Investigation of Hydrate Formation in Natural Gas Transmission Pipelines

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ABSTRACT: Gas hydrates are ice-like crystals that form because of free water crystallization around guest gas molecules present in the flow line, at certain pressure and temperature conditions. Natural gas hydrates in transmission pipelines pose a great flow assurance problem in the energy industries. Common natural gas guest molecules that form hydrates are methane, ethane, propane, iso-butane, n-butane, nitrogen, carbon dioxide and hydrogen sulphide. The main factors that affect hydrate formation are temperature, pressure, and composition.

This study investigates the formation of natural gas hydrates and the effect of different parameters optimized to retard the formation and growth of natural gas hydrate in transmission lines, such as; pipeline diameter, inlet temperature, inlet pressure, natural gas composition, and thermodynamic inhibitors. The study uses the Schlumberger PIPESIM software for the thermodynamic simulation and MATLAB software for the kinetic model. PIPESIM was set to utilize the Cupic Plus Association equation of state, the Multiflash PVT package, and the OLGAS flow correlation for multiphase flow. The kinetic model used to estimate the growth rate of natural gas hydrate was adapted from already existing model that utilizes the mass transfer and intrinsic kinetic mechanism of hydrate growth, the Arrhenius type equation for the reaction rate constant, and fugacity as the driving force for hydrate growth.

The key findings from this study show that the change in natural gas composition does not significantly affect hydrate formation. Decrease in temperature, reduces the rate of hydrate growth. Hydrate formation is inhibited by decreasing the pipeline diameter, increasing the inlet temperature and reducing the flow pressure. In addition, hydrate can be inhibited by the use of thermodynamic inhibitors. Alcohols and glycol reduce the hydrate formation temperature of natural gas. However, glycols have proven to be more effective than alcohols in inhibiting hydrate formation, with mono-ethylene glycol showing an even more favourable effect as compared to tri- ethylene glycol.

KEYWORDS: Hydrate, mono-ethylene glycol.

I. INTRODUCTION

An energy source that is fast becoming a preferred alternative source of energy is Natural Gas (NG). According to Hari et al. natural gas is arguably the cleanest burning fossil fuel which also plays an essential role in meeting the global energy demand. It currently supplying up to 24% of the worldwide energy demand that is projected to increase at a rate of about 2% per annum until 2040. Natural gas is also considered as the bridging fuel to transition into a world with reduced carbon emissions while catering to the high-energy demand [1, 2]. Natural gas is the most energy efficient fossil fuel as it offers essential energy saving benefits when compared to others like oil or coal. Although the primary use of natural gas is as a fuel, it is also a source of hydrocarbons for petrochemical feedstock and a major source of elemental sulphur, which is an important industrial chemical. Its popularity as an energy source is expected to grow substantially in the future as its share in the world energy balance [3] increased from 0 to 0.25 between the year 1950 and 2000 with expected share growth to 0.4 by the year 2050. With natural gas two essential energy goals for the twenty-first century can be achieved such as providing the viable energy demands needed for social and economic advancement, and reducing adverse impacts on world climate and the environment in general [4].

The sources of natural gas, either from the reservoir or from the refineries, are not found very close to consumers. Hence, it is transported downstream from the reservoir to the refinery down

to the consumer [4] with optimal level of flow assurance, which ensures the safe, reliable and economical flow of the natural gas at low risk and in a cost-effective manner. It is necessary to produce, process and transport the natural gas under high pressure for effective transport. However, at high pressure and low temperature conditions it was discovered that the production and transmission pipelines were becoming blocked with ice like solids [5] and in 1934, Hammer Schmidt found that these ice-like solids causing the blockages in natural gas pipelines are actually gas hydrates [6].

Natural Gas hydrate forms because of the crystallization of free water molecules present in the flow line, around guest gas molecules, which are usually hydrocarbon, at a certain pressure and temperature conditions. The most common guest molecules are methane, ethane, propane, iso-butane, n-butane, nitrogen, carbon dioxide and hydrogen sulphide, of which methane is predominant as it occurs more abundantly in natural gases. The main factors that affect hydrate formation are temperature, pressure, and composition. Free water only enhances hydrate formation, but it is not necessary for hydrate formation. Other factors such as the reaction kinetics, superficial surface area for crystal formation, type of physical site, and agglomeration, also affect the rate of hydrate growth [4, 7].

II.   NATURAL GAS HYDRATES
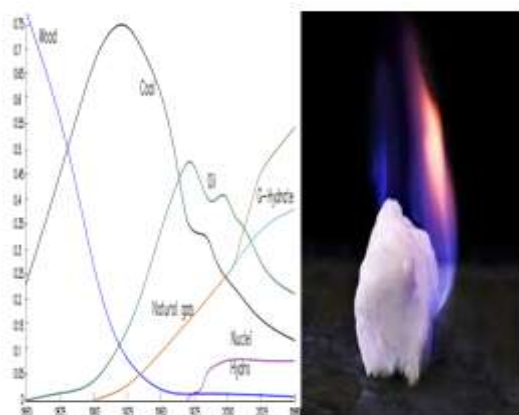
A gas hydrate or clathrate is a solid compound in which gas molecules are occluded in crystalline cells. They consist of water molecules retained by the energy of hydrogen bonds through a highly reversible chemical reaction to produce a solid, which has an ice-like appearance but possesses a different structure than ice. Gas hydrates can be stable over a wide range of pressures and temperatures. Formation of gas hydrate occurs when water and gas are present at low temperature and high pressure. Englezos reviewed clathrate hydrates stating that clathrates compounds are divided into two, they hydrates having water as the host species are called aqueous (water) clathrates, while the other category of clathrates in which the host is not water are called non-aqueous clathrates. Natural gas pipelines contain some amounts of free water or water vapour of about 30-40 mg of water per standard meter cube of gas, Methane is a dominant gas in natural gases, but traces of other hydrocarbon gases may also occur [1, 11, 12, 17, 19].

The physical properties of gas hydrates depend on the composition of the hydrate. Hydrates have a lower density than water, a low thermal conductivity and a large heat of dissociation, hence hydrates requires significant amount of energy to convert stable hydrate to liquid and gas [20].

Table 2.1: Typical physical properties of gas hydrates, adapted from [20]

Physical property	Thermal conductivity	Density	Heat of dissociation
Value	0.5 W/m K	900-950 kg m^{-3}	450-500 kJ

In 1778, Pristley obtained the first gas-hydrates by bubbling SO_2 through water at $0\circ C$ temperature and atmospheric pressure under laboratory conditions at low room temperature, and 33 years later, Sir Humphry Davy in 1811 reported the discovery of gas hydrates formed from aqueous chlorine chlorate gas hydrates during his Bakerian lecture to the Royal Society of London [15]. This lead some scientist to consider him the discoverer of gas hydrates, which is agreeable because even though Pristley was the first to discover gas hydrate in 1778, he did not name it gas hydrate. However, Veluswamy [2] argues in his work that Villard only first reported methane hydrates in 1888. Nonetheless, it was not until 1934 before gas hydrate started getting attention when Hammerschmidt [6] noted during the inspection of gas pipes, that the USA pipeline was complicated by the formation of solid plugs in the wintertime. From the examination, the plugs were assumed to be ice from the hydro test and condensed water. Relying on these laboratory investigations, he showed that the solid plugs consisted not of ice, but of hydrate of the transported gas [1-3, 8].

Hydrate plugs can damage equipment of gas transport system, leading to petroleum industries spending over two million US$ each day to prevent hydrate formation in wells, pipelines, and equipment [1]. The need to investigate in detail the conditions of natural gas hydrates formation and to find an

effective means of preventing solid hydrate plugs in pipelines became essential. Which explains the considerable interest in gas hydrates over the past 100 years, especially in the petroleum industry where the flow is slowed down, or entirely obstructed by large hydrated masses occurring in the natural gas pipelines, in the sea and Arctic regions [14, 16].

Although, natural gas hydrates present flow assurance problems in transmission pipelines. Natural gas from non-conventional sources are found abundantly trapped on the seabed in natural gas hydrates as almost pure methane. Japan has earnestly started extracting natural gas from hydrates, although the technology is quite expensive. We are undoubtedly going to move towards this technology in the future, as purification of the natural gas will not be necessary because natural gas from hydrates is almost pure methane, unlike natural gas from reservoirs that go through many purification stages to extract the pure hydrocarbons. Regarding quantity, there are huge amount of natural gas hydrates on the seabed, with an estimated amount of gas in hydrate accumulations of the world significantly exceeding the volume of known conventional gas resources [17, 18].

There are three primary conditions for hydrate to form in pipelines and process;

- Presence of free water and natural gas molecules ranging in size from methane to butane including CO_2 and H_2S. The free water can be produced from the reservoir or from the condensation of wet gas as the gas phase is gradually expanded and cooled along the pipeline. Hence, even though the wellhead may not have free water, if the vapour at the wellhead is saturated, it can condense to free water along the pipeline.
- Cold temperatures are essential for hydrate formation, as hydrate readily forms in freezing temperatures of about 2-4 ∘C at high pressures.
- High pressures promote hydrate formation. At 2-4 ∘C, hydrates can form at pressures as low as 7 bar. At higher pressures, hydrates form at higher temperatures. [11, 20, 21].

Hydrate formation conditions can be estimated using any of the following three methods.

1.   Hydrate curve method

The simplest method for quantifying the hydrate formation condition is the gas gravity method. This method uses the gas specific gravity which is defined as the molecular weight of the gas divided by the molecular weight of air, and the gas specific gravity is then used in fig. 2.4 to determine the hydrate formation condition. The only limitation of the gas gravity method is that, one condition for hydrate formation has to be known in other to get the other condition, either a known hydrate formation temperature to get the hydrate formation pressure or vice versa [20, 24].

2.   K values method

Katz in 1940 [25] introduced correlations of hydrates formation which was a mile- stone as it offered acceptable predictions for hydrate formation in the industry as it was more accurate than the gas gravity method [26]. This method entails the equilibrium calculations using vapour-solid equilibrium constants (K) values from Gas Processors Suppliers Association (GPSA) charts for all the individual components present in the gas. All molecules including natural hydrocarbons that are larger than n-butane are considered too large to form hydrate and thus have a K-value of infinity [20].

The limitation of this method is, the method is an iterative calculation, which is like the conventional dew point calculation, and convergence is achieved only by interpolation to satisfy the objective function.

3.   Simulation method

The most accurate predictions of hydrate formation conditions are made using commercial computer programs [27]. There are two types of applications that can be utilized for the prediction of hydrate formation, the early hydrate formation programs, which predicted hydrate formation temperature and pressure, and the flash, or Gibbs energy minimization programs, which predicts higher pressures, and lower temperature amounts than the early hydrate program and predict all the phases. Examples of commercial computer programs for detecting hydrate formation conditions are process flow simulators such as ASPEN, ASPEN PLUS, ASPEN HYSIS, or PIPESIM. The flow simulators make use of equations of state (EOS) as a basis for the determination of the hydrate formation conditions. However, it is essential to check results obtained from the program by hydrate curves or hand calculations (if possible), to ascertain the program has not made any unusual predictions [20, 27].

The prevention of hydrate formation represents about 70% of flow-assurance challenges mostly in deep water, while the remaining 30% deal with other flow assurance problems such as waxes deposition, scale, corrosion, and asphaltenes [28]. There are generally three methods of preventing hydrate formation and growth.

1.   Water removal

Free water is a critical component for hydrate formation, which is present in flow lines in the form of formation water, condensed water vapour, or process water [18]. Therefore, removal of free water will inhibit hydrate formation. Free water and dissolved water can be removed from the gas can be removed by separation, or drying with glycol which is a water absorber, further drying can be down using a molecular sieve to adsorb any remaining water in the gas to obtain water content sufficient enough to prevent condensation of the vapour in the transmission pipelines. The average pipeline entry water content allowed is 35 mg water/Sm3 [20]. For subsea developments, this method is not feasible where unprocessed hydrocarbons from the reservoir are transported to a host installation.

2.   Maintain temperature above hydrate formation temperature

As hydrocarbons are transported from the reservoir, especially in subsea pipelines, heat is lost from the fluid to the surroundings, causing a gradual reduction in fluid temperature and thus favouring hydrate formation. High reservoir fluid can be maintained by insulating the pipeline with materials of very low thermal conductivity such as polyurethane [29] or silica aerogels [30], to reduce the heat transfer from the fluid to the surroundings.Which can be feasible for some subsea applications depending on the transported fluid and the tie back distance, with a balance between the high cost of insulation and acceptable risk level [7]. Heat can also be added to the fluid by electrical heating [20] to maintain the flowing fluid outside the hydrate formation range.

3.   Addition of hydrate inhibitors

In locations where it is difficult to remove the water before transporting hydrocarbon, flow channels are frequently operated with inhibitor injection at the wellhead after which dehydration removes the inhibitor at the downstream point [28]. Generally, the two types of inhibitors are the thermodynamic hydrate inhibitors (THIs) and the low dosage hydrate inhibitors (LDHIs) [20].

3.1Thermodynamic hydrate inhibitors

These inhibitors suppress the formation of hydrates, by reducing the temperature at which hydrates form such as lowering the freezing point of water by adding antifreeze. The inhibition process normally occurs in the aqueous phase, rather than in the vapour. The most common thermodynamic inhibitors are methanol (MeOH), ethanol (EtOH), mono-ethylene glycol (MEG), and tri-ethylene glycol (TEG). Al- though salts can be effectively used to inhibit hydrates, it is not recommended for use in pipelines, as it causes corrosion problems in the pipelines [20, 31].

III.   EXPERIMENTATION
1.Thermodynamic Simulation

Simulating pipeline flow is a common practice by gas transmission operators to ensure a balanced system and maintain adequate gas delivery. The efficient and safe transmission of gas entails adequate balancing of the gas system, this being   a necessary criterion for the correct technical operation of the network, pipeline operators, and their dispatch centres, controlling parameters such as pressure, flow rates, and temperature using real-time simulators based on flow models [56].

PIPESIM is a steady-state multiphase flow simulator, which offers workflows for both front-end system design and production operations. The PIPESIM simulator is frequently used for situations that requires more detailed transient simulation. Such conditions may include shut-in, start-up, ramp-up, terrain-induced slugging, severe slugging, slug tracking, hydrate and wellbore clean up. These situations associated with the transportation of fluids can lead to severe operational hazards and give rise to quite a number of problems related to flow instabilities or solids formation that may potentially block the flow path [57].

PIPESIM utilizes equations of state (EOS) which includes the Peng-Robinson (PR) equation, Soave-Redlich-Kwong (SRK) equation, Benedict-Webb-Rubin (BWR) equation, and the Cubic Plus Association (CPA), with a different range of applica- tion for each equation of state.

2. Simulation model

PIPESIM is set to utilize the CPA EOS, the Multiflash PVT package, and the OLGAS flow correlation for multiphase flow. The fluid components and compositional properties are set up using the base data in table 3.1 and table 3.4.

Roughness is assumed constant throughout the pipe as it has only a small effect on the pressure and temperature variation in a steel pipe [27]. The simulated result shown in the PIPESIM system analysis window by sheets and graphs from which the change in pressure, temperature, flow velocity, distance and pressure gradient are intuitively observed.

3. Thermodynamic inhibitors

Thermodynamic inhibitors also known as anti-freeze changes the thermodynamic properties of a fluid by decreasing the hydrate formation temperature and increasing the hydrate formation pressure [20, 59]. Thus, shifting the equilibrium conditions for hydrate formation. Usually, alcohols and glycols are the most widely used inhibitors, which can be added in a batch or continues process;also, they are both economical and efficient. Gao et al. [67] presented at the 2012 fourth international conference on computational and information sciences. Stated that in order to inhibit hydrate formation, additives such as methanol, ethanol, and glycol are used to decrease the freezing point of the free water gotten because of the cooling of the gas during transmission, which causes the water vapour to become free water. Inhibitors are also used to reduce the free water content of the gas, to meet the minimum water vapour content of the flowing natural gas in a pipeline system in other to avoid hydrate formation problems [74, 75]. In this study, the effect of thermodynamic inhibitors on hydrate formation temperature and pressure is going to be evaluated by analyzing the various percentage of methanol (MeOH), ethanol (EtOH), mono-ethylene glycol (MEG), and tri-ethylene glycol (TEG) injected in the natural gas stream as shown in table 3.3.

Table 3.3: Dosage of Inhibitors Used in the System

Inhibitor	Amount, %			
MeOH	5	10	15	20
EtOH	5	10	15	20
MEG	5	10	15	20
TEG	5	10	15	20

Inhibitors should be used only when it is entirely necessary as they are associated with certain operational challenges such as high volume of inhibitors will result in a high cost of transportation and large storage tanks. Methanol is highly flammable. Methanol and glycols have discharge
Table 3.2: Pipeline data for fulmar pipeline from the North Sea to St. Fergus [71].
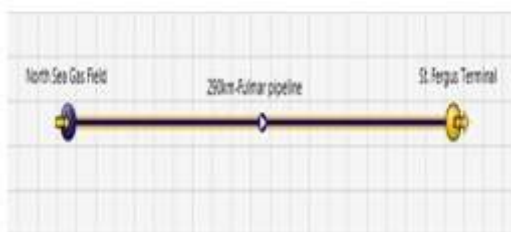
Model of subsea transmission pipeline from North

limits. Cost of building and maintaining inhibitor regeneration facilities is high.

Table 3.1: Composition of natural gas extracted from various regions, adapted from [45, 68-7

Component	Mole %			Eccentric Factor (w)	Critical temp. (K)	Critical pressure (MPa)
	St. Fergus	Union Gas	Turkman gas			
C1	93.63	93.9	94.21	0.0115	190.67	4.6408
C2	3.25	4.2	2.25	0.0908	303.5	4.8835
C3	0.69	0.3	0.53	0.1454	370	4.2568
iC4	0	0.03	0.36	0.1756	408.11	3.648
nC4	0.27	0.03	0	0.1928	425.39	3.7928
iC5	0	0.01	0.26	0.2273	460.89	3.3336
nC5	0.25	0.01	0	0.251	470.11	3.377
nC6	0	0.01	0.17	0.2957	507.89	3.0344
N2	1.78	1	1.9	0.0355	126.11	3.3936
CO2	0.13	0.5	0.14	0.225	304.17	7.3787

Parameters	Value
Liquid flow rates for 4 wells [72]	14000000sm3/d
Ambient Sea temperature	4℃
Fluid inlet pressure at well head [72]	18.1bara
Fluid inlet temperature at well head [72]	65℃
Flow line (horizontal distance) [72]	290 km
Wall thickness [70]	0.625 in
Roughness [45]	0.000046 m
Depth [73]	460 ft
Flow line diameter [72]	20 in
Pipeline thermal conductivity (CS) [72]	54 W/m K

Sea gas field to the St. Fergus terminal through the fulmar pipeline

IV.   RESULTS AND ANALYSIS
4.1Validation of EOS

The result from PIPESIM using the cubic plus association (CPA) EOS as shown in fig. 4.1, has been compared with the previous works of Farzaneh [45] and Schorre [83], who used the AGA8 EOS to calculate the flow temperature gradient in natural gas underground pipelines respectively.
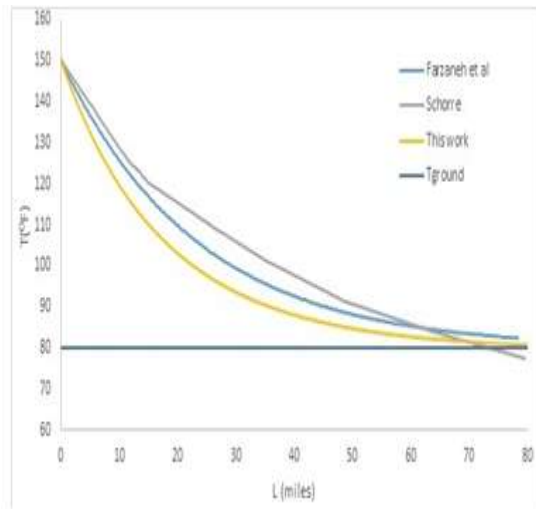
Figure 4.1: Comparison of temperature profile with previous work

The figure shows the temperature profile for 80 miles long pipeline with an inlet temperature and ambient temperature of 150^0F and 80^0F respectively. Comparing the results, the result obtained from PIPESIM using CPA EOS shows about 3% difference with the Farzaneh [45] APA8 EOS and a 5% difference with the work of Schorre [83].

4.2 Hydrate Formation Condition
The phase envelope plot as shown in figure 4.2 shows the system analysis of the pipeline and the condition at which hydrate will form in the pipeline. The hydrate formation point is the point where the system analysis line intersects with the hydrate formation line. Thus, it can be inferred from the plot that, the condition for hydrate formation in the fulmar transmission pipeline is at 19.76 ∘C and 174.66 bar. For safety, 5 ∘C should be added to the hydrate formation temperature. Figure 4.3 shows that the temperature and pressure will drop steadily in the pipeline and will eventually reach the hydrate formation temperature at 30 km distance.
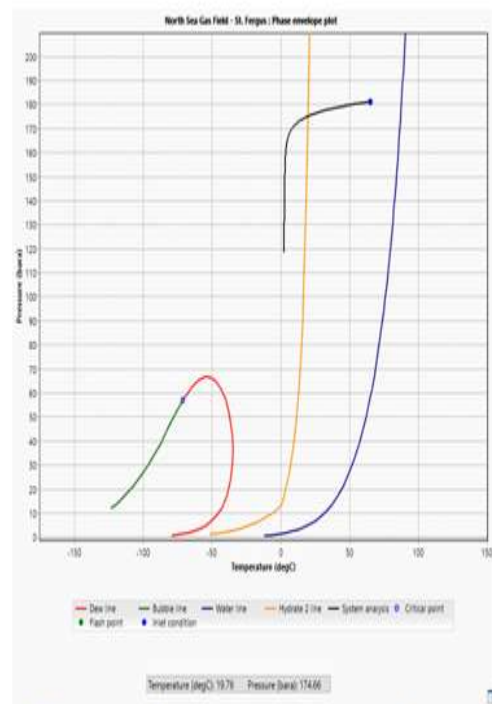
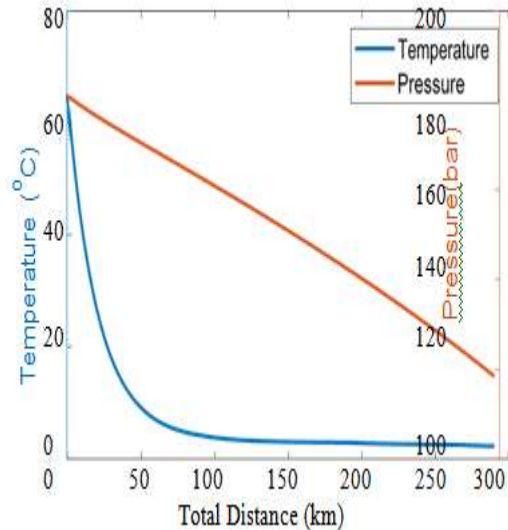Figure 4.2: Predicting hydrate formation condition for St. Fergus natural gas.

Figure 4.3: Temperature and Pressure Change along Pipeline

4.3 Effect of Pipeline Diameter on Hydrate Formation Conditions.
In this section, the effect of pipeline diameter on the hydrate formation condition is being discussed. Fig. 4.4 shows temperature profiles for three different pipeline diameters. From fig. 4.4, the 30-inch pipeline will form hydrates at 19 km while 20-inch pipeline under same inlet conditions will form hydrates at 30 km. A decrease in pipeline

diameter increases the time it takes the temperature to drop to the hydrate formation temperature. Hence, the longer it takes for before hydrates start to form in the pipeline. Another advantage of using a smaller diameter pipeline is that, they are more cost effective. It can also be seen from fig. 4.4 that at 80 km distance the temperature becomes uniform at 4 ∘C which is the ambient sea temperature, regardless of the size of the pipe. Therefore, a smaller diameter pipe may reduce the tendency for hydrate to form, but not for a very long distance.

It can be inferred that, decrease in pipeline diameter, increases pressure drop along the pipeline. The 30-inch pipeline gives a pressure drop of 6 bar along the pipe, while the 20-inch gives a pressure drop of 65 bar. Since the outlet pressure is still very high, the hydrate formation will be more dependent on the temperature   of the natural gas. To stop hydrate formation, it is better to use a smaller diameter pipeline, as the pressure will drop faster below the hydrate formation pressure, as compared to a larger diameter pipeline.
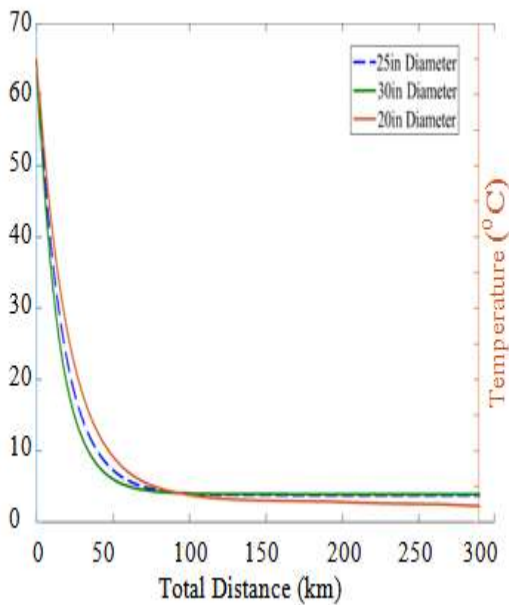

Figure 4.4: Temperature Profile for Various Pipeline Diameter

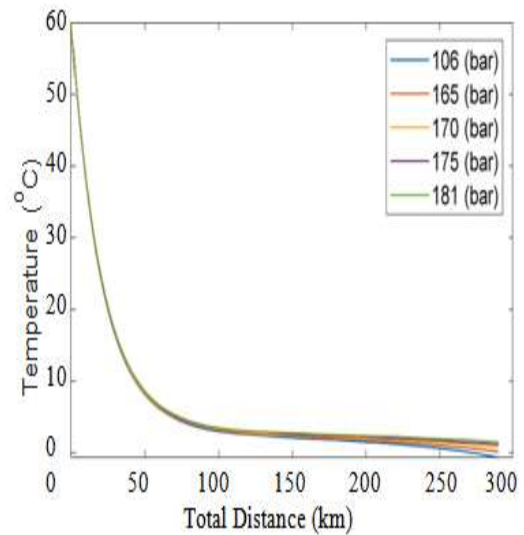### 4.4 Effect of Inlet Pressure on Temperature Profile

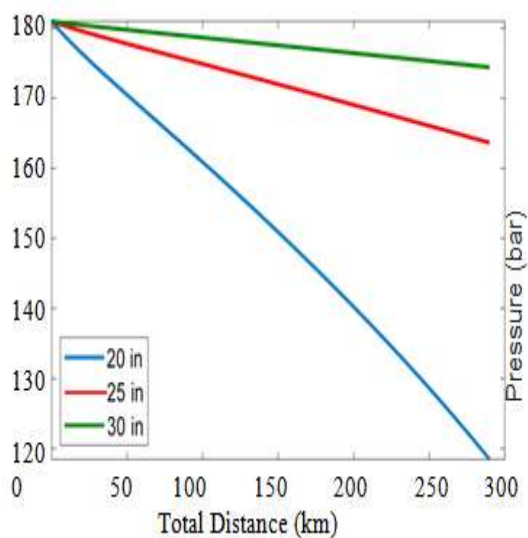Figure 4.6: Temperature Profile for Different Inlet Pressures.

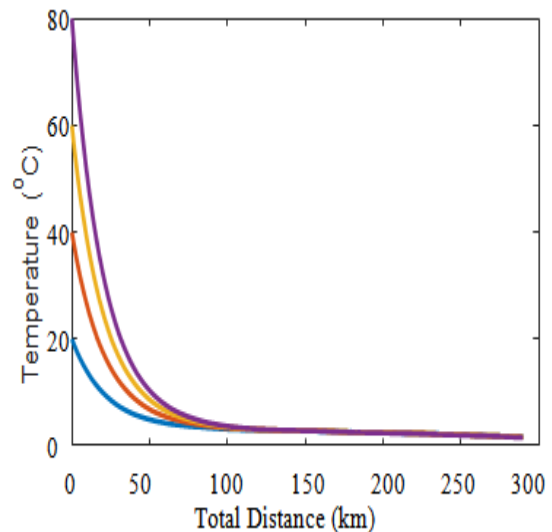Figure 4.5: Pressure Profile for Various Pipeline Diameter.

Figure 4.7: Temperature Profile for Different Inlet Temperatures

Fig. 4.6 shows the temperature profile for six different inlet pressures. From fig. 4.6, it is seen that change in the inlet pressure does not show any significant effect on temperature propagation along the pipeline until about 100 km where the temperature drop starts to increase for lower inlet pressures. Therefore, the increase in inlet pressure only shows a slight change in the outlet temperature and not through out the flow line. This result also supports my earlier claim in section 4.3 stating that, in high-pressure pipeline such as in this case, inlet pressure change will have little effect on the hydrate formation conditions, as can be seen from fig. 4.6 the temperature propagation distance remains constant for various inlet pressures right until the hydrate formation temperature. From 225 km, the temperature profile for inlet pressures of 160, 165, and 170 bar is seen to go below the ambient temperature. Probably, the change in temperature after a long distance of transmission could be because of Joule Thompson effect, which causes the gas to cool below ambient temperature due to expansion.

4.5 Effect of Inlet Temperature on Temperature Propagation Distance

The inlet temperature was varied as shown in figure 4.7, and the effect on the temperature profile was determined at a constant inlet pressure of 180 bar. The higher the inlet temperature, the more the temperature propagation distance, and hence the more the distance before hydrate starts to form. However, regardless of the inlet temperature, at about 90 km the temperature of the gas will be in equilibrium with the sea temperature of 4∘C.

4.6 Effect of Composition on Hydrate Formation Conditions

Figure 4.8 shows the temperature profile for different compositions of natural gas. From the plot, it is seen that temperature decreases steadily along the pipeline   till about 100 km after which the change in temperature became negligible until it reached a final value which is about the temperature of the surrounding seawaterof 4 ∘C. More importantly, it should be noted from the plot that the difference in the composition has little or no effect on the temperature profile.
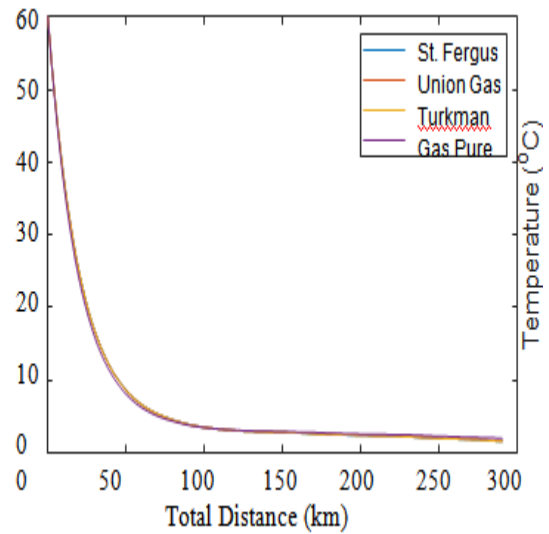

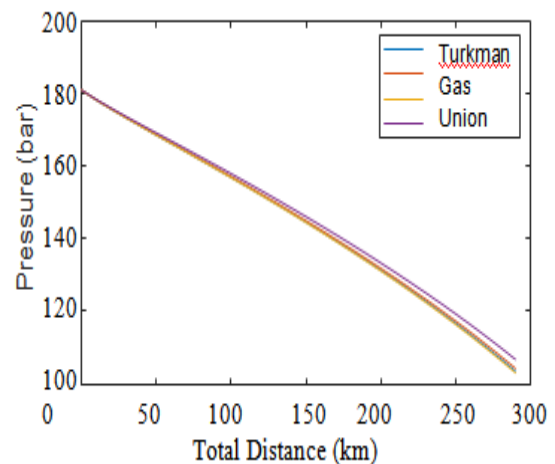Figure 4.8: Effect of Natural Gas Composition on Temperature Profile.

Figure 4.9: Effect of Natural Gas Composition on Pressure Profile.

The pressure decreases steadily throughout the pipeline for all gas compositions, but there is a slight change in outlet pressure for the various gas composition with a final pressure difference of about 5 bar. Therefore, the gas composition has no significant effect on the temperature and pressure profile in the natural gas transmission pipeline, which is supported by the work of Farzaneh et al. (2013) [45] showing a similar effect of natural gas composition in an underground pipeline. Hence, the hydrate formation condition is not affected by the change in composition.

4.7 Kinetic Hydrate Formation

The MATLAB code is used to estimate the rate of hydrate growth and temperature change in the pipeline.
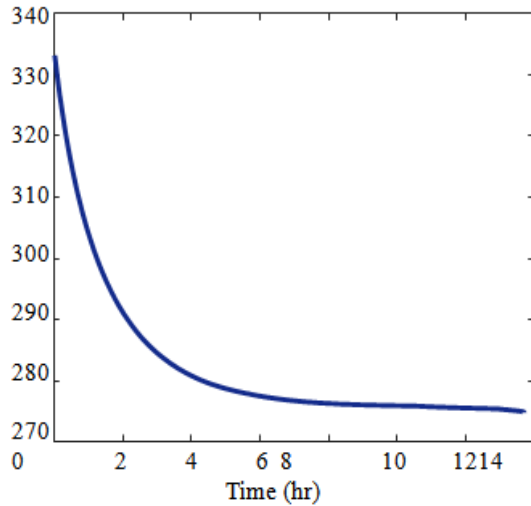

Figure 4.10: Rate of change in temperature of natural gas.

From the estimation of temperature over time in the hydrate formation of the natural gas, It takes 2 hours for the temperature to gradually decrease to 19.76 ∘C, which is the time taken for microscopic hydrate nuclei to form. Therefore, as the hydrate forming gas is been consumed, the time taken for a detectable volume of gas hydrate to be seen is 2 hours, which is also known as the induction time.
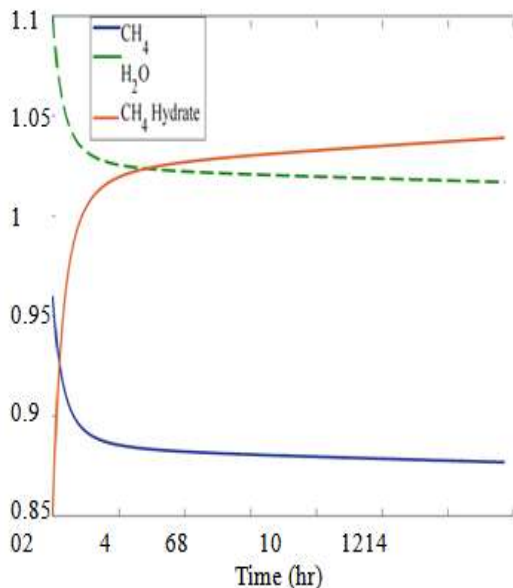

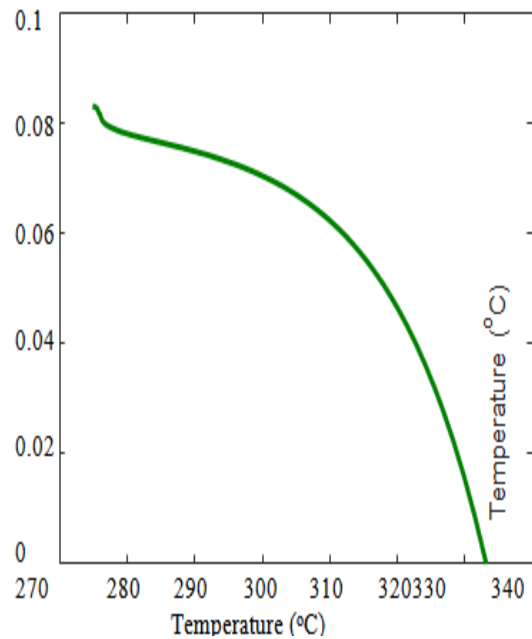Figure 4.11: Rate of methane gas consumption and methane hydrate formation

Figure 4.12: Effect of temperature change on methane hydrate growth rate (mol/s m^3)

As the methane gas is been consumed due to crystallization, methane hydrates are been formed, which agrees to the earlier assertion, the rate of hydrate growth is a function of the rate of natural gas consumption. There is a rapid decrease of methane gas consumption from 1.03 mol/s m3 to 0.95 mol/s m^3 in 2 hours, which results in a rapid hydrate growth from 0 mol/s m3 to 0.0627 mol/s m^3, this signifies the hydrate nucleation rate. After 2 hrs, methane gas starts to grow at a steady consumption rate of 1.07 mol/s m^3. From figure 4.12, the effect of pipeline temperature on the rate of methane hydrate growth is also evaluated. Decrease in temperature increases the rate of methane hydrate growth. Therefore, increasing pipeline temperature can also inhibit methane hydrate growth in the pipeline.

Although the natural gas considered in this work is mainly composed of methane at 93.63%, other gas components such as ethane, propane, butane and carbon dioxide could also form hydrate in the transmission pipelines.
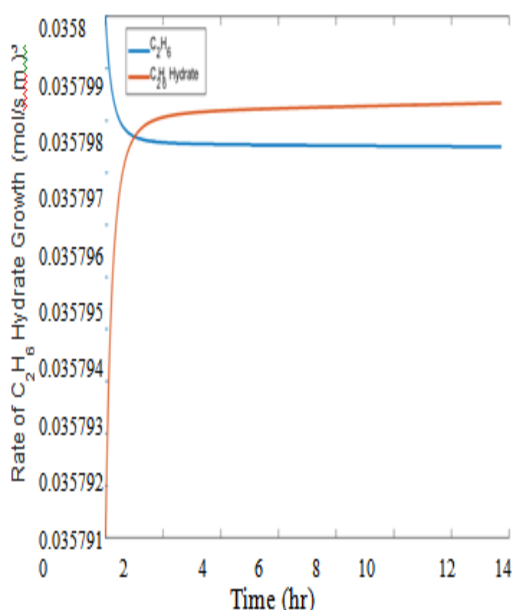
Figure 4.13: Rate of ethane gas consumption and ethane hydrate formation

Figure 4.14: Effect of temperature change on ethane hydrate growth rate

Ethane gas consumption decreased from 0.0358 mol/sm^3 to 0.0357975 mol/sm^3 after 1.5 hours. While, the rate of ethane hydrate formation gradually increases from 0 mol/sm^3 to 2.5e−6 mol/sm3 after 1.5 hours, and this signifies ethane hydrate nucleation time. After 1.5 hours, ethane hydrate starts growing at a steady rate of 2.5e^{-6} mol/sm^3. From the results obtained, it shows that the nucleation time for ethane hydrate is quite smaller than that of methane hydrate;hence, methane hydrate will invariably dominate the pipeline.

From figure 4.14, the effect of pipeline temperature on the rate of ethane hydrate growth is also evaluated. Decrease in temperature increases the rate of ethane hydrate growth. Therefore, increasing pipeline temperature can also inhibit ethane hydrate growth in the pipeline.
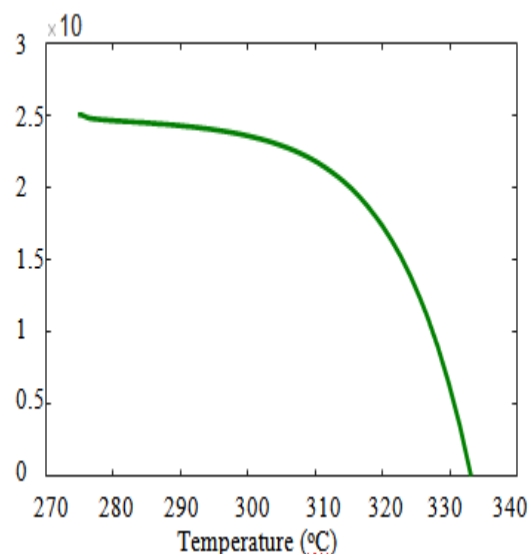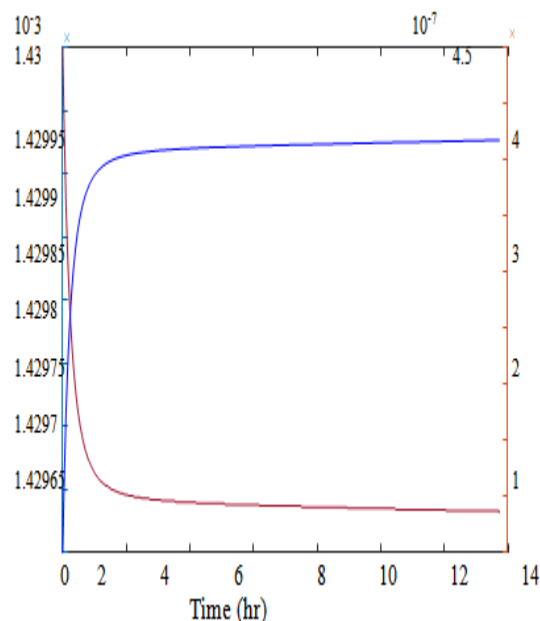

Figure 4.15: Rate of Carbon (II) oxide gas consumption and carbon (II) oxide hydrate formation

From figure 4.15, the rate of carbon (II) oxide gas consumption decreased from 1.43e^{-3} mol/sm^3 to 1.42965e^{-3} mol/sm^3 and rate of formation of carbon (II) oxide hydrate increased from 0 mol/sm^3 to 3.7e^{-7} mol/sm^3. After 1.5 hours, carbon (II) oxide hydrate starts growing at a steady rate of 3.7e^{-7} mol/sm^3. The rate of consumption of ethane and carbon (II) oxide gas is significantly low as compared with the rate of consumption of methane, as well as the rate of formation of methane gas hydrate. Therefore, it is safe to consider only

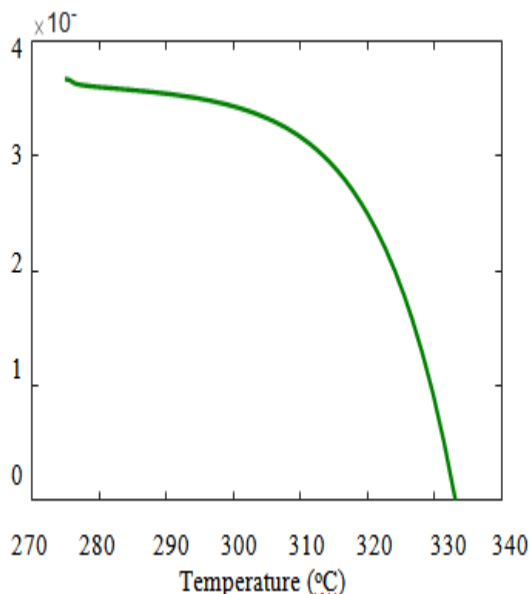methane gas when evaluating the formation of hydrate in natural gas pipelines.

Figure 4.16: Effect of temperature change on carbon (II) oxide hydrate growth rate (mol/s m^3)

The effect of pipeline temperature on the rate of carbon (II) oxide hydrate growth is also evaluated. Decrease in temperature increases the rate of carbon (II) oxide hydrate growth. Therefore, increasing pipeline temperature can also inhibit carbon (II) oxide hydrate growth in the pipeline.

4.8 Thermodynamic Inhibitors

This section shows the effect of various types of thermodynamic hydrate inhibitors such as EtOH, MeOH, TEG, and MEG, on the natural gas hydrate formation condition. Appendix B shows more details on the effect of the inhibitor on hydrate formation curve of the natural gas. The curve shifts to the left with an increase in inhibitor concentration.

Table 4.1: Effect of ethanol on hydrate formation

Amount %	HFT (∘C)	HFP (bara)	Distance (km)
5	16.52	173.91	32.5
10	12.66	172.42	40.1
15	8.71	170.06	52.2
20	5.1	165.34	76
25	-	-	-

The addition of 5% ethanol will decrease the hydrate formation temperature. Thereby, increasing the distance from 30 km to 32.5 km before hy- drate formation in the pipeline. Although,

table 4.1 shows that ethanol reduces the hydrate formation temperature and inhibit hydrate formation over a long distance in the pipeline. High amount of ethanol is needed to completely shift the system out of the hydrate formation zone as shown in figure B.1, where about 25% of ethanol is needed to inhibit hydrate formation throughout the pipeline, and this is not cost effective.

Methanol is more effective than ethanol in inhibiting hydrate growth, as 5% of methanol will reduce the hydrate formation temperature to 14.8 ∘C, as shown in table 4.2. This signifies that hydrate will start forming after 35.4 km. 10% methanol shifts the hydrate line further away to 49.9 km and with 15% methanol, hydrates will not form inside the pipeline. Whereas if 15% ethanol was injected hydrate will still form at 52.2 km, this goes to say that methanol is far more effective in hydrate inhibition than ethanol.

Table 4.2: Effect of methanol on hydrate formation

Amount %	HFT (∘C)	HFP (bara)	Distance (km)
5	14.8	173.33	35.4
10	9.3	170.45	49.9
15	-	-	-

Using glycols as hydrate inhibitors have proved to improve hydrate inhibition better than alcohols. 5% MEG as shown in table 4.3 will further reduce the hydrate formation temperature to 11.38 ∘C, causing hydrate to form at 42.5 km, and as little as 10% MEG will inhibit hydrate formation throughout the 290 km pipeline. This is quite impressive because unlike alcohols that are flammable, toxic and very expensive to recover, glycols are very easy to recover, with a recovering of 99%.

Table 4.3: Effect of MEG on hydrate formation

Amount %	HFT (∘C)	HFP (bara)	Distance (km)
5	11.38	171.62	42.5
10	-	-	-

The effect of TEG was also evaluated as shown in table 4.4. 5% TEG is more effective than 5% of MEG. 5% TEG pushes the hydration point further to 44 km as compared to 5% MEG which shows hydrate formation at 42.5 km. This signifies that TEG is slightly better than MEG at inhibiting hydrates when considering small amounts of inhibitors. However, above 5%, TEG is less effective than MEG. 10% of TEG will reduce the hydrate formation temperature to 3.93 ∘C causing hydrate to form at 93.4 km in the pipeline as

compared to 10% MEG that completely inhibits hydrate formation throughout the 290 km pipeline.

Table 4.4: Effect of TEG on hydrate formation

Amount %	HFT ($\circ$C)	HFP (bara)	Distance (km)
5	10.89	171.32	44
10	3.93	161.02	93.4
15	-	-	-

In general, comparing both the alcohol inhibitors and the glycol inhibitors as shown in figure 4.17, glycols are better hydrate inhibitors than alcohols, and there   is a slight difference between the effects of MEG and TEG as shown in figure 4.17, making MEG the most effective thermodynamic hydrate inhibitor in natural gas transmission pipelines.

V.   CONCLUSION
- Decreasing transmission pipeline diameter increases the temperature propagation distance and increases pressure drop along the pipeline. Therefore, decreasing the pipeline diameter does not favour hydrate formation in natural gas pipelines.
- Change in inlet pressure does not show much influence on the temperature propagation in the pipeline, as such the difference between the fluid temperature and the saturation temperature (sub-cooling) is not affected by inlet pressure change. If the pressure in the pipeline is well above the hydrate formation pressure, hydrates will form at hydrate formation temperatures. Therefore, the pressure in the system should be just high enough to deliver the gas at the required outlet pressure.
- Increasing the inlet temperature decreases sub-cooling and thus reduces the tendency for hydrates to form in the pipeline.
- Change in the gas composition has a negligible effect on the temperature and pressure profile in natural gas pipelines. Therefore, the composition of the natural gas has no significant impact on hydrate formation.
- Alcohols and glycol serve as powerful thermodynamic hydrate inhibitors, by reducing the hydrate formation temperature of the natural gas. However, glycols have proven to be more effective than alcohols in inhibiting hydrate formation, with mono-ethylene glycol (MEG) showing an even better effect as compared to tri-ethylene glycol (TEG).
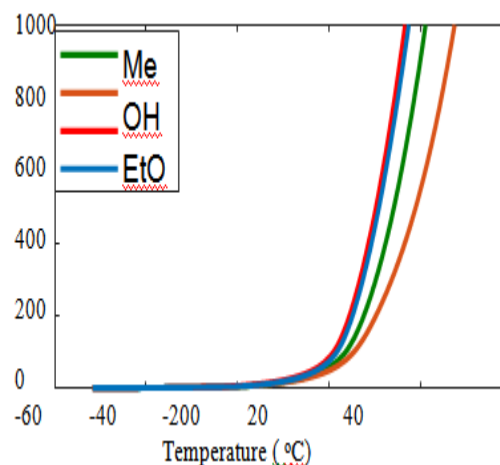

Figure 4.17: Comparing various types of thermodynamic inhibitor

- Increase in temperature reduces hydrate growth rate of natural gas in trans- mission pipelines.

VI.   RECOMMENDATIONS FOR FUTURE WORK
The following are recommendations for future work on the investigation of hydrate growth in the natural gas pipeline.
- The model adopted in this work is restricted to SI structured hydrate; an interesting future work would be to develop a hydrate growth model for SII and SH structured hydrates.
- Laboratory experiments play a vital role in enhancing the understanding thebehaviour of gas hydrate growth. In-depth gas hydrate formation experiment should be conducted to improve the predictability and applicability of these models.
- The study can be further developed by using linear growth rate to determine the size of the hydrate formed inside the pipeline. This can then be used to determine when hydrates will plug the pipeline.

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