MPRI-JAER INTERNATIONAL JOURNAL OF
APPLIED & ADVANCED ENGINEERING RES.
VOL. 1 NO. 1 JUN-2022

SIMULATION OF HYDRATE FORMATION AND PREVENTION IN SUBSEA WELLS USING UNISIM

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Abstract

The oil and gas industry has been taking stringent measures to prevent the formation of hydrates which cause severe flow assurance issues due to pipe blockage, production loss and pose safety and environmental hazards due to pipe rupture and leakages. In this work the Process Simulation and Modeling software Unit Simulation (UNISIM) was used for the simulation of hydrate formation and prevention in subsea wells. To prevent the deposition of natural gas hydrate in subsea oil and gas wells, the hydrate formation area in wellbore must be predicted. The simulation results established methanol as a thermodynamic inhibitor and agree with literature as the 0%, 30% and 70% methanol injection composition respectively causes shifting to the left of the hydrate equilibrium curve reducing the hydrate formation area thus preventing its formation.

[redacted]

KEYWORDS:
Clathrates, Equilibrium, Hydrates, Natural Gas, Simulation,

Introduction

Clathrates are crystalline compounds in which one group of molecules "host" form a lattice of cages in which "guest" molecules are encaged. Hydrates are clathrates in which the lattice is constructed from hydrogen bonded water molecules. For a clathrate hydrate to be stable it is essential that guest molecules occupy at least some of the cages. Clathrate hydrate formation is favored by low temperature and high pressure conditions. Clathrate hydrates may be formed from water and gaseous guests such as methane and carbon dioxide or water and liquid guests such as cyclopentane. Natural gas hydrates refer to clathrate hydrates in which the guest molecules consist of constituents of natural gas (Sloan & Koh, 2007).

Brief history of gas clathrate hydrates

The first documentation of what would now be recognized as a clathrate hydrate was first observed by (Priestly, 1790) . Priestly had cooled an aqueous solution of sulfur dioxide to approximately -8 °C and as the ice melted, it sank to the bottom of the liquor and what he was in fact observing was sulfur dioxide hydrate. Later it was observed by (Davy, 1811) that "the solution of chlorine in water freezes more readily than pure water". Under the supervision of Faraday (1823) made a more definitive discovery of clathrate hydrate. He studied the solid formed in an aqueous chlorine solution and determined its composition to be $Cl_2 \cdot 10H_2O$. The most pertinent observation made by these early hydrate scientists was the ice-like appearance of clathrate hydrates. Since Faraday's work a wide range of gases of small molecular volume have been observed to form clathrate hydrates, including simple hydrocarbons and noble gases. Clathrate hydrates of liquids with small molecular volumes such as chloroform, tetrahydrofuran and acetone have also been reported.

Low temperature and high pressure make it easy for the formations and deposition of natural gas hydrate in deep water and gas fields, and more attention has been drawn to this through flow assurance evaluations (Chin, 2000). To prevent the blockages caused by hydrate in deep water gas well, the prediction of hydrate formation conditions must be performed. Several authors have proposed methods for the prediction of natural gas hydrate formation (W.F. Prassl, 2004); (Zhiyuan Wang, 2008) ; (J. Rornero, 1998). However, the effectiveness of these methods have been based on some assumptions which tend to compromise their accuracy.

Structure of gas clathrate hydrates

Natural hydrates (e.g. water and gas) are crystalline solids. The gas molecules (guests) are trapped in the cavities of water which are hydrogen bonded water molecules (host) as shown in Figure 1.

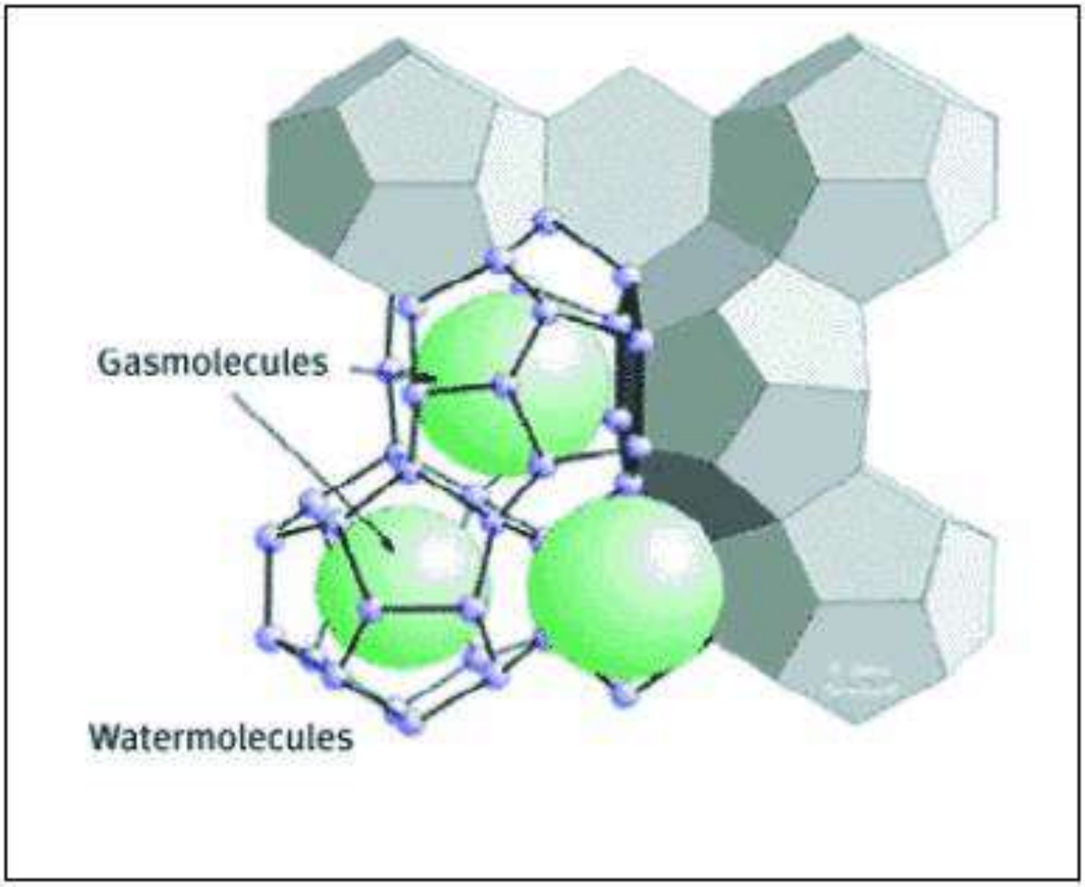


Fig 1: Hydrate Structure

Composition (SI), composition (SII) and Composition (SH) isometric lattice are the three gas hydrate structures that have been found (Sloan & Koh, 2007). The cages of Structure I are organized in a body center wide enough for methane, ethane and alike molecular gasses, for example carbon dioxide and hydrogen sulfide, packing is like a diamond in structure II, which results in some cages being big enough, not only to include methane and ethane gas, but gas molecules as big as propane, composition H takes small molecules and also the larger molecules, typical of the gas or oil portion. Amongst these three, structure I is the most common one. According to Sloan, Figure 2 shows the three common structures of gas hydrate.

Gas hydrates are clathrates that develop under certain conditions (low temperature, high pressure) and may be present at increased temperature than the water freezing point. High pressure (typically > 30 bar) and low (typically < 20 ° C) conditions support hydrate formation, precise conditions in terms of pressure and temperature depend on the composition of the fluids. These conditions could exist offshore in shallow depths below the ocean floor (Sinquin A, 2004)

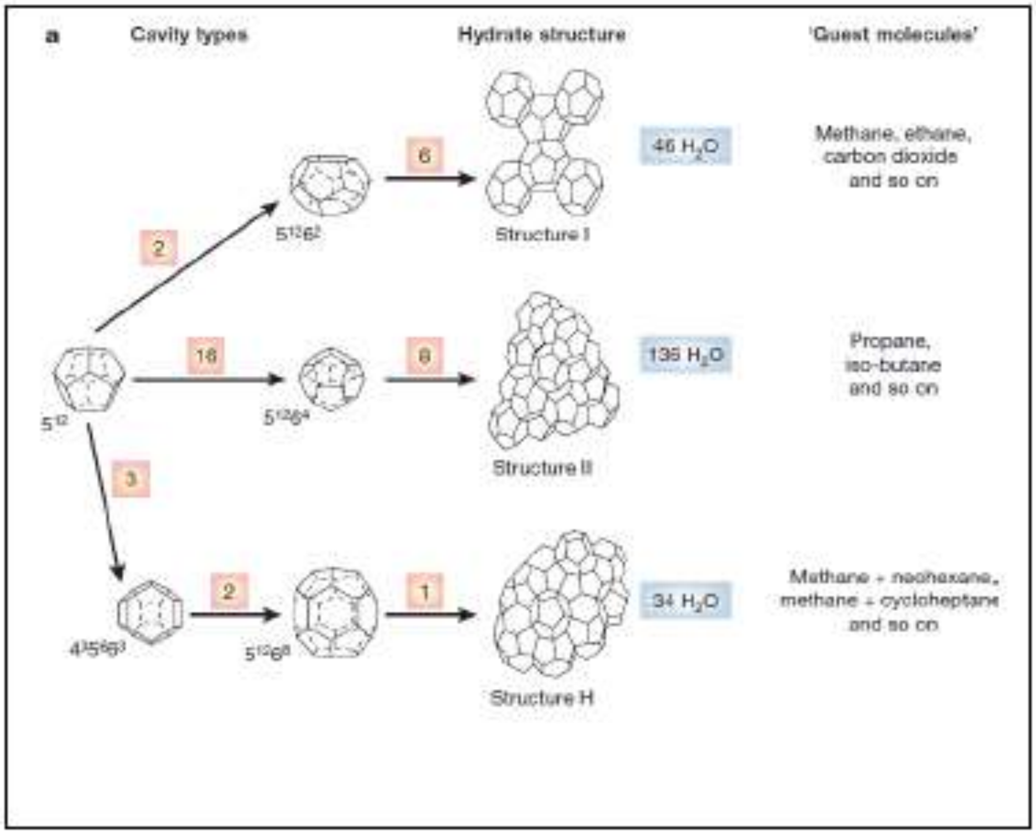


Figure 2: Common types of crystal hydrate structures

The simulation method for the prediction of the hydrate formation is done by the UNISIM software. The prevention method used is the injection of a thermodynamic inhibitor methanol which reduces the temperature of the hydrate formation equilibrium curve hereby shifting the curve to the left hence reducing the hydrate formation area.

In order to prevent the deposition and accumulation of natural gas hydrate in subsea wells, the hydrate formation area in wellbore must be predicted by simulation by comparing four prediction methods of temperature in pipe with field data and comparing five prediction methods of hydrate formation with experiment data. A method was proposed using two software the oil and gas simulator (OLGA) and the Reservoir, Flow and Process Simulator, PVTSIM for predicting the hydrate formation area in wellbore (Guo et. al., 2016).

Temperature and Pressure Models

The main flow pattern in the deep water gas well is gas-liquid annular flow and is based on the assumption that a layer of liquid film slowly rises along a pipe wall dragged by a column of high speed gas flow containing lots of liquid droplets (Chenwei Liu, 2010). Theoretically, the extended two-fluid model applied by OLGA includes three separate continuity equations, two momentum equations and one mixture energy-conservation equation (Bendiksen, 1991). These are presented as follows:

1. Continuity equation for gas phase

$$\frac{\partial(V_g\rho_g)}{\partial t} = -\frac{\partial\left(AV_g\rho_g v_g\right)}{A\partial z} + \varphi_g + G_g \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

For the liquid film

$$\frac{\partial(V_l\rho_l)}{\partial t} = -\frac{\partial\left(AV_l\rho_l v_l\right)}{A\partial z} - \varphi_g \frac{V_l}{V_l+V_d} - \varphi_l + \varphi_d + G_g \ldots\ldots\ldots\ldots\ (2)$$

For liquid droplet

$$\frac{\partial(V_d\rho_l)}{\partial t} = -\frac{\partial\left(AV_l\rho_l v_l\right)}{A\partial z} - \varphi_g \frac{V_d}{V_l+V_d} + \varphi_t - \varphi_d + G_d \ldots\ldots\ldots\ldots\ (3)$$

2. Momentum equations.

A combined momentum equation for the gas phase and possible liquid droplets,

$$\frac{\partial\left(V_g\rho_g v_g + V_d\rho_l v_d\right)}{\partial t} = -\left(V_g + V_d\right)\frac{\partial p}{\partial z} - \frac{1}{A}\frac{\partial\left(AV_g\rho_g v_g^2 + AV_d\rho_l v_d^2\right)}{\partial z} - \lambda_g \frac{\rho_g}{2}\left|v_g\right|v_g \frac{S_g}{4A} - \lambda_i \frac{\rho_g}{2}\left|v_r\right|v_r \frac{S_i}{4A} + \left(V_{g\rho_g} + V_{d\rho_l}\right) g\cos\alpha + \varphi_g \frac{V_l}{V_l+V_d} v_a + \varphi_e v_i - \varphi_d v_d \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

A separate equation for the liquid film,

$$\frac{\partial\left(V_l\rho_l v_l\right)}{\partial t} = -(V_l)\frac{\partial p}{\partial z} - \frac{1}{A}\frac{\partial\left(AV_l\rho_l v_l^2\right)}{\partial z} - \lambda_i \frac{\rho_l}{2}\left|v_l\right|v_l \frac{S_l}{4A} + \lambda_i \frac{\rho_g}{2}\left|v_r\right|v_r \frac{S_i}{4A} + \left(V_{l\rho_l}\right)g\cos\alpha - \varphi_g \frac{V_l}{V_l+V_d} v_a - \varphi_e v_i + \varphi_d v_d - V_l d\left(\rho_l - \rho_g\right)g \frac{\partial V_l}{\partial z}\sin\alpha \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

3. Energy equation.

A mixture energy-conservation equation,

$$\frac{\partial\left[m_g\left(E_g+\frac{v_g^2}{2}+gh\right)+m_l\left(E_l+\frac{v_l^2}{2}+gh\right)+m_d\left(E_d+\frac{v_d^2}{2}+gh\right)\right]}{\partial t}=$$
$$-\frac{\partial\left[m_g v_g\left(H_g+\frac{v_g^2}{2}+gh\right)+m_l v_l\left(H_l+\frac{v_l^2}{2}+gh\right)+m_d v_d\left(H_d+\frac{v_d^2}{2}+gh\right)\right]}{\partial z}+\ H_s+U$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (6)$$

where,
V is volume fraction;
ρ is density, kg/m^3;
v is velocity, m/s;
A is the pipe cross-sectional area, m^2;
Subscripts g; l; i; d indicate the gas, liquid, interface and droplets, respectively;
φ_g is the mass transfer rate between the phases, kg/m^3 s;
φ_l, φ_d are the entrainment and deposition rates, kg/m^3. s:
G_f is the possible mass source of Phase f, assumed to enter at a 90° angle to the pipe wall, carrying no net momentum, kg/m^3 s;
p is pressure, Pa;
S_g; S_l; S_i are the wetted perimeter of the gas, liquid and interface, respectively, m;
α is the pipe obliquity, rad;
H_s is the enthalpy from mass source, J/kg;
E is the internal energy per unit mass, J/kg;
h is elevation, m;
U is the heat transfer from pipe walls, J/m^3;
g is gravitational acceleration, m/s^2.

Natural Gas Hydrate Equilibrium Model

The multiphase flows always develop towards the minimized state of chemical potential. Therefore, the hydrate phase equilibrium model applied in the use of PVTSIM is established using the chemical potential theory as observed by several authors (Erickson, 1983); (J. Munck, 1988); (J.H. Vander Waals, 1959).
The difference between the chemical potential of water in the hydrate state and in the pure water state can be expressed as:

$$\mu^H-\mu^\alpha=\left(\mu^H-\ \mu^\beta\right)+\left(\mu^\beta-\mu^\alpha\right)\ \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(7)$$

where, α; β and H are used to identify each of the three states considered. $\left(\mu^{H} - \mu^{\beta}\right)$ is regarded as the stabilizing effect on the hydrate lattice caused by the adsorption of gas molecules, calculated as follows:

$$\left(\mu^{H} - \mu^{\beta}\right) = RT \sum_{i=1}^{NCAV} v_i \ln\left(1 - \sum_{K=1}^{N} Y_{Ki}\right) + RT \ln\left({f_w}/{f_w^o}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where, v_i is the number of cavities of type i; Y_{Ki} denotes the
possibility that a cavity i is occupied by a gas molecule of type K;
NCAV is the number of cavities per unit cell in the hydrate lattice;
N is the number of components present, which may enter into a
cavity in the hydrate lattice; R is the gas constant; $\ln\left({f_w}/{f_w^o}\right) = \ln(x_w)$

if injecting the inhibitors into the drilling fluids, ; $\ln\left({f_w}/{f_w^o}\right) = \ln(y_w\ x_w)$

y_w, x_w is the activity coefficient and the molar fraction of the water in the water-rich phase respectively $(\mu^{\beta} - \mu^{\alpha})$ is the difference between the chemical potentials
of water in the empty hydrate lattice and water in the form of
liquid or ice, calculated as:

$$\frac{(\mu^{\beta} - \mu^{\alpha})}{RT} = \frac{\Delta\mu(T_o P_o)}{RT_o} - \int_{T_o}^{T} \frac{\Delta H}{\mathrm{R}T^2} dT + \int_{P_o}^{P} \frac{\Delta V}{\mathrm{RT}} dP \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

where,
ΔH , ΔV are the changes in molar enthalpy and molar volume associated with the transition.
T_o is the temperature under the standard condition, °C;
P_o is the pressure under the standard condition, Pa.
$(\mu^{H} - \mu^{\alpha})$ can now be calculated using Equations (7) - (9).
$(\mu^{H} - \mu^{\alpha})$ = 0 indicates that the hydrate state and the liquid or solid water states are equally favorable;
$(\mu^{H} - \mu^{\alpha})$ <0 indicates that hydrate can exist and some of the water will at equilibrium be in a hydrate form.
$(\mu^{H} - \mu^{\alpha})$ a > 0 indicates that no hydrate can exist and the water will be in the form of either liquid or ice.

Prediction Method of Natural Gas Hydrate Formation Area in Wellbore

OLGA is the industry standard tool for transient simulation of multiphase petroleum production (Bendiksen, 1991). Its models cover from bottom hole into the production system, involving the wells, flow lines, pipelines and process equipment. It is being used for design and engineering, mapping of operational limits and safety analysis. The fluid physical property parameters are calculated using PVTSIM and for the simulation with OLGA

Coupling optimum temperature and pressure model with natural gas hydrate equilibrium model, the method based on OLGA and PVTSIM for predicting the natural gas hydrate formation area in wellbore was obtained. The prediction procedure is shown in Figure 3, as follows:

(1) Drawing the temperature profile curve in wellbore using the temperature model.

(2) Drawing the pressure profile curve in wellbore using the pressure model.

(3) Drawing the temperature profile curve of natural gas hydrate equilibrium in wellbore based on the pressure profile and the gas hydrate equilibrium model.

(4) Comparing the temperature profile curve and the natural gas hydrate equilibrium curve in wellbore (Zhiyuan Wang, 2008). The natural gas hydrate formation area in wellbore is the area enclosed by the temperature profile curve and the natural gas hydrate equilibrium curve. The longer the area's vertical length is, the broader the hydrate formation's scope is. The wider the area's horizontal width is, the more easily the hydrate forms. The method can directly and accurately reflect the hydrate formation conditions in wellbore.

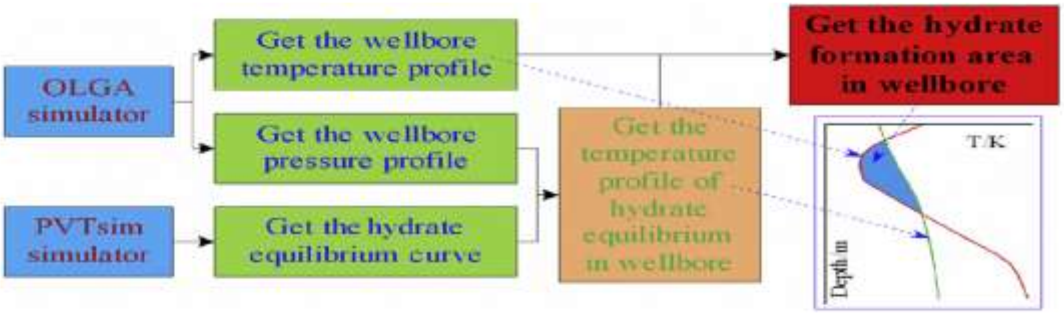


Fig3: The computational scheme for calculating the hydrate formation area in wellbore *(Guo et. al., 2016).*

METHODOLOGY

Simulation Materials

The simulation tool is a simulating software Unit Simulation (UNISIM) which comprises of fluid packages with various equations of state for operational calculations for the simulation of the pipe line in south sea China with the given parameters and conditions.

Table 1: Composition of Inlet Stream

Component	Mole %
N_2	2.525
CO_2	5.262
CH_4	81.006
C_2H_6	5.027
C_3H_8	1.150
H_2O	1.384
i-Butane	0.40
n-Butane	0.83
i-Pentane	0.281
n-Pentane	0.308
Hexane	0.352
Heptane	0.469
Octane	0.407
Nonane	0.203
Decane +	0.397

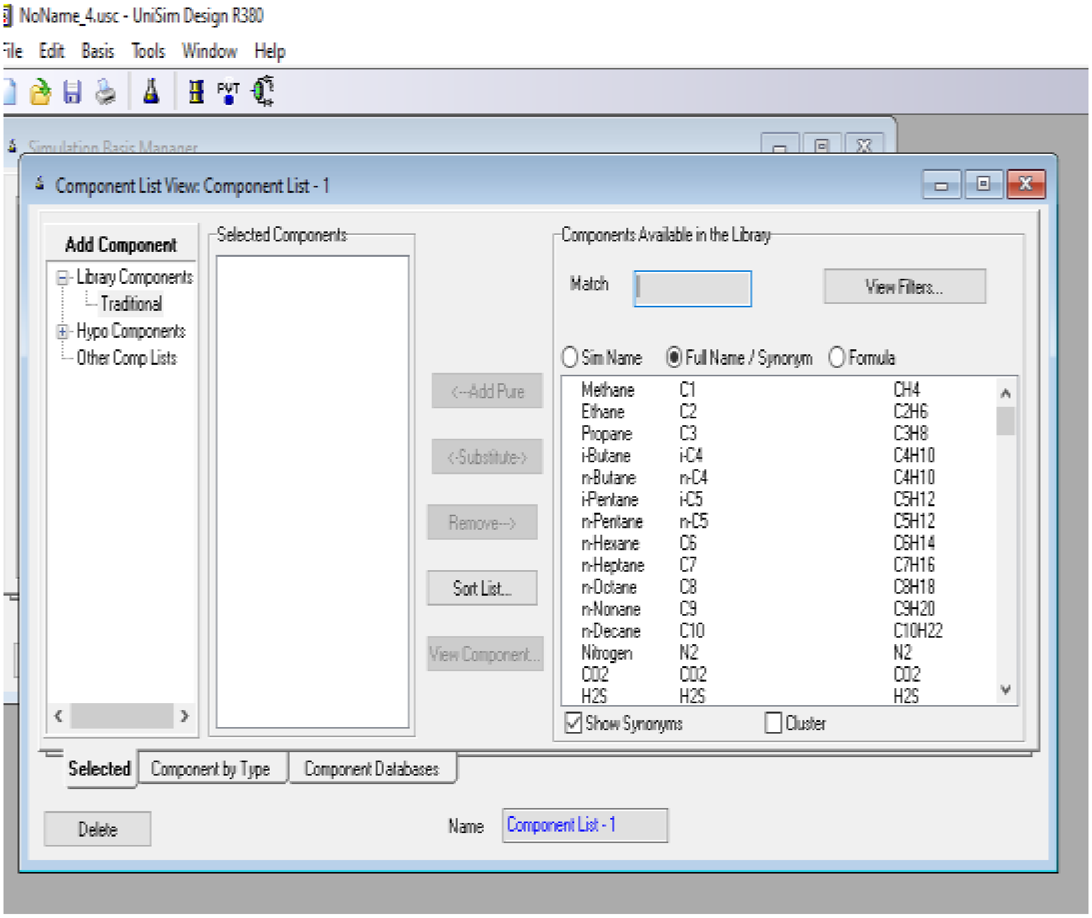
Inlet temperature = 67°C,
Inlet pressure = 1157 kpa, with
Pipe specification of length = 158km
Elevation change = 450m,
Outer diameter = 777.0mm,
Inner diameter = 678.0mm, pipe material is mild steel
Overall heat transfer coefficient = 18kJ/h.m^2.C
Sea bed temperature = 6°C.

Simulation Methods

The procedure on the UNISIM simulation interphase is itemized as follows:

1. Open simulation environment 'component' and add components in Table 1 above
2. Choose a suitable fluid package. (Peng-Robinson fluid package was chosen which utilizes the (Peng D.B, 1976) equation of state.
3. Enter simulation environment and define the composition and condition of the inlet and methanol streams.
4. Introduce a mixer from the unit operation palette making the inlets to be 'inlet' and 'methanol' stream to ensure mixing and outlet the 'upstream'.

5. Introduce pipe from the unit operation palette making the inlet ‘upstream’ and outlet to be ‘outlet’ stream.
6. Define the pipe by clicking the ‘rating’ and filling out the pipe specifications (sizing and heat transfer coefficient).
7. The blue line of all the process streams insinuates the converges.
8. Click on the outlet stream utility to obtain phase envelope and hydrate formation curves



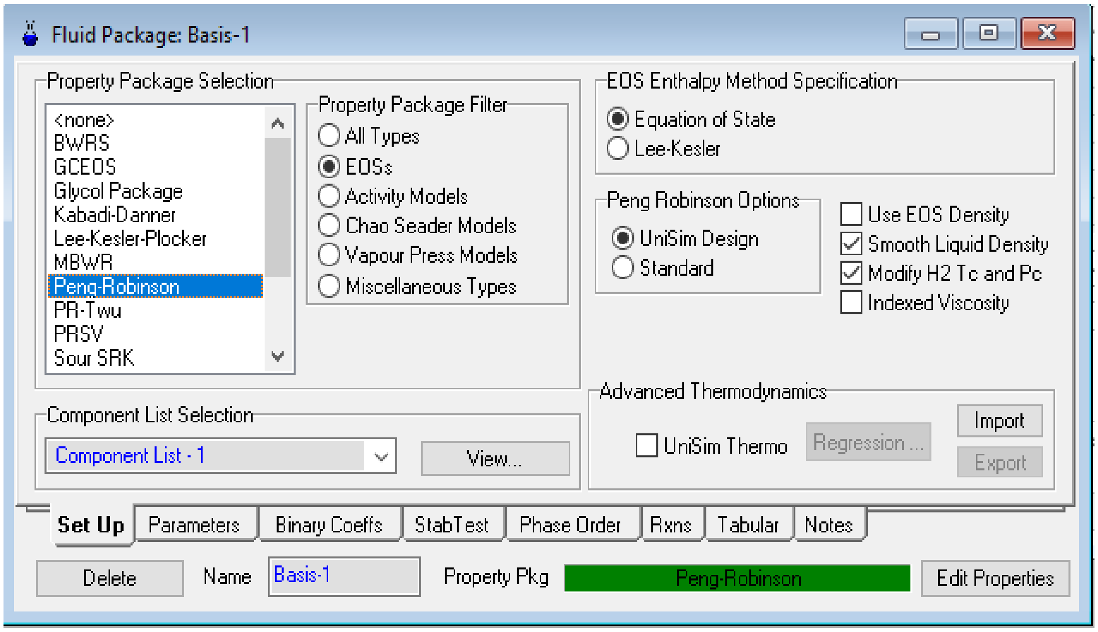
○ Sim Name ● Full Name / Synonym ○ Formula

Methane	C1	CH4
Ethane	C2	C2H6
Propane	C3	C3H8
i-Butane	i-C4	C4H10
n-Butane	n-C4	C4H10
i-Pentane	i-C5	C5H12
n-Pentane	n-C5	C5H12
n-Hexane	C6	C6H14
n-Heptane	C7	C7H16
n-Octane	C8	C8H18
n-Nonane	C9	C9H20
n-Decane	C10	C10H22
Nitrogen	N2	N2
CO2	CO2	CO2
H2S	H2S	H2S

☑ Show Synonyms ☐ Cluster

Name: Component List - 1

Fig 4: Selecting Simulation Components



Fluid Package: Basis-1

Property Package Selection

- <none>
- BWRS
- GCEOS
- Glycol Package
- Kabadi-Danner
- Lee-Kesler-Plocker
- MBWR
- Peng-Robinson
- PR-Twu
- PRSV
- Sour SRK

Property Package Filter

○ All Types
● EOSs
○ Activity Models
○ Chao Seader Models
○ Vapour Press Models
○ Miscellaneous Types

EOS Enthalpy Method Specification

● Equation of State
○ Lee-Kesler

Peng Robinson Options

● UniSim Design
○ Standard

☐ Use EOS Density
☑ Smooth Liquid Density
☑ Modify H2 Tc and Pc
☐ Indexed Viscosity

Advanced Thermodynamics

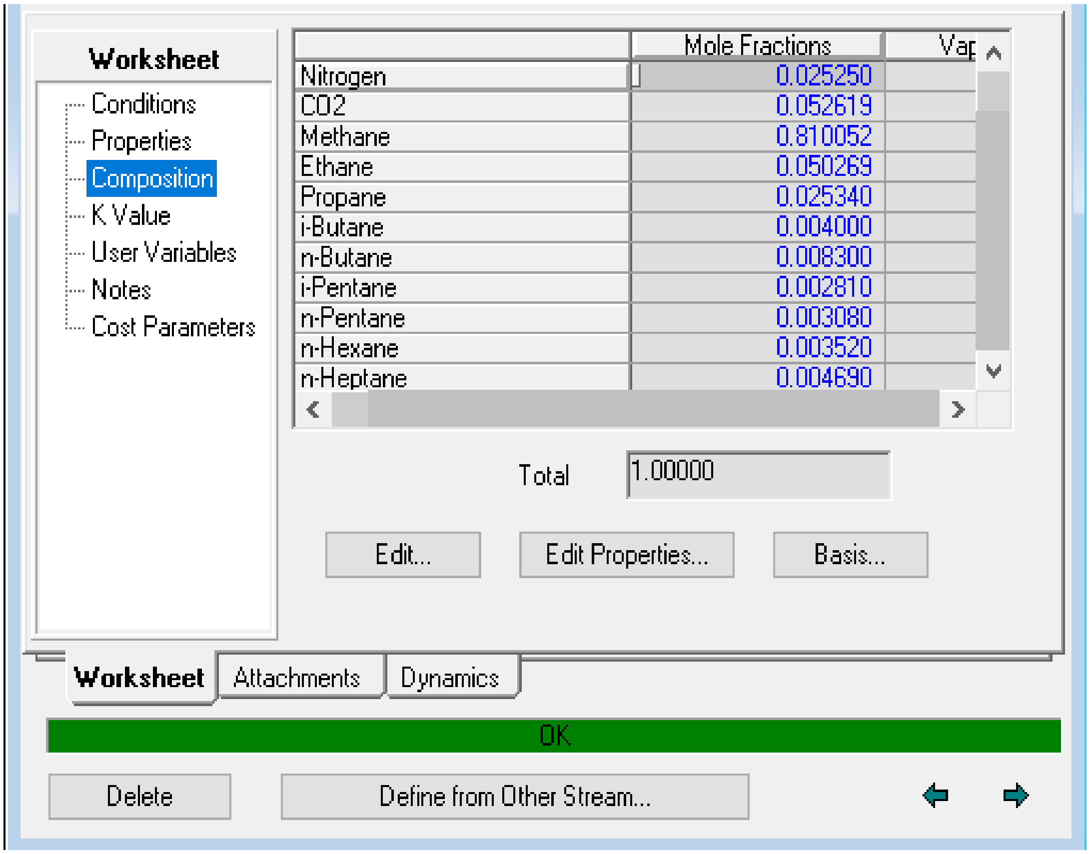
☐ UniSim Thermo

Component List Selection: Component List - 1

Name: Basis-1

Property Pkg: Peng-Robinson

Figure 5: Choosing Simulation Fluid Package



Worksheet

- Conditions
- Properties
- Composition
- K Value
- User Variables
- Notes
- Cost Parameters

	Mole Fractions	Vap
Nitrogen	0.025250	
CO2	0.052619	
Methane	0.810052	
Ethane	0.050269	
Propane	0.025340	
i-Butane	0.004000	
n-Butane	0.008300	
i-Pentane	0.002810	
n-Pentane	0.003080	
n-Hexane	0.003520	
n-Heptane	0.004690	

Total: 1.00000

Fig 6: Defining Stream Composition

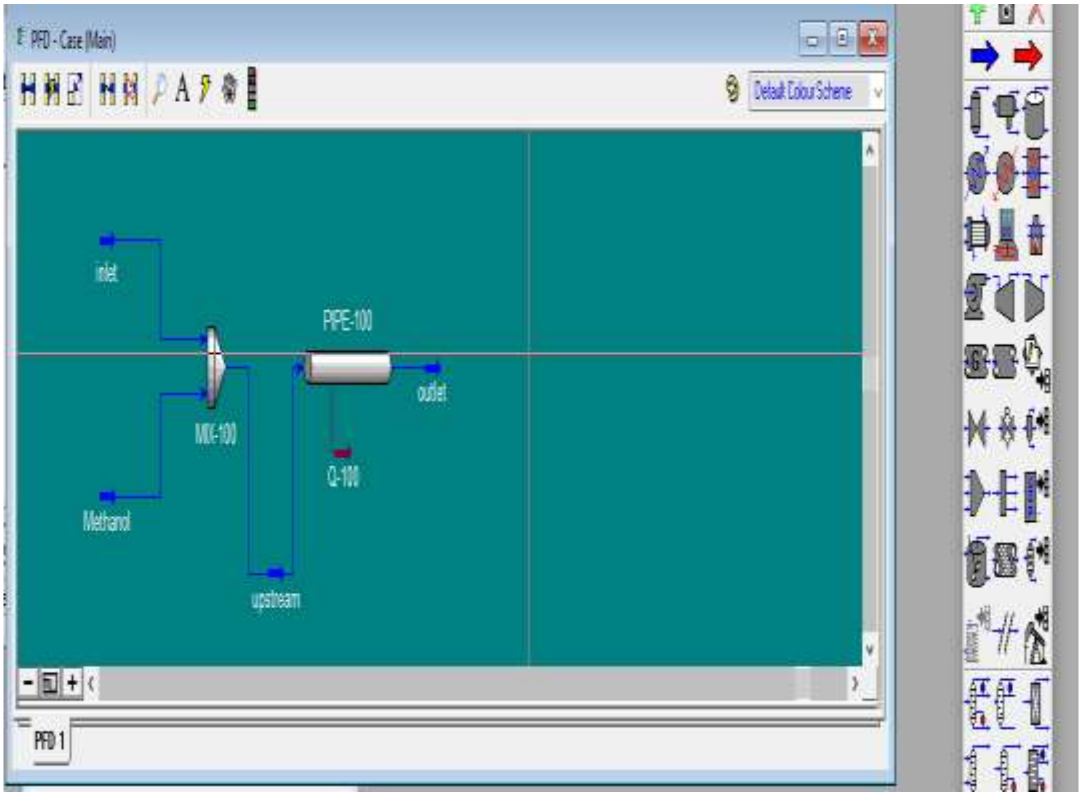


Fig 7: Process Flow Diagram on Simulation Environment

Data Analysis Method

After simulation prediction have been done, comparative graphs of hydrate formation curve for the different composition of methanol 0, 30 and 70% were plotted on a single graph to ascertain the effect of methanol composition on the hydrate formation curve.

RESULTS AND DISCUSSION

Data Presentation and Analyses

The data obtained from the temperature and pressure profiles were plotted to show the hydrate formation curve for different methanol composition as shown in Figure 8.

Table2: Temperature and Pressure Values for Hydrate Formation Plot

0% Methanol		30% Methanol		70% Methanol	
T_1 (C)	P_1 (bar)	T_2 (C)	P_2 (bar)	T_3 (C)	P_3 (bar)
-5	3	-30	3	-30	25.48
0	4	-25	4	-28	34.9
3	5	-20	5	-26.58	44.9

5	6	-15	6	-25.6	54.9
10	10	-10	10	-24.91	64.9
15	20	-5	20	-24.44	74.9
20	50	0	50	-24.12	84.9
25	100	3	100	-23.92	94.9
30	200	5	200	-23.78	104.9
				-23.67	114.9
				-23.56	124.9
				-23.45	134.9
				-23.33	144.9
				-23.19	154.9
				-23.05	164.9
				-22.9	174.9
				-22.75	184.9
				-22.59	194.9
				-22.51	200

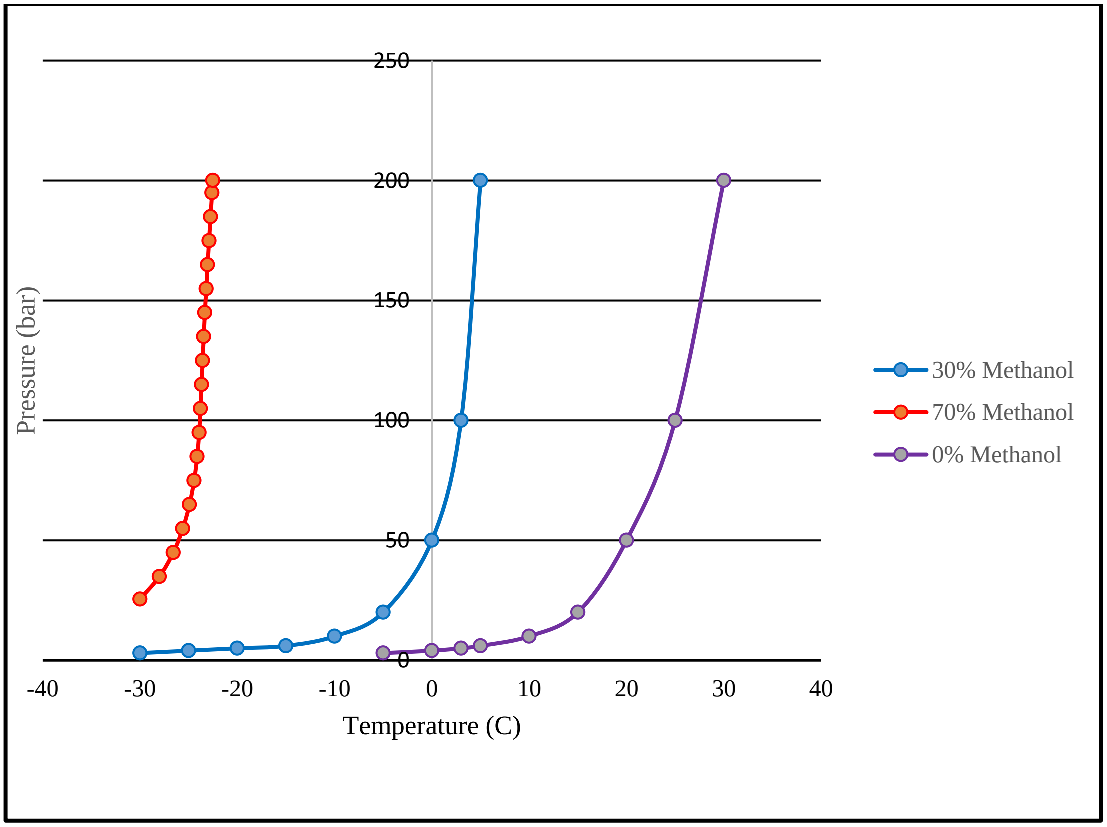


Fig 8: Hydrate Formation Curve for Different Methanol Composition

Table 3: Temperature and Pressure values for Phase Envelope Plot

T (C)	P (kpa)
77.2976	202.650
91.8818	429.010
106.8627	901.379
121.1200	1879.754
131.9616	3899.324
134.3821	5915.852
132.4658	8085.424
123.3482	11633.520
100.3562	16512.360
71.1749	20051.000
38.1643	21678.290
31.62093	21723.420
1.863895	20710.730
-41.9696	15309.350
-47.8293	14195.380
-52.8456	13162.470
-59.1750	11752.300
-66.7066	9915.180
-72.5605	8365.250
-77.2077	7057.604
-80.9505	5954.365
-85.3059	4614.267
-88.5533	3575.773
-91.0012	2771.005
-92.4416	2288.694
-92.6805	2208.086
-92.8538	2149.498
-92.8963	2135.096
-92.9016	2133.302
-92.9030	2132.854
-92.9036	2132.630

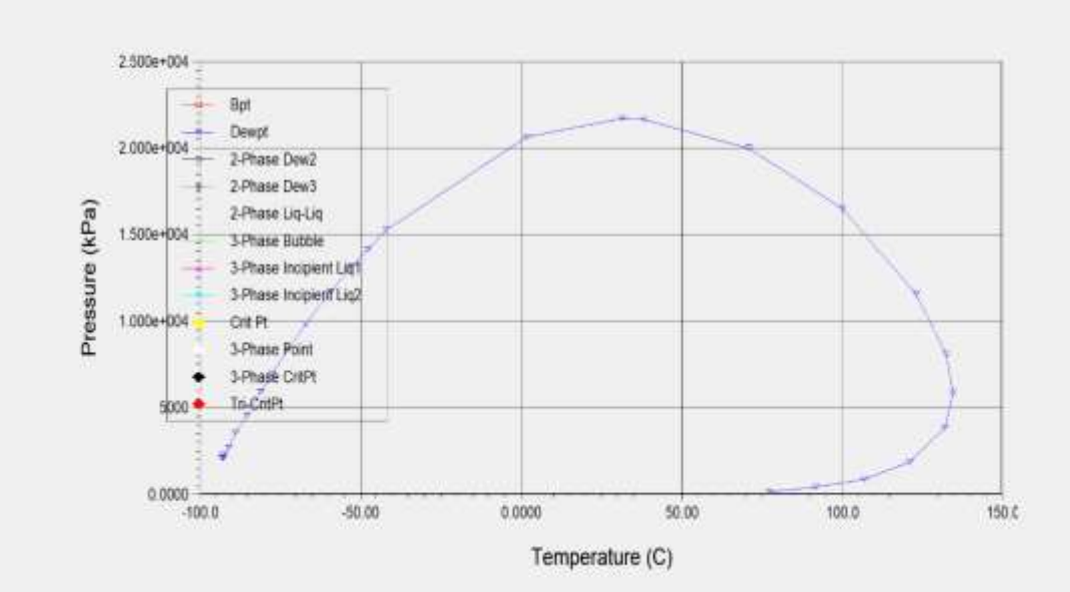


Fig 9: Phase Envelope Plot

Results from the hydrate equilibrium curve of Figure 8 compares different composition of methanol injected and it can be seen that increase in methanol composition shifts the hydrate equilibrium curve to the left hence reducing the area of hydrate formation corresponding to the temperature - pressure profile of the pipe. This clearly agrees with existing literature that injection of methanol prevents hydrate formation by acting as a thermodynamic inhibitor.

The phase envelope plot as shown in Figure 9 shows conditions at which thermodynamically distinct phases occur and coexist at equilibrium. This shows that the area above the curve comprises of gases while the area enclosed is the two phase (liquid – gases) region and the boundary is the dew point branch.

CONCLUSION

In this work the Process Simulation and Modeling software, UNISIM was used for the simulation of hydrate formation and prevention in subsea wells. To prevent the deposition of natural gas hydrate in subsea oil and gas wells, the hydrate formation area in wellbore must be predicted. The simulation results established methanol as a thermodynamic inhibitor and in line with literature as the 0%, 30% and 70% methanol injection composition respectively causes shifting to the left of the hydrate equilibrium curve reducing the hydrate formation area thus preventing its formation.

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