

Comparing the Effectiveness of Methanol, Ethanol and Monoethylene Glycol at Preventing Hydrate Formation in a Hydrate Flow Loop

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Abstract

Gas hydrates are formed when free water combines with natural gas under high pressure and low temperature, and they are a significant cause of plugged subsea flow lines. This research studied three thermodynamic hydrate inhibitors (methanol, ethanol and monoethylene glycol) in preventing hydrate formation in an experimental flow loop designed to model subsea flow lines. The closed flow loop was a 12meter ½' stainless steel pipe submerged in a 4' Polyvinylchloride(PVC) pipe containing cold water, mimicking the subsea pipelines on the waterbed. The hydrate formers (water and natural gas) were fed into the loop to check for hydrate formation, which was indicated by a rise in the loop temperature because hydrate formation is an exothermic reaction. 2wt% of the methanol, ethanol and monoethylene glycol (MEG) were used as hydrate inhibitors at different experimental runs. 2wt% monoethylene glycol could not prevent hydrate formation in the loop, but a higher concentration of 3wt% was efficient at preventing hydrate formation. To enhance the performance of monoethylene glycol, it was blended with methanol and ethanol. The best blend was 0.7wt% MEG combined with 0.3wt% methanol. It is imperative to use the blend of monoethylene glycol and methanol to reduce the volume requirement from only monoethylene glycol and reduce inhibition cost.

Keywords: Flow assurance, Thermodynamic hydrate inhibitors, Flow loop, Gas dominated system, Temperature depression

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1. Introduction

Natural gas hydrates are a curious kind of chemical compound called clathrates. Clathrates consist of two dissimilar molecules mechanically intermingled but not truly chemically bonded; instead, one molecule forms a framework that traps the other molecule. They are formed when small gas molecules are trapped inside polyhedral cages of hydrogen-bonded water molecules at high pressures (3-10 MPa) and low temperatures (275 K - 285 K) (Koh and Sloan, 2007). Most natural gases such as methane, carbon dioxide, hydrogen sulfide and propane, will form hydrates at suitable temperatures and pressures. Natural gas hydrates can be considered modified ice structures enclosing methane and other hydrocarbons, but they can melt at temperatures well above regular ice.

At 30 atmospheres pressure, methane hydrate begins to be stable with temperatures above 0°C, and at 100 atmospheres, it is stable at 15°C. This behaviour has two critical practical implications (Báez and Clancy, 1994). First, it's a nuisance to the

gas company. They must dehydrate natural gas thoroughly to prevent methane hydrates from forming in high-pressure gas lines. Second, methane hydrates will be stable on the seafloor at depths below a few hundred meters and will be solid within seafloor sediments. Dissociation of methane hydrates in ocean sediments leads to emission of methane gas, may have an adverse impact on global warming and climate change. The dissociation of gas hydrates could also decrease the shear strength in continental sediments, making the sediments unstable.

Beyond the environmental impact of gas hydrates, there have also been serious concerns from the gas and oil industries. In 1934, Hammerschmidt first recognized that natural gas hydrates rather than ice were a major potential cause of pipeline occlusion (Hammerschmidt, 1934). As the working areas of the gas and oil production are usually in the deep ocean, the conditions there are favourable for the water and gas to form hydrates, leading to blockages clogging

the gas flow in pipelines. Considering the safety risks and economic loss caused by hydrate blockages, many methods have been employed to prevent their formation. Typical methods are heating the system to a temperature above the hydrate formation at the system pressure (Lili *et al.*, 2021), drying the gas (Hubbard, 1991), and chemical control using inhibitors (Odutola *et al.*, 2014). Chemical control of hydrates involves using chemicals to alter the hydrate formation condition of pressure and temperature or to delay hydrate nucleation, growth and agglomeration. Low Dosage Hydrate Inhibitors (LDHI) and Thermodynamic hydrate inhibitors (THI) are the chemicals used in hydrate inhibition.

THI comprise alcohols and glycols, while LDHIs are polymers and surfactants. THI are added at relatively high concentrations of about 10wt% - 60wt% in the aqueous phase (Kelland *et al.*, 1995). Their main benefits are their effectiveness, reliability and proven track records.

THI reduces the water activity by interfering with the hydrogen bond of water, thereby shifting the hydrate formation process outside the hydrate stability zone. This enables the system to operate in harsh conditions without hydrate formation (Jinhai *et al.*, 2011). There are two types of THI: polar THI and ionic THI. Methanol and glycols are polar THI, while salts are ionic THI. THIs are effective in melting hydrate plugs. The choice THI to use depends on the plug location, fluid effects and properties of the plug.

Alcohols (Methanol and Ethanol) and glycols (Monoethylene glycol, Diethylene glycol and Triethylene glycol) are usually used as polar thermodynamic inhibitors. They are typically injected before the fluid cools to hydrate formation temperature. They prevent hydrate formation by changing the thermodynamic properties, shifting the equilibrium temperature and pressure of hydrate formation leftward (Fig. 1). Polar THI are the most common chemicals used for hydrate inhibition.

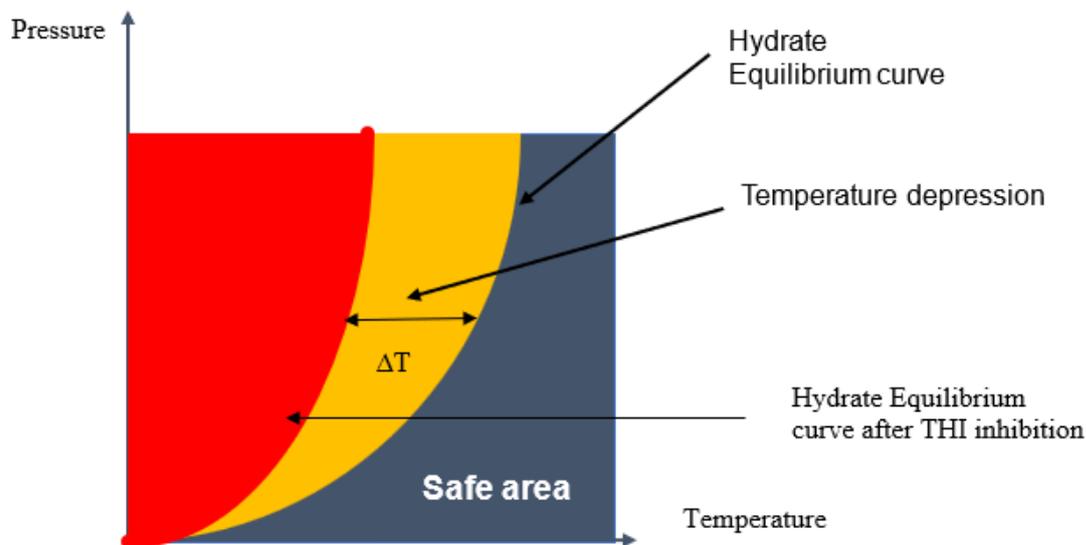


Fig. 1: Effect of THI on hydrate inhibition

Methanol (MeOH) is the simplest alcohol. It is colourless, volatile, highly flammable, and has a distinctive odour like that of ethanol. The chemical formula for methanol is CH_3OH . Methanol is mainly used in preventing hydrates in pipelines and topside on platforms (Jeong *et al.*, 2013) and for system restarts. Methanol has severe side effects, making its use less attractive in the petroleum industry: a tremendous amount of methanol is lost to the hydrocarbon phase during hydrate formation. Methanol in petroleum fluid reduces the market value of petroleum fluid. Also, methanol will increase the chances of pipe corrosion by

dissolving the alcohol-based corrosion inhibitor. Methanol loss is significant when a fraction of the hydrocarbon phase is very large relative to the water phase. Methanol recovery is costly and is seldom done. Ethanol (EtOH) is very effective at preventing hydrate formation. It is the most popular hydrate inhibitor in Brazil (Saeid *et al.*, 2011). However, like methanol, a significant portion of ethanol is lost to the hydrocarbon phase during hydrate inhibition, which may cause downstream production problems.

Monoethylene glycol (MEG) is also known as ethane-1,2-diol. Pure MEG is colourless, odourless,

syrupey, sweet-tasting and toxic. It is widely used as antifreeze because of its low freezing point and tendency to form glasses. MEG-Water mixture freezes at temperatures below $-45\text{ }^{\circ}\text{C}$ when 60wt% MEG and 40wt% water are mixed. MEG disrupts the hydrogen bond in water to alter the hydrate formation temperature to lower temperatures and hydrate formation pressure to higher pressures. MEG is a valuable desiccant. It is widely used in long multiphase pipelines that transport natural gas. MEG may be recovered and recycled more quickly than methanol because of its higher molecular weight and low volatility; however, this is rarely done because it can increase water salinity and cause more problems. The quantity of MEG lost to the vapour and condensates are very small compared to methanol. MEG is most appropriate when the hydrocarbon phase is very high, and the water phase is little. MEG injection is used when the required methanol injection rate exceeds 30gal/hr (Sloan, 1998). MEG low vapour pressure requires that it be atomized into a pipeline. MEG is hardly used to dissociate hydrate plug due to its high viscosity and density; MEG is seldom used to dissociate a hydrate plug unless the point at which MEG is injected is vertically above a hydrate plug such as plugs formed in risers or wells. Other glycols such as di-ethylene glycol, tri-ethylene glycol can be used in inhibition hydrates. The glycol chosen must be hygroscopic, non-corrosive, non-volatile, easily regenerated to high concentrations, insoluble in liquid hydrocarbons and non-reactive with hydrocarbon, CO_2 and sulfur compounds. This work compares MeOH, EtOH, and MEG's effectiveness in preventing hydrate formation in a gas dominated experiment

conducted in a laboratory flow loop. These chemicals depress hydrate formation temperature to enable the loop to operate at the hydrate risk zone without forming hydrates.

2. Materials and methods

2.1 Equipment

The equipment used in this research was a mini loop that simulated the offshore environment (Odutola et al., 2017). The laboratory flow mini-loop, essentially composed of a $\frac{1}{2}$ inch pipe embedded in a 4inch PVC pipe containing cold water. The $\frac{1}{2}$ inch pipe simulated the subsea flowline lying on the seabed with surrounding cold water. The flow loop has been used to evaluate the effectiveness of kinetic hydrate inhibitors such as: modified starch (Odutola et al., 2019), N vinyl caprolactam (Odutola et al., 2016), Poly Vinyl Caprolactam (Odutola and Okomo, 2021), and plant polymers (Odutola and Utobivi, 2021).

The flow loop was situated in a temperature-controlled room to avoid temperature gradients between the flowing media and the surrounding. The PVC pipe was also insulated with amaflex and fibre wool to prevent external temperature influence. The flow loop was designed to withstand the pressure of 3500 psi. Water was injected into the loop using an electromotor pump, and flow was implemented with a Kracht screw pump with variable rates. Cooling was achieved by circulating water from the refrigerator around the loop at a cooling rate of 2°C/hr . The loop was monitored by three temperature sensors (platinum resistance thermometers). A schematic of the laboratory mini loop is presented in Fig. 2.

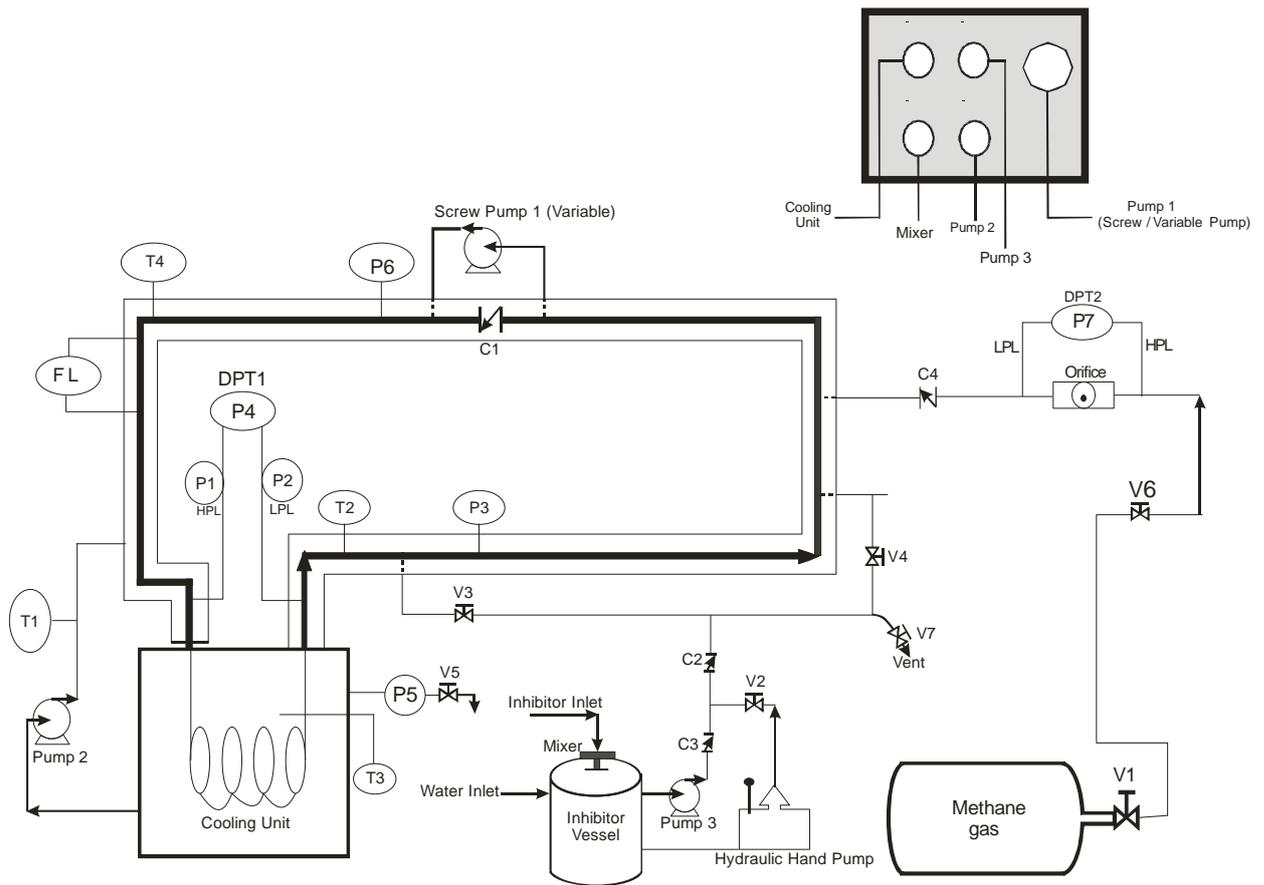


Fig. 2: High-pressure laboratory scale for flow mini-loop apparatus (Odutola et al., 2017)

2.2 Materials

The materials used in this research include water for the hydrate formation experiment, ice to accelerate the loop temperature reduction, natural gas of specific gravity 0.5 as the hydrate former and

three thermodynamic hydrate inhibitors (Monoethylene glycol, ethanol and methanol) from JHD chemicals. The chemical and physical properties of THI used in this research are summarized in Table 1.

Table 1: Properties of THI

Property	MEG	Ethanol	Methanol
purity	99%	99%	99%
Chemical formula	C ₂ H ₆ O ₂	C ₂ H ₅ OH	CH ₃ OH
Molecular weight	62.07 gm/mol	46.07 gm/mol	32.042 gm/mol
Specific Gravity	1.116	0.791	0.7866
Boiling point	197.3 (°C)	78.50 (°C)	64.7 °C
Heat of combustion at 25°C	5625 (KJ/gmol)	5625 (kcal/l)	726.1 kJ mol ⁻¹

2.3 Experimental procedure

A control experiment was first conducted without a hydrate inhibitor. The water and gas were fed into the loop, and the loop temperature was reduced by circulating cold water around the loop. Changes in the loop pressure and temperature were closely monitored as a sign of hydrate

formation. In the experiments conducted to study the inhibitor effectiveness, a mixture of water and inhibitor was fed into the inhibitor vessel and stirred to ensure the homogeneous mixing of the water and inhibitor. The water inhibitor mixture was pumped into the loop, and the gas was fed into the loop through the orifice. The screw pump was

turned on to ensure agitation in the loop, and the cooling water was circulated around the loop. Temperature and pressure reading of the loop were taken at an interval of 15 minutes during the 2-hour experiment. The equivalent weight of inhibitor used in the experiments was calculated from the concentration by weight of inhibitor using Equations (1) and (2).

$$wt\ of\ inhibitor\ required = \frac{x}{100} \times 3000g \quad (1)$$

$$wt\ of\ water\ required = \frac{(1-x)}{100} \times 3000g \quad (2)$$

where x = concentration by weight of inhibitor. 3000g is the total mass of water and inhibitor fed into the loop

3. Results and discussion

The experiment conducted is a constant volume batch experiment. The reactants (water and gas) were fed into the loop and the loop was closed at a pressure of 210psia while the loop temperature was conditioned to hydrate formation temperature. A drop in the loop pressure is an indication that gas was used up in forming hydrates and the inhibitor was not efficient. The plot of pressure against time (Fig. 3) showed that 2wt% MEG was the least effective inhibitor. This is seen as the loop pressure declined from 210psia to 115psia when 2wt% MEG was used as inhibitor. This implies that most of the gas was used up in forming hydrates. The methanol performed best as the loop pressure declined from 210psia to 145psia when 2wt% MeOH was used as inhibitor.

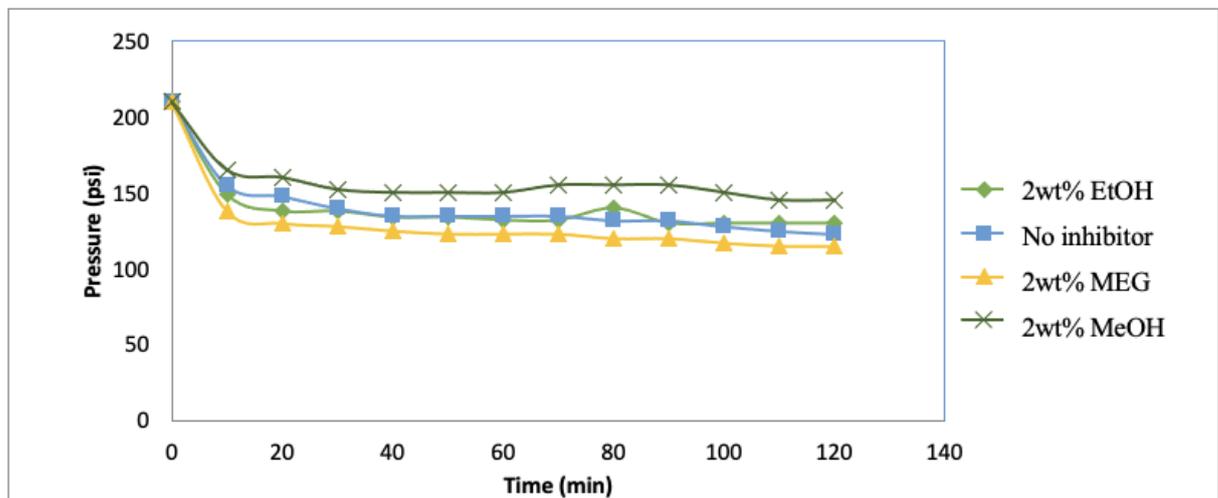


Fig. 3: Pressure versus time for 2wt% ethanol, 2wt% methanol, 2wt% monoethylene glycol and the uninhibited system

Hydrate formation is an exothermic reaction. Therefore, heat is released during hydrate formation. Fig. 4 shows the temperature plot against time for the experiments conducted with inhibitors. In the uninhibited experiment, the loop temperature reduced consistently until the 50th

minute, where temperature was increased (Fig. 4). This increased temperature, signifying hydrate formation, peaked at the 60th minute with a value of 10°C and subsequently declined to and remained at 7°C till the end of the experiment.

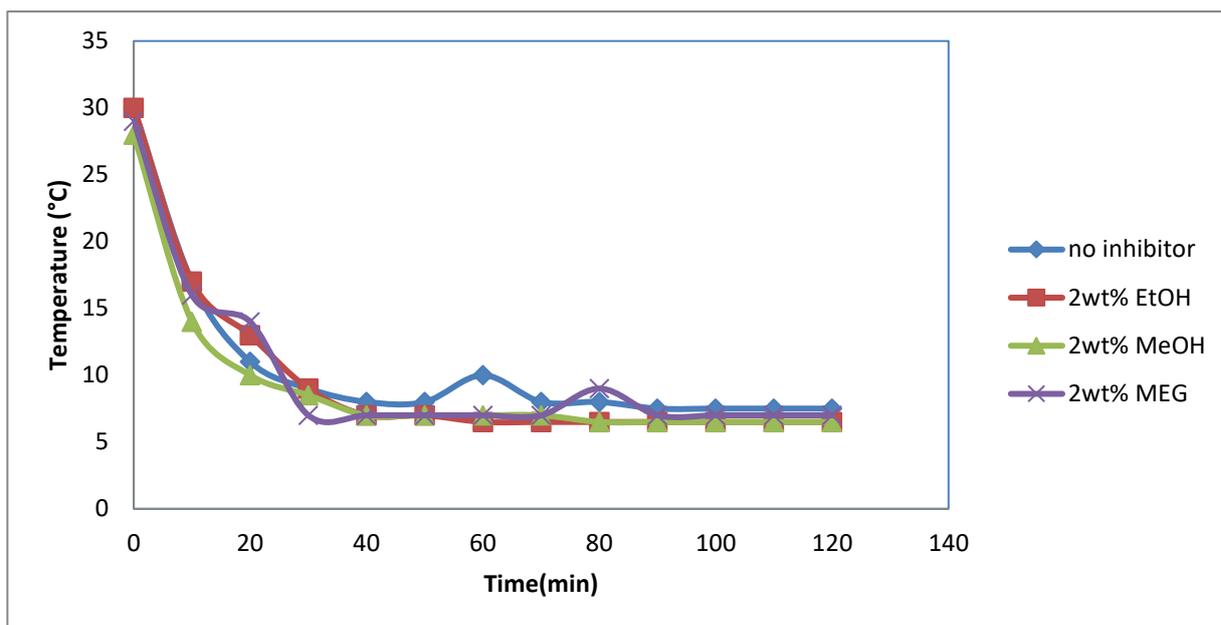


Fig. 4: Temperature versus time for EtOH, MeOH and MEG

When 2wt% ethanol was used as an inhibitor, no temperature increase was recorded. The temperature declined from the start of the experiment till the 60th minute when the temperature attained a value of 7°C (Fig. 4). This implies that 2wt% ethanol was effective at preventing hydrate formation in the loop at 210psi. No temperature increase was recorded when 2wt% (20000ppmw) of methanol was used as an inhibitor confirming the effectiveness of this dosage of methanol at inhibiting hydrate formation in the loop at 210psi. Note that at the end of the experimental run conducted with methanol and ethanol as inhibitors, valve v5 (Fig. 2) was opened, and the effluents gushed out freely. No hydrate plug was noticed.

The trend was different for Monoethylene glycol. At 2wt% of MEG, the temperature declined consistently from the start of the experiment until the 70th minute, when a temperature rise was noticed. At the 80th minute, a temperature peak of about 8.5°C was attained, after which temperature decreased gradually until the experiment was terminated at 120 minutes with a temperature of 7°C (Fig. 4). At the end of the experiment, valve v5 was plugged. The temperature rises and the plugged valve v5 signified that an exothermic reaction of hydrate formation took place, and 2wt% (20000ppmw) MEG could not adequately prevent hydrate formation in laboratory hydrate loop at 210 psi.

Table 2: Effect of THI on hydrate inhibition

Inhibitor	Conc. of inhibitor (wt%)	Hydrate formation
MeOH	2	No
MEG	2	Yes
EtOH	2	No
MEG	3	No

A summary of results obtained using various concentrations of THI is tabulated in Table 2. It shows that 2wt% MeOH and 2wt% EtOH were effective at preventing hydrate formation in the loop. However, 2wt% MEG was insufficient in preventing hydrate formation in the loop. An increased concentration of MEG to 3wt%

prevented hydrate formation in the loop. To improve the performance of MEG, it was mixed with ethanol and methanol, as shown in Table 3. The blend that prevented the occurrence of hydrate formation in the loop is the mixture of 0.7 wt% MEG and 0.3wt% MeOH (Table 3).

Table 3: Effect of hybrid of THI on hydrate inhibition

Inhibitor	Hydrate formation
0.5wt% MEG + 0.5 wt% EtOH	Yes
0.5 wt% MEG + 0.5wt% MeOH	Yes
0.7 wt% MEG + 0.3wt% MeOH	No
0.7wt% MeOH + 0.3 wt% EtOH	No
0.3wt% MeOH + 0.7 wt% EtOH	No

4. Conclusion

The performance of three thermodynamic inhibitors, namely ethanol, methanol and monoethylene glycol, on hydrate inhibition in a horizontal flow loop was studied. Ethanol and methanol prevented hydrate formation in the loop at a dosage of 2wt% respectively. However, monoethylene glycol required a higher dosage of 3wt% to prevent hydrate formation in the loop. The best hybrid of THI to prevent hydrate formation in the loop was the hybrid of 0.7wt% MEG and 0.3wt% MeOH. It is advised that the blend of MEG and MeOH be used during hydrate inhibition to prevent the high dosage requirement of MEG alone.

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