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An Evaluation of Triethylene Glycol in Associated Natural Gas

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ABSTRACT

LEAN and RICH triethylene glycol (TEG) obtained upstream and downstream of the contactor of a TEG unit in an oil and gas installation were characterized to obtain the pH, salinity, water content and % efficiency respectively. Results obtained show that the characteristics of the LEAN TEG were within acceptable limits unlike those of the RICH TEG which were off specification stipulate by the American Petroleum Institute (API). LEAN TEG with acidic pH (<6.5) and high salinity (> 1000 mg/l) can cause corrosion of the metallic parts of the TEG unit while alkaline pH (>8.5) causes foaming of the TEG which increases TEG loss. LEAN TEG with high water content (>1.5%) reduces the efficiency of the TEG as a moisture stripping agent. A known volume of 5000 liters of LEAN TEG was used as a moisture stripping agent for a 9000 KSm3/d of associated natural gas to obtain an acceptable glycol circulation flow rate of 60 kg of TEG for every kilogram of water removed at 10 oC dew point depression, with a contactor pressure and temperature of 75 barg and 45 oC respectively. Gas chromatographic (GC) analyses were carried out on associated natural gas before and after treatment with TEG, results obtained shows that the molar concentration of carbon dioxide (CO2) and water in the natural gas reduced by 87 and >90 % respectively bringing both parameters to acceptable limits. The molar concentrations of helium and nitrogen remained unchanged before/after treatment with TEG and there was no hydrogen sulphide in the natural gas even before treatment. Analyses of the natural gas using a Shaw meter shows that the dew point, moisture content and absolute humidity of the gas were above acceptable limits before treatment with TEG. The moisture content and absolute humidity of the gas were reduced by 90 % respectively with the dew point of the gas depressed to an acceptable level after treatment with TEG. A LEAN and RICH TEG refers to TEG before and after use as a moisture stripping agent for gas. Water vapor in gas reduces the ability of the gas to flow in the flow lines and process systems, it also causes corrosion in lines and equipment.

Keywords: Moisture; Corrosion; Dew point; Hydrate, Humidity; Methane

Introduction

Natural gas can be defined as a gaseous mixture of hydrocarbons made up of basically methane (CH4)[1,2]. Natural gas also contains smaller amounts of liquids which are hydrocarbon gas liquids which occur as liquids under higher pressures and as gasses at atmospheric pressure examples are ethane (C2H6), propane (C3H8) and butane (C4H10)[3]. In addition, natural gas contains nonhydrocarbon gasses such carbon dioxide, hydrogen sulphide, helium, nitrogen and water vapor. Natural gas is a fossil fuel formed millions to hundreds of million years ago from the remains of plants and animals deposited in thick layers on the earth's surface and ocean floors mixed with sand, calcium carbonate and silt. These thick layers buried under rock, sand

and silt are converted under pressure and heat to form crude oil, coal and natural gas which are all fossil fuels[4,5]. Natural gas is classified into associated and non-associated based on their sources. Associated natural gas are produced with crude oil while non associated natural gas occurs with deposits of coal and are called coalbed methane. Before the 18th century, natural gas obtained from crude oil and coal exploration were either flared into the environment causing a lot of harm and damage to the ecosystem or reinjected into gas well[6]. Flaring of natural gas introduces toxic pollutants such as sulphur dioxide (SO2), carbon dioxide (CO2), volatile organic compounds (VOCs) and methane (CH4) to the environment. Greenhouse gases such as CO2 and CH4 contributes to global climate change[7]. Though CO2 has a longer-lasting effect, CH4 which is the principal component of natural gas is more dangerous than CO2 because it is more prevalent in flares that burn at lower efficiency as such sets the pace for global warming in the near term. At least 25% of today's global warming is driven by CH4[6]. Currently, natural gas flaring is highly prohibited, it is however processed to produce various products such as synthesis gas, ammonia, urea, methanol and petrochemical feedstocks such as propylene, ethylene, acrylonitrile, acrylic acid etc. Non associated natural gas or coal bed methane are extracted from coal deposits before or during coal mining and can be added to natural gas pipelines without any special treatment, on the other hand associated natural gas obtained from crude oil wells contain a lot of impurities capable of jeopardizing the optimal use of the gas and therefore requires a lot of processing[8]. Triethylene glycol (TEG) is a very important chemical used in the processing of natural gas, it has a higher boiling point and can achieve a larger dew point drop than diethylene glycol. Triethylene glycol (TEG) is very effective in stripping off moisture from natural gas because of its excellent thermal stability and low vapor pressure[9]. The chemical structure of TEG is shown in **(Figure 1)**. When gasses come in contact with TEG, water vapors entrained in the gas are absorbed in the TEG making the gas moisture free. TEG has a minimal regeneration loss owing to its thermal stability thereby making it very cost effective in the Oil and Gas industry. TEG before use as a moisture stripping agent for natural gas is said to be lean while after use is referred to as a rich TEG[10]. The aim of this study is to analytically evaluate both the lean and the rich TEG to ascertain the impact of the TEG's composition on its moisture stripping ability. The study is also aimed at envisaging the impact of the TEG on the characteristics of the natural gas as well as that of the natural gas on the efficiency and durability of the TEG **(Figure1)**.

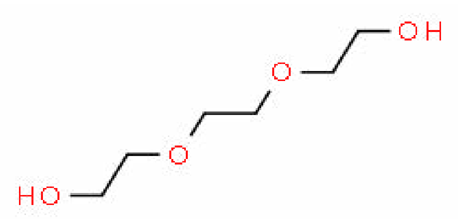

Figure 1: Chemical structure of TEG.

Both the "wet" and "rich" gas means the gas is rich in water and "dry" and "lean" gas means the gas is lean in water. Similarly, the "wet" and "rich" TEG means the glycol is rich in water and "dry" and "lean" TEG means the gas is lean in water. The separator is often referred to as the scrubber, the glycol gas absorber as contactor, the still column as stripper and glycol regenerator as glycol reconcentrator[11].

Materials and Methods

The equipment and reagent used for analyses include: Hach pH meter, Karl Fischer titrator, Agilent Gas Chromatography, shaw meter, hygrometer, graduated glass sampling tubes for carbon dioxide, drager pump, sampling balloons, silver nitrate solution, potassium dichromate indicator, coulomat standards, hydrogen and helium gas.

Sample Collection / Preparation

Pure samples of Lean TEG were obtained upstream the TEG contactor unit in an oil and gas installation using a glass bottle previously cleaned with acetone and dried in an oven. Samples of Rich TEG were also obtained downstream the contactor unit (upstream the TEG recovery drum) after contact with associated natural gas using a clean dry glass bottle. Analytical evaluations were carried out on both the Lean and Rich TEG samples. The compositions of the associated natural gas before and after contact with TEG were also determined. A 5000 liter of Lean TEG contained in the surge drum of the TEG unit was used in the treatment of 9000 KSm3/d of natural gas at a contactor pressure and temperature of 75 barg and 45 0C respectively. The glycol circulation flow rate was obtained by circulating 60 kg of TEG for every kilogram of water removed at 10 0C dew point depression.

pH Determination of Teg Samples

A 50 ml of deionized water was introduced into 50 ml of TEG sample and stirred adequately using a magnetic stirrer. The pH meter and associated electrodes were standardized using two reference buffer solutions within the range of the anticipated sample pH. The sample measurements were made under strict controlled conditions and prescribed techniques. The already calibrated electrodes were immersed into the 50 / 50 TEG / water sample. As soon as the electrode output stabilizes, the stability indicator appears displaying the pH and temperature (ASTM D 1293, 2018).

Determination of The Salinity of Teg Samples

A 5 ml of the TEG sample was added into 50 ml of deionized water, sample was vigorously stirred to ensure complete homogeneity and then titrated with silver nitrate solution in the presence of 1 ml potassium chromate indicator. The persistence of a brick red silver chromate color indicated the end point of the titration (ASTM E202, 2016). The salinity of the TEG sample can be calculated using equation 1:

$$\text{Salinity of TEG (mg/l)} = (((V2-V1)\times N\times 580000))/S \quad \ldots\ldots\ldots\ldots (1)$$

Where:

V1 = Volume of silver nitrate used for 50 ml deionized water

V2 = Volume of silver nitrate used for 5 ml of TEG in water

N = Normality of silver nitrate

S = Volume of TEG sample (5 ml)

Water Content Determination of Teg Samples

The test sample was agitated vigorously to obtain a homogenous solution. The Karl Fischer titrator was operated with a central processing unit, a keyboard and a monitor. The entire system was put on with a click which commences the stirring of the coulomat with a magnetic stirrer. After one minute of stirring the coulomat, 0.1 ml of the TEG sample was injected into the reaction bottle containing the coulomat which was still been stirred. Measurement commences after selecting the appropriate parameters. Results of the moisture content was displayed on the monitor at the end of analyses.

Gas Chromatographic Analyses of Associated Natural Gas

The Gas Chromatographic (GC) equipment was started by switching on the flame gas (hydrogen) and carrier gas (helium) and was adequately calibrated until the base line of the recorder was perfectly horizontal indicating that the GC is properly stabilized and conditioned. The cylinder containing the gas was connected to the hexport gas sampling valve of the GC. The temperature of the sample injection port was kept at 20-25 0C above the column temperature. The gas was introduced into the GC through the injection port through the columns. Measurement commences through the start button and the peaks of the chromatogram at the various retention times displayed on the recorder. The gas composition was determined after 10 minutes of analyses[4].

Carbon Dioxide (CO_2) Determination of Associated Natural Gas

The associated natural gas was obtained with a gas sampling balloon containing an inlet valve after introducing the same gas through the balloon to displace any form of residual gas. Both ends of the graduated gas sampling tube was carefully broken with the aid of a cutter. The arrow end of the glass sampling tube was inserted into the flared open end of the drager pump while the other end inserted into the inlet valve of the sampling balloon. A 1 liter of gas was introduced into the sampling tube by stroking the dragger pump 10 times. The sampling tube was removed from the pump, the length at which the color change extends through the graduated glass sampling tube determines the CO2 concentration of the gas[12].

Determination of Dew Point and Moisture Content of Associated Natural Gas

The head of the shaw meter was raised three times and left in an upward position to calibrate the equipment using air. The equipment was adjusted to read the dew point of air which was affirmed with the help of a hygrometer. The head of the equipment was depressed and reading allowed to stabilize. A gas sample was released through the sampling point into a dry napkin to verify the content and then flushed to the atmosphere for two minutes. Gas sample was introduced into the equipment gently at atmospheric pressure, covering the gas outlet of the equipment with the tip of the finger until the head of the shaw meter was lifted. Gas was allowed through the equipment at atmospheric pressure until a stable reading of the dew point was obtained. The dew point and moisture content of the gas at line pressure were obtained by calculation[13].

Discussion

Triethylene glycol (TEG) is a very essential moisture stripping agent for natural gas. The presence of moisture and other non-hydrocarbon components in natural gas is very detrimental to its usage and application hence the essence of treating natural gas with moisture dehydrating agents such as TEG[14]. Apart from the features and components of the TEG unit such as the contactor pressure and temperature, the volume and the characteristic of the TEG also determines its effectiveness in stripping moisture off the natural gas. The contactor pressure and temperature refer to the pressure and temperature at which the TEG contacts with the gas[9]. The moisture content of the gas decreases with increase in contactor pressure at a constant temperature. Excellent gas dehydration can be achieved at any pressure below 200 barg inasmuch as the contactor pressure is kept constant at a constant Temperature. A contactor pressure of 75 barg at a constant temperature of 45 0C was used for this study in order to optimize cost associated with the procurement of high-pressure equipment[15]. **(Table 1)** shows the characteristics of both the Lean and Rich TEG. The characteristics of the TEG before usage which is represented by the Lean TEG is very essential in guarantying its effectiveness as a moisture stripping agent. From Table 1 it can be deduced that the pH of the lean TEG was within specification while that of the rich TEG was slightly acidic and below specification. The use of acidic pH as a moisture stripping agent for gas can cause corrosion within the metallic parts of the TEG unit, this tendency increases when the water content and salinity of the TEG are above acceptable limits. On the other hand, an alkaline TEG increases the foaming tendency of the TEG resulting in the emulsification of the TEG with the gas thereby leading to high TEG loss. TEG with pH within the alkaline range also reduces the intimate contact between the gas stream and the absorbent agent (TEG) thereby reducing the moisture stripping tendency of the TEG which ultimately results in higher dew point of the gas. Consistent monitoring of the TEG pH is very critical to ensure its stability, pH stabilizers such as de-ethanol amine stabilizes TEG with low pH while alkaline neutralizers stabilize TEG with high pH[14,10]. Results also show that the salinity, water content and the TEG concentration of the Lean TEG were within acceptable limits unlike those of the Rich TEG. The higher the water content, the higher the salinity and the lower the TEG concentration. TEG with high salinity increases the corrosion tendency of the TEG while the ability of the TEG to strip moisture off the gas reduces as the TEG concentration reduces. The % efficiency of the TEG which refers to the TEG's potential to be regenerated is calculated from the TEG's concentration and water content. The % efficiency of the TEG is inversely proportional to the water content of the TEG and directly proportional to the TEG's concentration[9]. Results obtained from Table 1 also shows that the % efficiency of the TEG which represents the ability of the TEG to be regenerated after use as a stripping agent for the natural gas was > 90% which is within specification, indicating that the natural gas do not have a negative impact on the TEG. It is however important to note that the negative impact of the gas on the TEG may increase with time after prolonged usage[10].

Table 1: Characteristics of LEAN and RICH Triethylene Glycol (TEG).

Parameters (Average Results)	LEAN TEG	RICH TEG	LEAN TEG Specification
pH	7.80	6.05	6.8-8.5
Salinity (mg/l)	750.00	12500.00	600-1000
Water content (%)	0.25	8.00	<1.5
TEG Conc. (%)	99.75	92.00	98.5 - 99.0
% Efficiency (TEG Regeneration)	96.88	96.88	>90

The composition of the natural gas before and after treatment with TEG were shown in **(Table 2)**. Results obtained shows that the non-hydrocarbon components such as carbon dioxide (CO_2), nitrogen and helium in the natural gas before treatment with TEG were within acceptable limit. The molar concentrations of hydrogen sulphide (H_2S) in the natural gas before and after treatment with TEG was zero respectively. There is a pronounced reduction in the molar concentration of CO_2 in the natural gas after treatment with TEG while the concentrations of helium and nitrogen remain unchanged before and after treatment with TEG respectively. The water content in the natural gas before treatment with TEG was well above acceptable limit whereas the water content in the same natural gas reduced remarkably to within specification after treatment with TEG. The reduced CO_2 in the natural gas after treatment with TEG is associated to the reduced water content. CO_2 readily dissolves in water to form carbonic acid which is the principal precursor for corrosion especially in oil and gas installations[13]. Helium and nitrogen are inert gasses whose presence do not interfere with other components of the gas in terms of reaction. The total absence of H2S in the natural gas is an advantage as sulphides are the principal cause of souring in a process which can result to a lot of challenges such as corrosion, pitting and line blockage which negatively affect the integrity of an installation[14]. Results obtained from **(Table 2)** also shows an increase in the hydrocarbon components of C1-C4 after treatment with TEG which is an advantage especially the improved percentage in methane. The higher the percentage of methane the purer the natural gas and the better its functionality as a starting material in the production of petrochemical feedstocks[4].

Table 2: Composition of Natural Gas using Gas Chromatographic Analyses.

Composition	Molar Conc. Without TEG (%)	**Molar Conc. With TEG (%)**	**API Specification**
Methane	91.6	92.7	>85
Ethane	3.9	4.0964	8-Mar
Propane	1.2	1.21	2-Jan
Butane	0.7	0.87	<1
Pentane	0.52	0.52	<1
Carbon dioxide	1.5	0.2	2-Jan
Hydrogen Sulphide	0	0	<1
Nitrogen	0.3	0.3	5-Jan
Helium	0.1	0.1	<0.5
Water	0.18	0.0036	0.01
Total	100	100	

Results obtained from **(Table 3)** shows that the dew point, moisture content and absolute humidity of the natural gas before treatment with TEG were above acceptable limit, these same parameters were drastically reduced to specification after treating the natural gas with TEG thereby confirming the effectiveness of the TEG in stripping the moisture content off the gas. The dew point of a gas at line pressure refers to the temperature and pressure at which the first water vapor condenses into liquid, it is used to measure the water vapour content of natural gas[9]. Results obtained from **(Table 3)** shows that treating the natural gas with TEG resulted in the dew point depression of the natural gas thereby reducing the moisture content and absolute humidity by about 90%. When contacted with wet natural gas, the Lean TEG strips off the water vapor from the gas stream through the process of absorption. Water vapor in gas reduces the ability of the gas to flow in the flow lines and process systems, it also causes corrosion in lines and equipment[10]. At low temperatures, water vapor in gas forms hydrates which are complicated molecules of hydrocarbon liquid and water capable of blocking expedition lines and causing equipment breakdown[16]. A bar chart showing the composition of natural gas with/without treatment with TEG is represented in **(Figure 2)** while other parameters of natural gas (with/without treatment with TEG) are represented in a bar chart shown in (**Figure 3)**.

Table 3: Natural Gas Parameters using Shaw Meter.

Gas Parameters	**Without TEG**	**With TEG**	**API Specification**
Flow line Pressure (barg)	50.00	50.00	NA
Dew Point @ atm Pressure (⁰C)	-28.70	-49.80	<10
Dew Point @ line Pressure (⁰C)	19.20	-12.60	<10
Moisture Content (ppmV)	429.00	40.00	100
Moisture Content (ppmW)	266.00	25.00	100
Absolute Humidity (g/m3)	0.30	0.03	<0.1

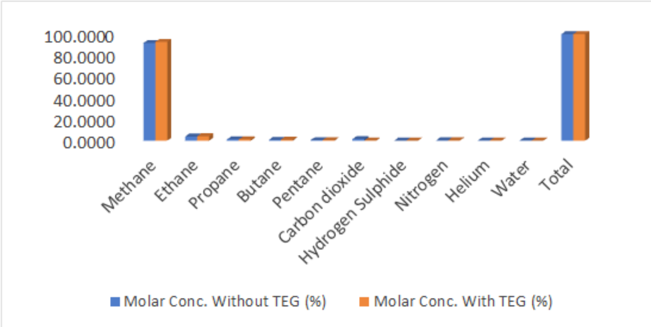

Figure 2: Composition of Natural Gas with/without TEG Treatment.

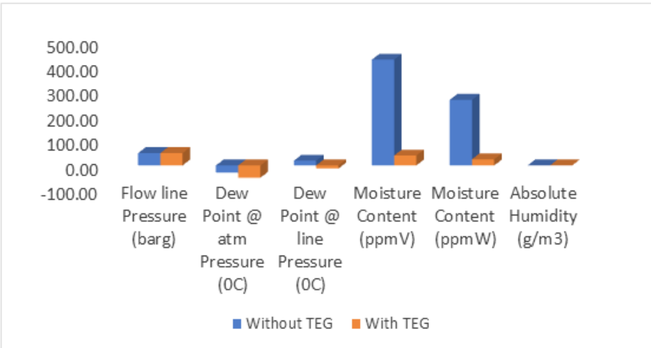

Figure 3: Natural Gas Parameters with/without TEG Treatment.

Conclusion

The presence of non-hydrocarbon components such as CO_2, H_2S, inert gases and water vapor in natural gas, negatively affect their industrial uses for instance in the production of petrochemical feedstock such as acrylic acid, acrylonitrile, synthesis gas, propylene, ethylene etc. Most non-hydrocarbon components in gasses are water soluble as such exist in the water phase, therefore proper dehydration of the gas with an adequate moisture dehydrating agent such as TEG reduces these components within acceptable limit. Triethylene glycol (TEG) is very effective in stripping off moisture from natural gas because of its excellent thermal stability and low vapor pressure. The volume of TEG contained in the surge drum of the TEG unit must depend on the gas flow rate as this guarantees the acceptable glycol circulation per kilogram of water removed in the gas. The characteristics of the TEG such as pH, salinity, water content are very critical in the efficiency of the TEG as a moisture striping agent as well as the safety and preservation of the installation.

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