



## Exergy Analysis of Monoethylene glycol recovery processes for hydrate inhibition in offshore natural gas fields



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### ABSTRACT

Gas hydrate formation is an issue in natural gas production. In offshore deepwater scenarios the situation is aggravated by the inaccessibility, salinity, low temperatures and high pressures. Monoethylene glycol (MEG) injection in well-heads is one of the used technologies for flow assurance in gas flowlines. Rich MEG is processed in MEG Recovery Units (MRU) to be recovered as Lean MEG returned to well-heads. In offshore rigs, besides determining energy requirements, the assessment of energy degradation is also important, which can be done by Exergy Analysis. In this work, an exergy formulation is developed and three technologies of offshore MRUs are assessed. Since exergy is a property that depends on the definition of a reference environment reservoir (RER), Exergy Analysis is performed via two RER approaches, both presenting consistent results. Approach #1 prescribes the usual standard atmosphere, with the addend that it is saturated by equilibrium with an infinite body of liquid water and MEG is in chemical equilibrium with air species. Since MEG is spontaneously oxidizable, this entails very high exergy flows for MRU streams with MEG. As MEG is practically conserved, high exergy efficiencies result for all MRUs hindering their discrimination. Approach #2 prescribes also the standard atmosphere in equilibrium with liquid water containing MEG at infinite dilution, but not in chemical equilibrium with air. The MEG condition in MRU streams is now more akin with the MEG state in this RER, resulting that MEG streams have lower magnitude of exergy flow, leading to realistic exergy efficiencies that allow MRU discrimination. The underlying reason is that the input exergy flows now have magnitude comparable with exergy losses.

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## 1. Introduction

One major concern in offshore natural gas (NG) production, particularly in deepwater fields, is the formation of gas hydrate in subsea pipelines, which is considered as the most critical aspect in flow assurance strategies. Gas hydrate plugs can have tremendous safety and economic impacts on gas flowline operation and can stop production completely for several days or months, and in the worst case, can result in pipeline loss. Furthermore, the removal of plugs of gas hydrate and remediation can be costly and time-consuming, emphasizing the relevancy of inhibition of hydrate formation (Nazeri et al., 2012).

Natural gas hydrates are crystalline water-based solids

physically resembling ice, with a crystalline structure comprised of water and light hydrocarbon molecules (mainly CH<sub>4</sub>). Hydrate structures are characterized by repetitive crystal units composed of asymmetric, spherical-like “cages” of hydrogen-bonded water molecules, each cage typically containing one (or more) guest molecule(s) held in its interior by dispersion forces. Common hydrate crystalline structures are cubic structure I (sI), cubic structure II (sII), or hexagonal structure H (sH). Type I cubic structure sI is formed with guest molecules having diameters between 4.2 and 6 Å, such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, and H<sub>2</sub>S, therefore being directly associated to natural gas hydrates, but the other two structures can also occur in the NG context. Cubic structure sII is more common with larger hydrocarbon molecules like C<sub>3</sub>H<sub>8</sub> and i-C<sub>4</sub>H<sub>10</sub>, while the hexagonal structure sH is associated with multicomponent cages that encapsulates two hydrocarbon molecules like CH<sub>4</sub> with C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub>H<sub>12</sub> or C<sub>6</sub>H<sub>14</sub> (Sloan and Koh, 2008). Such solids can be formed above the freezing temperature of water and, for this reason,

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represent a major flow assurance concern. Gas flowline hydrate formation occurs as consequence of favorable thermodynamic conditions, which are defined basically by three factors: (i) presence of production water along with the gas, (ii) high operating pressures in flowlines, and (iii) low temperature close to 0 °C (Gupta and Singh, 2012). Those conditions are typically found in deepwater subsea gas flowlines and therefore the prevention or control of hydrates formation is necessary in order to avoid safety hazards in flowlines and the consequent production losses (Sloan and Koh, 2008).

In this context, the most adopted strategy for gas hydrate inhibition is the continuous injection of a hydrate inhibitor in the well-heads, so as to avoid hydrate formation and consequently ensure unimpeded flow. Regarding thermodynamic inhibitors of hydrates, MEG injection has been widely used because of its relative advantages over other inhibitors, namely: low losses to vapor phase, low solubility in condensate phase, high depression of water freezing point, high depression of hydrate formation temperature and good attenuation of corrosion. Furthermore, MEG can be easily recovered and effectively regenerated and recycled, configuring a cost effective choice for hydrate inhibition (Haghighi et al., 2009). In addition, the latest MEG reclamation plant designs are cheaper to build and to operate, they have simpler equipment and offer substantially better performance, especially in terms of reliability, high recovery of MEG, energy consumption, low carbon emission, adequate disposal of salt and water back in the sea with environmentally acceptable levels of contamination, and they also comply with the best Health, Safety & Environment (HSE) standards (Nazzer and Keogh, 2006).

### 1.1. MEG Recovery Unit: MRU

After injection, MEG flows along with the production fluids towards the platform, where the incoming stream has its three phases separated: (i) an aqueous bottom phase, comprised mainly of MEG, water and salts; (ii) an intermediate hydrocarbon liquid phase (condensate), and (iii) an upper gas phase of NG with low water content. The aqueous phase, after removal of hydrocarbons in a pre-treatment step, is also known as Rich MEG, aqueous MEG containing at least 25% w/w of water and salts (Bikkina et al., 2012). The Rich MEG is sent to the MEG Recovery Unit (MRU) in order to remove water, salts and other impurities. The recovered MEG is known as Lean MEG containing a minimum of 80% w/w MEG. Lean MEG is returned to be re-injected into the well-heads, thereby completing the MEG loop. Currently, there are three main technologies for offshore MRUs, namely: Traditional Process (TP), Full-Stream Process (FS) and Slip-Stream Process (SS).

TP simply processes Rich MEG with an atmospheric distillation column (ADC) to distillate part of the water producing the re-concentrated Lean MEG as bottoms at a temperature near to 140 °C. TP usually works well when there is no formation water with the produced gas. However, formation water is usually associated with raw NG and therefore the Lean MEG from TP retains inorganics (NaCl, Ca<sup>2+</sup>, carbonates, oxides and sulfides), which accumulate overtime and deposit as scale on filters, piping and exchanger surfaces, deteriorating MRU capacity and facilitating corrosion and thermal degradation of glycol (Nazzer and Keogh, 2006).

FS treats Rich MEG with three serial steps: (i) ADC again for the first removal of water with bottoms temperature below 140 °C; (ii) Flash-Evaporator (FLS) operating under vacuum (0.2 bar A) at vapor temperatures below 120 °C, wherein the feed instantaneously vaporizes after mixing with the recycled hot liquor (with MEG above 90% w/w), while salts precipitate as a slurry in the concentrated liquor; and (iii) the vapor stream from the FLS, containing only MEG

and water, feeds a sub-atmospheric distillation column (SDC) at 0.2 bar A to be separated into pure water (top) and Lean MEG (Nazzer and Keogh, 2006). FLS operates under vacuum to ensure low operating temperatures in the hot liquor recycle ( $T \leq 140$  °C) preventing thermal degradation of MEG, which starts at 162 °C. This degradation produces oxidized species (e.g. acetic and formic acids; Alharooni et al., 2015) leading to a weakening of hydrate inhibition, which in turn entails make-up of fresh MEG to re-compose the inhibitor (Montazaud, 2011). Furthermore, the heater of liquor recycle is a critical item that must reliably heat a high flow rate of salty recycle liquor without exposing it to high skin temperatures that might promote thermal degradation and/or vaporization with salt precipitation, leading to fouling (Nazzer and Keogh, 2006). Since the liquor heater must not allow suspended particulate matter to settle and incrust, a spiral heat exchanger (SHE) is the preferred design, as it avoids solids build up through a high velocity field that prevents stagnant areas (Latta et al., 2016).

SS process is a combination of the aforementioned Traditional and Full-Stream processes, wherein only a fraction (the Slip-Stream) of the ADC bottoms is treated in a FLS + SDC train and then mixed with the untreated MEG from ADC. This arrangement depends on the salt incoming rate. If it is not too high, it is possible to remove a good part of the water in the pre-concentrator ADC and control the salt content in the lean MEG by running the slip-stream through the FLS (reclaimer) followed by the SDC to finish the removal of water from the slip fraction (Seiersten et al., 2010). The final concentration of salts in the Lean MEG should therefore be kept below a precipitation limit that is acceptable for service.

### 1.2. Power, heating and cooling resources available to offshore MRUs

Depending on the adopted MRU technology and process conditions, there will be different requirements of heating, cooling and electric energy (EE) for operation. Since only MRUs located on offshore platforms are considered here, it is critical to minimize heating, cooling and EE requirements and also the extent of energy degradation. Moreover, the platform environment molds the available options of cooling, heating and EE resources.

The EE supply on offshore oil and gas rigs is normally provided by gas turbines. Gas turbines are widely used for onsite power generation and as mechanical drives in offshore oil and gas production facilities such as FPSOs (Araújo et al., 2016). The temperature of exhaust from gas turbines with power output rating up to 50 MW (both industrial heavy-duty and aero-derivatives) range between 400 °C and 600 °C (Bianchi et al., 2014; GE Aviation, 2013). In offshore rigs the waste heat from the exhaust gases is partly recovered to increase the temperature of a liquid heating medium, such as mineral oil or pressurized hot water (PHW), which circulates in a closed loop supplying heat to facilities (Nguyen et al., 2013). The most common heating medium in topside facilities is PHW, which is easily produced via Heat Recovery Water Heaters (HRWH) (Araújo et al., 2016) with low safety risk compared to mineral oil or high pressure steam (PARAT Halvorsen AS, 2008). Although it is not uncommon to utilize direct EE for heat supply on offshore rigs (Myhre, 2001), up-to-date systems adopt PHW as a low cost heating solution for reboilers and heaters operating below 180 °C (Araújo et al., 2016). In this work all considered MRU heating duties are supplied by PHW supposed available at 200 °C. FPSO gas turbine power stations are designed with capacity near to 100 MW of EE at full service, not counting the spare machines. At 100 MW of EE, most vendors guarantee a minimum heat recovery of 75 MW in the HRWH (Araújo et al., 2016). Thus, it is reasonable to assume that the PHW circuit has a maximum capacity of 75 MW of heat supply in typical scenarios, which is perfectly suitable to MRU

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