO process achieved the most significant improvement of water dew point followed by conventional stripping gas dehydration process. Moreover, TEG modification using potassium formate as additive was investigated. The results showed that the absorption capacity of TEG was improved significantly. This modification suggests a higher performance of the proposed mixture when compared to the original TEG.

**Table 1 – The composition of the natural gas employed in this study.**

H <sub>2</sub> O	0.002	cyc-C <sub>6</sub> (cyclo hexane)	0.002
CO <sub>2</sub>	0.084	i-C <sub>6</sub>	0.006
N <sub>2</sub>	0.005	n-C <sub>7</sub>	0.001
C <sub>1</sub>	0.386	i-C <sub>7</sub>	0.001
C <sub>2</sub>	0.129	c-C <sub>7</sub>	0.002
C <sub>3</sub>	0.158	i-C <sub>8</sub>	432 ppm
n-C <sub>4</sub>	0.097	c-C <sub>8</sub>	807 ppm
i-C <sub>4</sub> (isobutane)	0.052	C <sub>6</sub> H <sub>6</sub> (benzene)	857 ppm
n-C <sub>5</sub>	0.032	C <sub>7</sub> H <sub>8</sub> (toluene)	697 ppm
i-C <sub>5</sub>	0.033	C <sub>8</sub> H <sub>10</sub> (xylene)	402 ppm
n-C <sub>6</sub>	0.006	C <sub>8</sub> H <sub>10</sub> (ethyl benzene)	40 ppm

## 2. Equilibrium correlations for predicting water dew point

Evaluation of TEG system involves the determination of minimum of TEG concentration required to meet the outlet gas water dew point specification (Bahadori, 2009). Several equilibrium correlations for predicting water dew point of natural gas in equilibrium with TEG solutions have been published since 1950 (Bahadori, 2009). However, it is important to have an easy-to-use correlation to predict accurately the equilibrium between the wet natural gas and TEG solution in the dehydration system. Using the correlation, a better approach to compare the theoretical data and simulation data could be reached (Bahadori et al., 2008). In this study values got from thermodynamic correlations are considered as the theoretical data while data from Hysys are considered as the prediction data. Water dew point ( $T_d$ ) of the natural gas stream in equilibrium with the concentration of TEG is predicted accurately using this simple correlation. This correlation developed by Bahadori (2009). It is a polynomial form and consists of several different coefficients so that it depends on the concentration of TEG used in the gas dehydration unit (GDU) and the contactor operating temperatures as well. This correlation is shown by Eq. (1) while the rest of the coefficients are shown by Eqs. (2)–(5).

$$T_d = a + bT + cT^2 + dT^3 \quad (1)$$

where

$$a = A_1 + B_1 W + C_1 W^2 + D_1 W^3 \quad (2)$$

$$b = A_2 + B_2 W + C_2 W^2 + D_2 W^3 \quad (3)$$

$$c = A_3 + B_3 W + C_3 W^2 + D_3 W^3 \quad (4)$$

$$d = A_4 + B_4 W + C_4 W^2 + D_4 W^3 \quad (5)$$

where  $T_d$  and  $T$  are the water dew point temperature and the contactor temperature respectively, and  $W$  is TEG purity in weight percent (wt.%) (Bahadori, 2009).

## 3. Methodology

Three natural gas dehydration processes were simulated using real data from actual plant (Naif et al., 2004). The composition of the natural gas employed in this study is shown in Table 1.

**Table 2 – physical properties of triethylene glycol.**

MW	150
Specific weight (g/cm <sup>3</sup> )	1.125
Melting point (°C)	-7
Boiling point (°C)	286
Vapor pressure (Pa) at 25 °C	0.05
Decomposition temperature (°C)	204

The theoretical number of trays was determined. It is proven that the conversion from equilibrium stages to real ones can be made assuming an overall tray's efficiency of 25–30% (Abdel-Aal and Aggour, 2008).

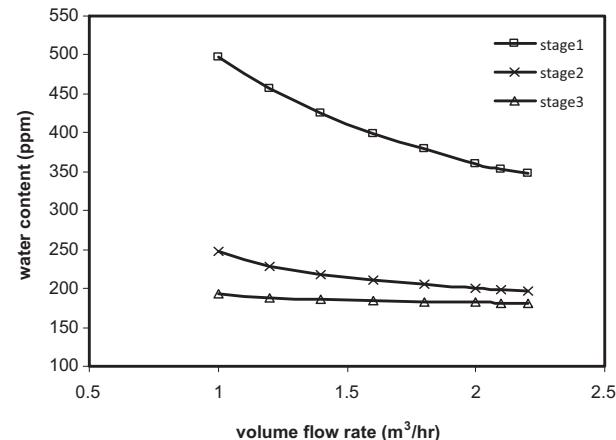
The effect of the reboiler temperature was assumed to be not higher than 204 °C to avoid the thermal decomposition of TEG. The effect of the stripping gas was determined for further enhancing of the existing GDU. The stripping gas volumetric flow rate has a greater effect than increasing the reboiler temperature. Optimization of TEG concentration against the dew point level is extremely important for high performance natural gas dehydration unit. In this study, an updated thermodynamic correlation was employed to estimate the minimum concentration of TEG necessary to achieve the desired dew point. Phase envelope of the gas stream at different dehydration processes was developed. This helped to figure out the high potential of DRIZO process compared to the other two processes. The profile of water dew point was estimated precisely to prove the high performance of DRIZO process. The behavior of BTEX in TEG–water system was investigated employing residue curve. Furthermore, it is shown that water and benzene tended to form a homogenous azeotrope in the TEG–water system. TEG modification using potassium formate as additive was investigated. The maximum solubility of potassium formate in TEG is 21 wt.% (Atkinson, 1994; Bahadori, 2007; John, 2001). Table 2 shows triethylene glycol (TEG) physical properties. The results were evaluated using the parameters of water vapor content in the outlet stream, and BTEX absorbed in the parent and the modified TEG.

#### 4. Results and discussion

The performance of different gas dehydration processes was investigated for the water/hydrocarbon dew point and concentration of regenerated TEG. This data was validated against the predicted data from the thermodynamic correlations. The generated data in terms of the water content remaining in the gas after it passed through the gas dehydration unit was 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 results are shown as a parametric study of a typical gas dehydration unit.

##### 4.1. Effect of number equilibrium stages in the contactor

The effect of the number of equilibrium stages on the water content of the dry gas is shown in Fig. 1. The re-boiler temperature of 202 °C was employed to regenerate the rich TEG. It is shown in Fig. 1 that the increasing of the number of equilibrium stages of the contactor increases water vapor to be removed and results in further reduction of the water content of the outlet dry gas. Lowering circulation of TEG with higher



**Fig. 1 – Effect of the number of equilibrium stages on the residual water content.**

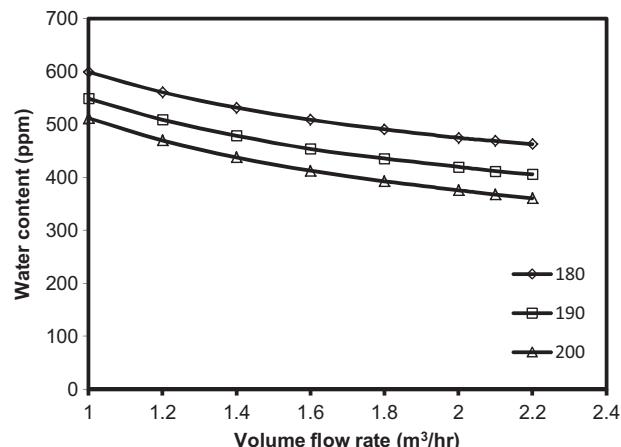
number of stages of the contactor is necessary to produce an acceptable amount of residual water content of the dry gas. This is because the increase of the number of stages allows the gas to reach equilibrium with the lean glycol at lower circulation rate of TEG (Moshfeghian, 2010a,b; Mohamadbeigy, 2008).

##### 4.2. Effect of re-boiler temperature

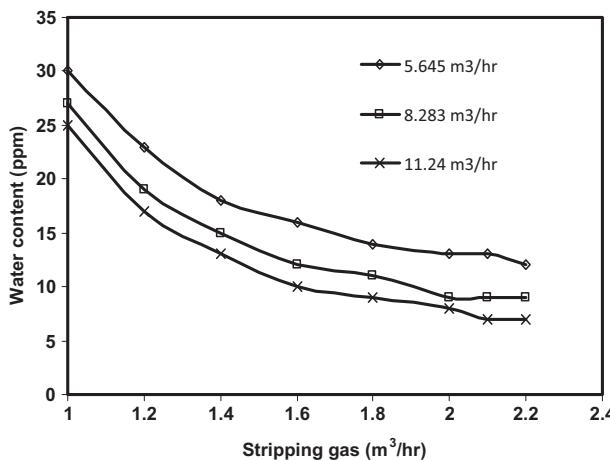
Increasing the re-boiler temperature at the regeneration column to a temperature higher than 204 °C will lead to thermal decomposition of TEG (Luká, 2009). Fig. 2 illustrates the residual water content of the dry gas from the contactor outlet with respect to the re-boiler temperature of the regenerator 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. The higher reboiler temperature, the higher the purity of regenerated TEG to absorb more water vapor from the wet gas (Bahadori and Hari, 2009a,b).

##### 4.3. Effect of stripping gas

Applications with high dew point depression will 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



**Fig. 2 – Effect of the reboiler temperature to the residual water content of TEG solution.**

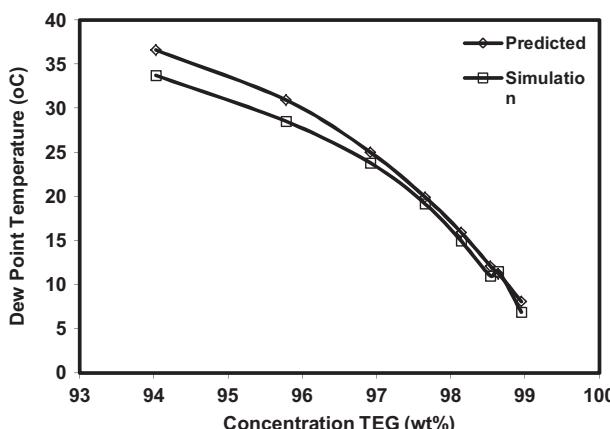


**Fig. 3 – Effect of stripping gas flow rate on the residual water content.**

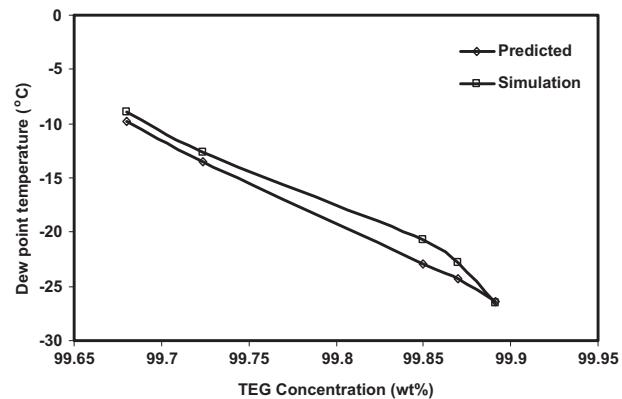
facilities are needed such as the use of stripping gas in the dehydration process. Fig. 3 illustrates the effect of stripping gas on the residual water content of the dry gas. Increasing the stripping gas volume flow rate will have much greater effect than increasing reboiler temperature. By reducing the partial water vapor pressure in the regenerator using the stripping gas, it will increase the tendency of water molecules in TEG to be vaporized hence reduce its boiling point as well. At constant reboiler temperature, more water will be extracted from TEG in the form of water vapor that comes out as the top product of the regeneration column with increasing stripping gas volume flow rate. Hence, the concentration of regenerated TEG will increase as well.

#### 4.4. Equilibrium correlations for predicting water dew point

Comparison between the prediction data generated using thermodynamic correlations and the data generated from the validated process has been done. The water dew point with respect to its regenerated TEG was determined for several TEG concentrations. Figs. 4–6 show the data generated using thermodynamic correlations and the data generated from the validated process. They are comparable since the deviation is mostly not exceeding 10%, which is acceptable in this case.



**Fig. 4 – Comparison of the water dew point ( $T_d$ ) from simulation to estimation for concentrations from 90 wt.% to 99 wt.%.**

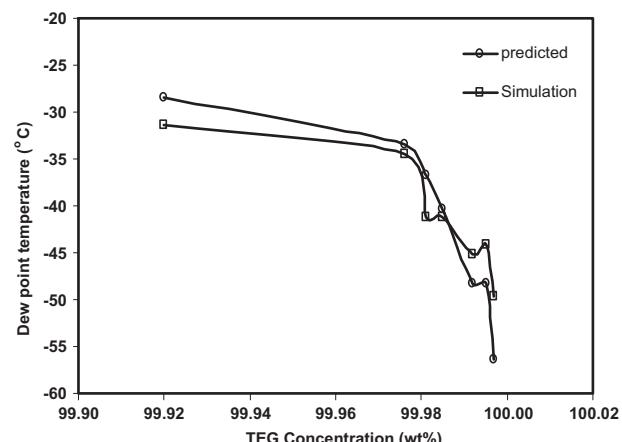


**Fig. 5 – Comparisons of the water dew point ( $T_d$ ) from simulation to estimation for concentrations from 99 wt.% to 99.9 wt.%.**

#### 4.5. Phase envelope of gas stream at different dehydration units

In this study, three gas dehydration units (GDUs) were simulated and validated using the real data plant (Naif et al., 2004). The gas dehydration units were a typical gas dehydration unit and the enhanced gas dehydration units such as the Striping gas Stahl column GDU and the DRIZO GDU. The performance of these gas dehydration units (GDUs) were investigated in terms of the water dew point and water content remaining in the dry gas after dehydration. Fig. 7 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 is shown from the P-T diagram of the wet gas that it is saturated with water vapor since the water dew point curve located at the right side of the hydrate curve. Under this condition free water forms and the hydrates may form.

Fig. 8 shows the P-T diagram for the dry gas after it passed through Stripping gas and Stahl column GDU while Fig. 9 shows the P-T diagram for the dry gas after it passed through the DRIZO GDU. Due to the removal of water vapor 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 operate at lower temperature since the water dew



**Fig. 6 – Comparisons of the water dew point ( $T_d$ ) from simulation to estimation for concentrations from 99.9 wt.% to 99.999 wt.%.**

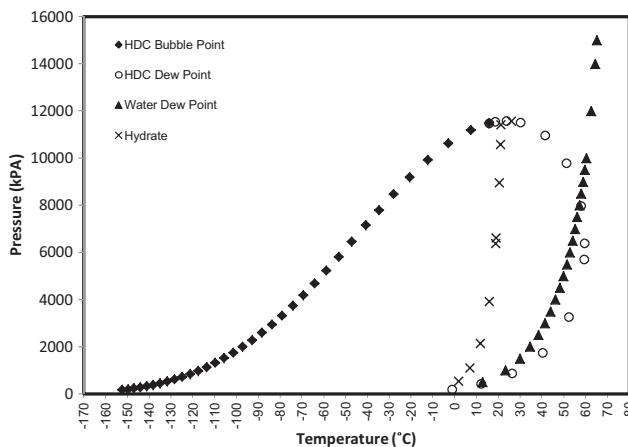


Fig. 7 – P-T diagram of the wet natural gas.

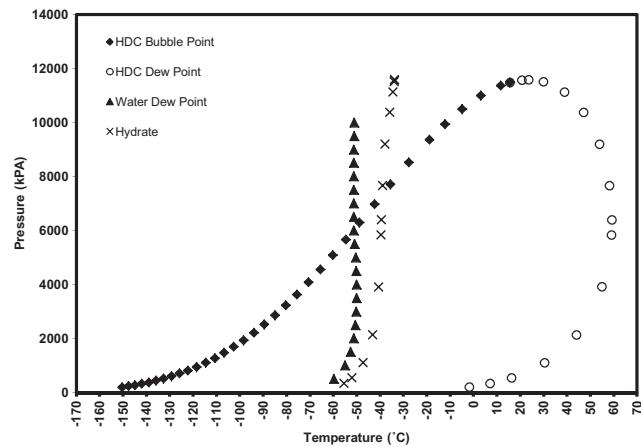


Fig. 10 – P-T diagram of the dry natural gas from DRIZO GDU.

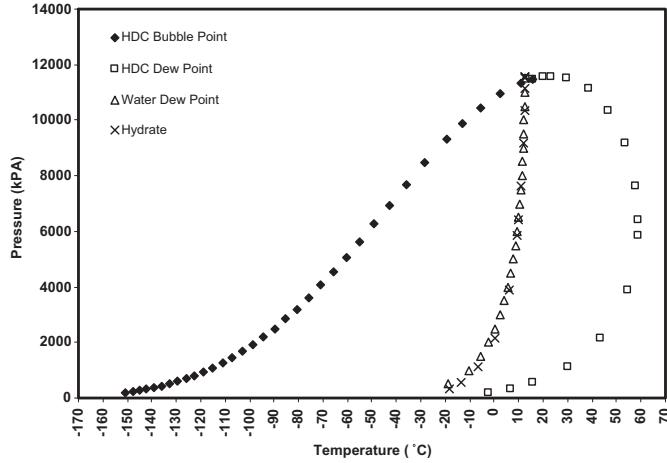


Fig. 8 – P-T diagram of the dry natural gas from typical GDU.

point has been shifted to lower temperature. This is due to the reason that at temperatures higher than water dew point temperature, the gas is under-saturated with water and will not form aqueous phase. Under this condition water vapor will not condense to water which can 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 the typical gas GDU. The results showed that the concentration of the regenerated

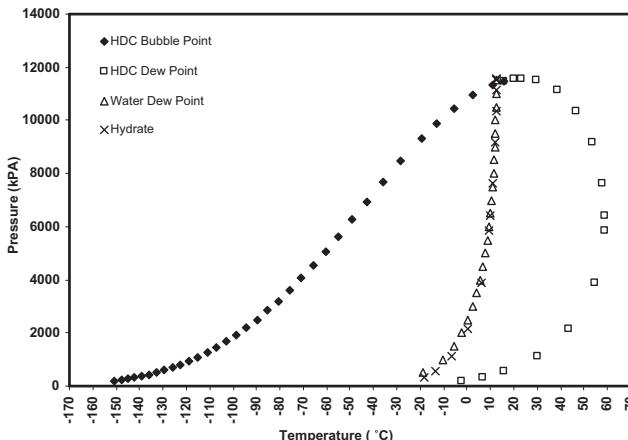


Fig. 9 – P-T diagram of the dry natural gas from the Stripping gas and Stahl column GDU.

TEG in DRIZO GDU the highest compared to the other two gas dehydration units.

Shown in Fig. 10 the water dew point curve of the dry gas has been shifted to the leftmost side of hydrocarbon dew point resulted in large depression of the water dew point. Thus, it is proven that largest water dew point depression is gained from DRIZO GDU compared to the other two gas dehydration units. The effect of having BTEX gases act as the entrainer in the DRIZO GDU in the azeotropic distillation between TEG and water are shown in Fig. 11. Benzene was used to represent the other BTEX gases since it is the major component. It is shown that benzene will form a homogeneous azeotrope with water that will later come out as the top product in the regeneration column. Furthermore, water and benzene tended to form a homogeneous azeotrope in the TEG–water system.

It is shown in Fig. 12 that a material balance line illustrated on the residue curve map showed a ‘bow-tie region’ of both the distillate and bottom product region. A feasible product composition region can be found for each of the distillation region. Data used for the illustrated region in Fig. 12 are based on the maximum amount of benzene needed to produce the least amount of water vapor remain in the dry gas in implementing the process of the azeotropic distillation between TEG and

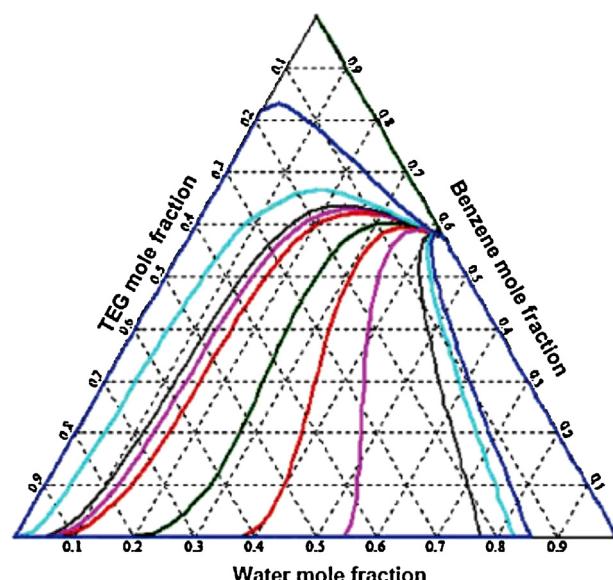


Fig. 11 – Residue curve map for the system TEG–water–benzene.

**Table 3 – Amount of water vapour in dry gas and BTEX by TEG with addition of potassium formate (KOOCH) at DRIZO GDU.**

Mass flow rate of makeup benzene (kg/h)	Mass flow rate KOOH (kg/h)	Water content in dry gas (ppm)	BTEX gases (kg/h)			
			Benzene	Toluene	Ethyl benzene	Xylenes
0.0	0.0	45.0				
0.0	162.21	38.0	0.44	0.35	0.20	0.02
0.0	282.77	32.0	0.52	0.43	0.27	0.02
0.0	378.88	30.0	0.62	0.52	0.33	0.03
0.0	518.49	28.0	0.77	0.67	0.43	0.04
0.0	771.74	25.0	1.09	0.97	0.64	0.06
2.0	518.49	18.0	1.45	1.21	0.80	0.07
4.0	518.49	11.0	1.83	1.50	1.00	0.09
6.0	518.49	6.0	2.51	1.88	1.23	0.12
8.0	518.49	3.0	3.02	2.06	1.30	0.12
9.0	518.49	1.0	3.54	2.29	1.45	0.14

water in DRIZO GDU. It is shown that comparison between data from simulation using HYSYS are comparable with the data on the residue curve map of TEG–water system since the mole fraction of products calculated for bottom and distillate product of the column using HYSYS are available in the distillation region as illustrated in Fig. 12.

Furthermore, it is previously shown on the P-T diagrams 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 (GDUs) since the hydrate formation curve is mostly controlled by lighter components and the major components of natural gas is methane that is 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 the gas dehydration process meets the criteria needed to be as the liquid desiccants as it has high affinity toward water and low affinity toward other components in the wet natural gas.

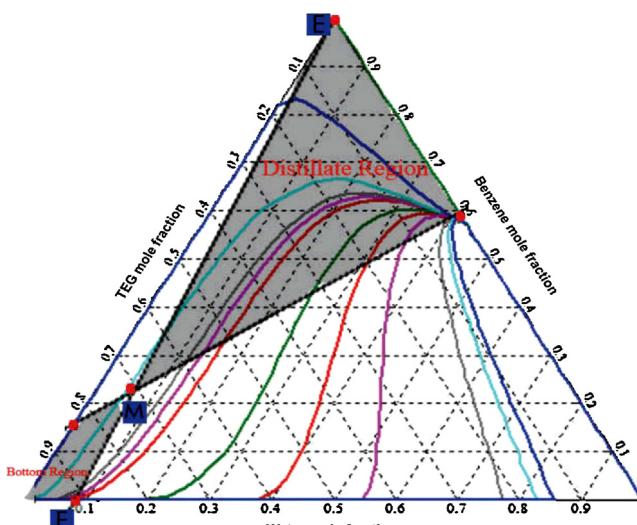
#### 4.6. TEG modifications by addition of additive to improve absorption capacity

Addition of salts namely potassium formate (KOOCH) aqueous solution as an additive to the anhydrous TEG solution was

investigated. The results show a higher removal of water vapor from wet natural gas was achieved; the details of these results are shown in Tables 3 and 4.

The results show that addition of potassium formate (KOOCH) results in rising the absorption capacity of TEG by double to triple. It is shown in Table 3 that the water vapor content in dry gas was reduced to 28 ppm as a result of KOOCH addition to the TEG. However, this water content still not acceptable since the maximum amount of water vapor content in the raw natural gas allowed by specifications is 6–8 ppm. Furthermore, it is shown that the amounts of BTEX gases absorbed by TEG are increased with the mass flow rate rise of potassium formate (KOOCH). It is recommended to recover this amount of BTEX for reuse. 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. In this case, the BTEX gases are condensed into liquid form to be introduced into the reboiler 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 toward BTEX gases was increased as well as the absorption capacity of TEG toward water vapor in the process. This can help to reduce the amounts of external solvents (e.g. Benzene solvent). Which can be used as the entrainer in the azeotropic distillation at the regeneration column. This approach will save costs in terms of amounts of make-up solvents to be used as the entrainer in the system. This because some of it may lose to the atmosphere through the flash tank due to its high value in vapor pressure. Shown in Table 4 by addition of potassium formate (KOOCH) into DRIZO gas dehydration unit, the reduced amount of benzene to be used as an external solvent for the entrainer in the process. In addition, aqueous solution of KOOCH has low vapor pressure even at a high temperature that is suitable to be used in the regeneration process of TEG since the only minimum amount of it will vaporize and lose to the atmosphere. This will reduce amounts of makeup KOOCH aqueous solutions to replace the lost one.

It is shown in Table 4 that without addition of potassium formate (KOOCH) solution, higher value of mass flow rate is needed to obtain the desired amount of water vapor content left in the dry gas. At the same mass flow rate of 9 kg/h of benzene into the re-boiler of the regeneration column, only certain amount of water vapor being absorbed. Thus leaving 19 ppm of water vapor content remained in the dry gas as compared to when KOOCH was added. Lower value of one



**Fig. 12 – Residue curve map for the system TEG–water–benzene with material balance lines.**

**Table 4 – Amount of water vapour in dry gas and BTEX by TEG without addition of potassium formate (KOOCH) at DRIZO GDU.**

Mass flow rate of makeup benzene (kg/h)	Mass flow rate KOOH (kg/h)	Water content in dry gas (ppm)	BTEX gases (kg/h)			
			Benzene	Toluene	Ethyl benzene	Xyelene
0.0	0.0	45.0	4.21	4.71	4.45	0.34
2.0	0.0	40.0	5.42	5.06	4.70	0.36
4.0	0.0	32.0	7.45	5.53	5.06	0.39
6.0	0.0	25.0	10.67	6.23	5.64	0.44
8.0	0.0	19.0	15.70	7.09	6.25	0.49
9.0	0.0	19.0	18.72	7.68	6.79	0.53
10.0	0.0	14.0	23.93	8.46	7.29	0.57
12.0	0.0	8.0	39.65	11.14	9.44	0.74
14.0	0.0	5.0	62.77	14.46	12.15	0.96
16.0	0.0	3.0	118.34	22.48	18.65	1.48
18.0	0.0	1.0	148.34	33.96	24.62	1.78

ppm water vapor of the dry gas was achieved. This is because, KOOCH addition to TEG solution helps to increase its absorption capacity toward water vapor and BTEX gases from the wet gas. Hence, the increase amount of 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.

## 5. Conclusions

In the enhanced gas dehydration process, the water content of natural gas has been reduced significantly as well as the water dew point. DRIZO GDU has showed the most significant improvement of the water dew point curve followed by conventional stripping gas dehydration process and typical gas dehydration process. This is related to the concentration of regenerated TEG, which was the highest in DRIZO GDU process compared to the other two employed processes. By implementing the concept of azeotropic distillation, it allows more water vapor to be separated from TEG in the regeneration column and resulted in higher concentration of the regenerated TEG. The addition of potassium formate (KOOCH) to TEG into the process was proven that it helps to increase the absorption capacity of TEG thus reduces the amount of water vapor remaining in the dry natural gas. It was proven that addition of potassium formate (KOOCH) caused a rise of the absorption capacity of TEG by 2–3 times. Furthermore, the addition of potassium formate resulted in reduction of the amount of makeup solvent with lower water vapor content. Therefore, it is recommended to be used in DRIZO GDU.

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