Mathematical Model of Energy Storage in Gas Hydrate and its Flow in Pipeline Systems*

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Abstract

Natural gas, one of the major sources of energy for the 21st Century, provides more than one-fifth of the worldwide energy needs. Storing this energy in gas hydrate form presents an alternative to its storage, and a smart solution to its flow it with the rest of the fluid without creating difficulty in gas pipeline systems due to pressure build-up. This study was design to achieve this situation in a controlled manner using a simple mathematical model, by applying mass and momentum conservation principles in canonical form to non-isothermal multiphase flow, for predicting the onset conditions of hydrate formation and storage capacity growth of the gas hydrate in pipeline systems. Results from this developed model show that the increase in hydrate growth, the more the hydrate storage capacity of gas within and along the gas pipeline. The developed model is therefore recommended for management of hydrate formation for natural gas storage and transportation in gas pipeline systems.

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Table of Contents

Introduction

- The growth in Global Energy Demand **led** oil and gas companies to seek for hydrocarbon in a more challenging environment of deep off-shore subsea.

- Of these hydrocarbon resources, Natural Gas is likely to dominate and remain as the foremost Source of Energy for the 21st Century due to its:

  – Relative abundance
  – Clean burning attributes and
  – Wide geographical distribution

- This energy resource for the future could also be found in enormous quantities in permafrost and offshore region of the world in Hydrate form.

Introduction

- Gas hydrates are ice-like crystalline inclusion compounds composed of hydrogen-bond water molecules structures that form cavities with specific geometry and size (Fig. 1), inside which gas molecules are enclathrated (Sarshar et al., 2010)

- Conditions favouring hydrate formation are:
  - Right combination of Pressure and Temperature
  - Presence of hydrate former (e.g. C_nH_{2n+2}, n = 1-5)
  - Sufficient amount of water
- Three known existing structures: S-I, S-II and S-H

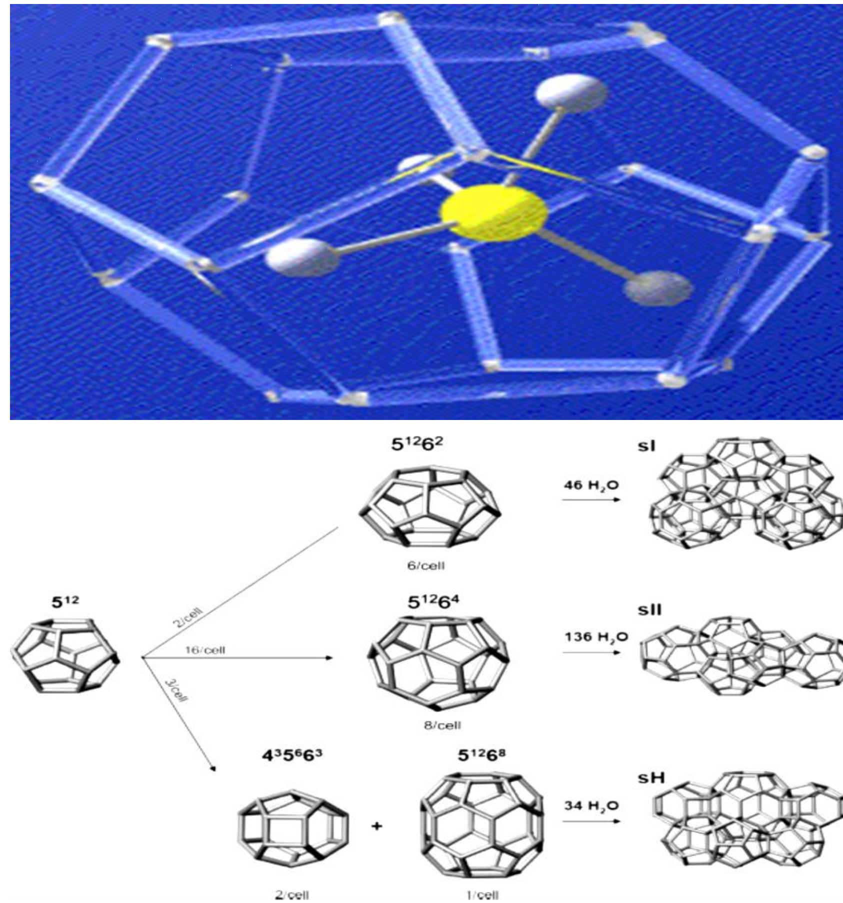


Figure 1: Gas Hydrate Structure

Source: www.pet.hw.ac.uk/hydrate/hydrates _what_ html

Mechanisms of Gas Storage in Hydrate

- Water molecule consists of a single atom of Oxygen (-ve) bonded to two (+ve) Hydrogen atoms.
- As a result of induced electrostatic charges on the molecules, the water molecules will align forming hexagonal pattern – *The hexagonal crystal structure of the host molecules (H_2O)* in hydrate.
- This alignment (of H and O_2 atom) is called hydrogen bond.
- The presence of hydrate formers stabilizes the aligned molecules – by Van der Waal forces.
- No bonding exists between guest and host molecules, hence guest molecules rotates freely inside the cage built by the host molecules.

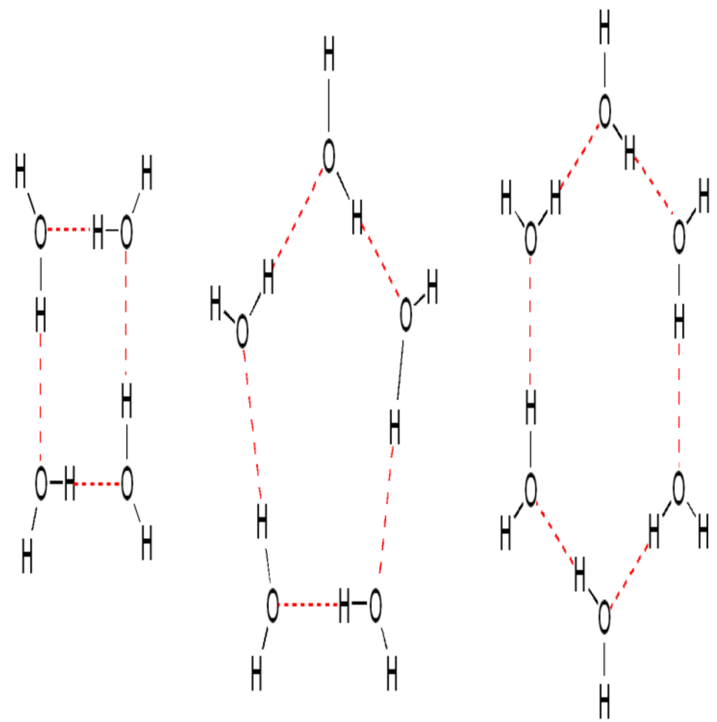
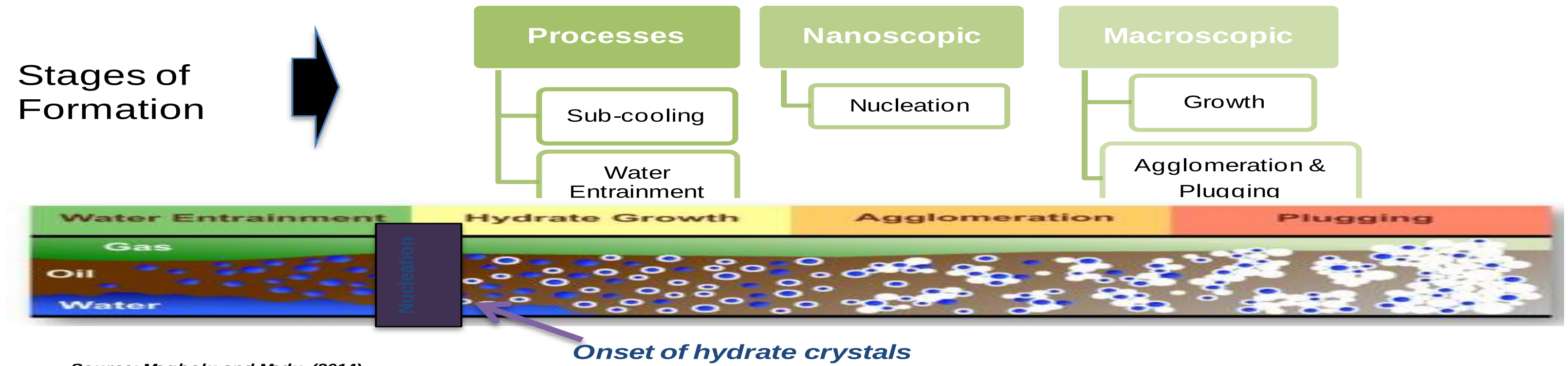


Figure 2: Hydrate cage faces

Source: Steed and Atwood, 2009

Flow of Hydrate in Pipeline



Source: Mogbolu and Madu (2014)

- For Natural Gas to dominate and remain as the foremost source of energy for the 21st Century, it must not only be produced but also be transported.
- Pipeline remain the cheapest, most efficient and safest means of transporting this valuable energy resource to the market.
- Water is often associated with produced natural gas.
- H_2O -Gas interphase is a good nucleation site where gas- H_2O clusters and grow to a critical size (growth stage), as more gas is supplied to the liquid phase.
- The crystals in the growth stage agglomerate into larger hydrate masses which in the long run may form a plug.

Objectives

- This study was designed by developing a Mathematical model applying mass and momentum conservation principles to multiphase flow in pipeline system.
  - Predict hydrate formation onset pressures.
  - Monitor and control hydrate growth (gas storage capacity) in gas pipeline system for different gas composition.

Methodology

- The governing equations employed are the conservation equations of mass and momentum.

- Conservation of Mass Equation

$$\frac{\partial}{\partial t}(\rho_k \alpha_k) + \frac{\partial}{\partial x}(\rho_k \alpha_k u_k) = 0 \qquad (1)$$

- Conservation of Momentum Equation

$$\frac{\partial}{\partial t}(\alpha_k \rho_k u_k) + \frac{\partial}{\partial x}(\alpha_k \rho_k u_k^2 + \alpha_k p) = \Gamma_k \qquad (2)$$

Characteristic Method – Technique for solving PDEs

- Writing the system of governing equations in composite form

$$\frac{\partial \hat{U}}{\partial t} + \frac{\partial F}{\partial x} + D = 0 \quad (3)$$

- In Primitive form

$$\Re \frac{\partial U}{\partial t} + \Re \breve{A} \frac{\partial U}{\partial x} + \Re \breve{C} = 0 \quad (4)$$

- Applying the mathematics of Eigenvalue and Eigenvector

$$\left| \breve{A} - \lambda I \right| = 0 \quad (5)$$

- Characteristic Equation

$$\lambda^4 + \lambda^3 X + \lambda^2 Y + \lambda Z + \Omega = 0 \quad (6)$$

- The characteristic zeros are:

$$\lambda_i^T = \left(u_1 - c_1, u_1 + c_1, u_2 - c_2, u_2 + c_2 \right) \quad (7)$$

- Characteristic Velocity:

$$\begin{aligned} \lambda_1 &= u_1 - c_1 \\ \lambda_2 &= u_1 + c_1 \\ \lambda_3 &= u_2 - c_2 \\ \lambda_4 &= u_2 + c_2 \end{aligned} \quad (8)$$

Presenter's notes: Method of Characteristic (MC)

1. PDEs are the basis for nearly all technical processes in fluid mechanics.
2. MC is a technique for solving PDEs
3. Valid for any hyperbolic PDE
4. The method aim is to reduce a PDE to ODE along which the solution can be Integrated.

Resulting into the General Equation for the system

$$\frac{dP}{\partial t}+\left(-\frac{2\alpha_2\rho_2c_2^2u_1}{P}-\frac{2\alpha_2\rho_2c_2^2c_1}{P}+\frac{2\alpha_1\rho_1c_1^2u_1}{P}-\frac{2\alpha_1\rho_1c_1^3}{P}\right)\frac{dP}{dx}$$
$$+\left(\frac{2\alpha_2\rho_2c_2^2u_1}{c_1}-2\alpha_2\rho_2c_2^2-2\alpha_1\rho_1c_1u_1+2\alpha_1\rho_1c_1^2\right)\frac{du_1}{dx}$$
$$+\left(-\frac{2\alpha_2\rho_2c_2^2u_1}{\alpha_1}+\frac{2\alpha_2\rho_2c_2^2c_1}{\alpha_1}+2\rho_1c_1^2u_1-2\rho_1c_1^3\right)\frac{d\alpha_1}{dx} \qquad (9)$$
$$+\left(\frac{\alpha_2\rho_2c_2^2}{c_1}-\alpha_1\rho_1c_1\right)\frac{du_1}{dt}-\frac{\rho_2c_2^2}{\alpha_1}\frac{d\alpha_1}{dt}=0$$

Presenter's notes: Significance of Characteristic Velocities

U_j – Local fluid Vel. C_j – Sonic Vel.

1. Sonic velocity generates **Shock waves** (i.e. pressure propagating waves)
2. These waves arises at the point of disturbances (caused by solid precipitation) along the flow path.
3. They are characterized by abrupt change in P, T and ρ
4. At that point(s) pressure progressively builds up.

Result

- The Pressure vs Time Equation

$$\Phi_{122} P_{out}^{2} + \Phi_{11} P_{out} + \Phi = 0 \qquad (10)$$

- Hydrate Volume Fraction

$$\Phi_{31} \alpha^{2} + \Phi_{32} \alpha - \Phi_{23} L = 0 \qquad (11)$$

- Pressure vs Pipe length

$$\ln\left(\frac{P_{out}^{2}}{P_{in}^{2}}\right) + \frac{\Phi_{12}}{\Phi_{141}}\left(P_{out} - P_{in}\right) - \frac{\Phi_{211}}{\Phi_{141}} L = 0 \qquad (12)$$

Table 1: Gas Compositional and Physical Data

Component	Mole Fraction				
	Gas A	Gas B	Gas C	Gas D	Gas E
CO_2	0.01349	0.01320	0.02094	0.00350	0.03110
N_2	0.01029	0.01380	0.01040	0.02490	0.00640
C1	0.91139	0.90000	0.89358	0.86560	0.73030
C2	0.05931	0.06700	0.06873	0.06780	0.08040
C3	0.00467	0.00510	0.00543	0.01530	0.04280
i-C4	0.00040	0.00040	0.00039	0.00510	0.00730
n-C4	0.00045	0.00050	0.00046	0.00610	0.01500
i-C5	0.00000	0.00000	0.00006	0.00370	0.00540
n-C5	0.00000	0.00000	0.00001	0.00370	0.00600
C6	0.00000	0.00000	0.00000	0.00430	0.07530

Parameter	Gas A	Gas B	Gas C	Gas D	Gas E
Gravity	0.61	0.61	0.62	0.62	0.63
M_a	17.54	17.69	17.91	17.94	25.42
P_{in} (psia)	3000	3000	3000	3000	3000
P_c (psia)	672	671	673	658	657
T_c (˚R)	359	360	362	377	435
L (miles)	900	900	900	900	900
D (mm)	304.8	304.8	304.8	304.8	304.8
θ	0˚	0˚	0˚	0˚	0˚
ε	0.0006	0.0006	0.0006	0.0006	0.0006

Pressure Buildup (MPa)	Onset Pressure (kPa)	Time (hr)	Pipeline Size (mm)	Gas Storage Capacity as a function of Hydrate Growth (Å)				
				C1 (91%)	C1 (90%)	C1 (89%)	C1 (86%)	C1 (73%)
0.0-1.4	6.48	0.08	304.8	1.531	1.474	1.474	1.468	1.460
0.0-3.3	144.26	7.48	254.0	1.555	1.503	1.502	1.497	1.489
0.0-9.0	487.70	11.22	203.2	1.615	1.561	1.561	1.556	1.548
0.0-33.0			152.4	1.709	1.650	1.650	1.644	1.635

Table 2: Pressure Buildup due to Hydrate Growth

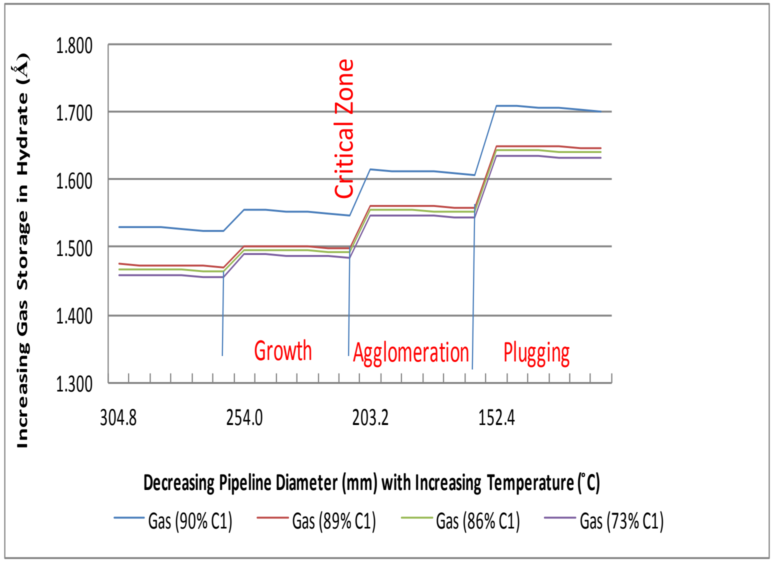


Chart 1: Gas hydrates storage capacity growth along pipeline

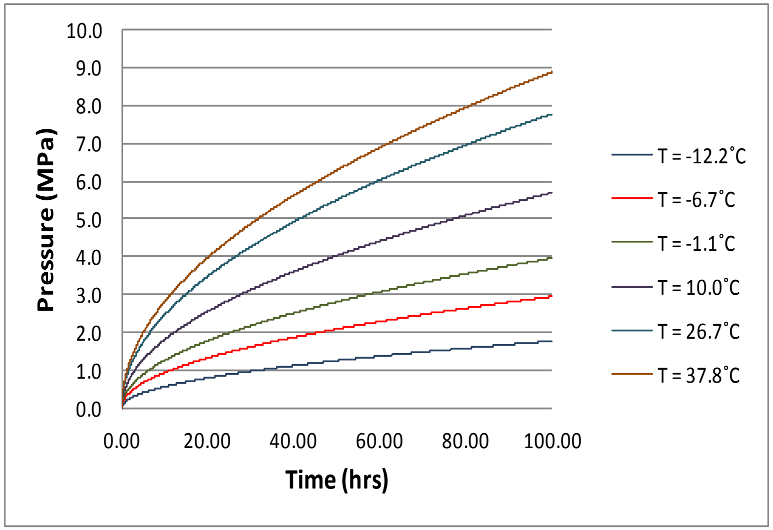


Chart 2: Pressure Build-up on Hydrate formation over time across temperature range -12.2 to 37.8 °C

Discussion

- One of the objective of this study is to predict onset pressures of hydrate formation along the pipeline:
- The process begins early as soon as gas is entrained in guest molecule. This provides early warning for detecting **minute hydrate particles**.
- As production continues and fluid flow along the pipeline, the hydrate precipitates growth enters the second stage "growth" - **Large number of hydrate crystal appearance occur with increase gas storage capacity**.
- Noteworthy in this study was the prediction of the Critical Zone - transitory zone between the "growth" and "agglomeration" stages.
- Below this critical zone the individual hydrate particles with stored gas can remain entrained to flow along with the fluid never (allowed) reaching the point of agglomeration.
- Conversely, when the critical zone is exceeded, the agglomeration stage sets in leading to the formation of larger hydrate masses which ultimately leads to complete plugging with its resultant negative effects.

Conclusion

- Simple but accurate time-dependent mathematical models were developed.
- Predict hydrate Storage Capacity – a function of Hydrate Growth
- Pressure predictive tool in giving early warning signal in detecting the onsets of minute hydrate particles appearance, large number of hydrate crystal appearance and point at which massive hydrate clustering sets in
- Detect a **critical zone** marked by critical maximum onset pressure (Optimum Operating Condition)

Recommendation

- The developed models are recommended for easier and faster monitoring and management of hydrate formation for natural gas storage and transportation in natural gas pipeline systems.

  (Because pipeline transportation could face difficult problems of solid deposition & blockages and causing serious economic implications – loss of production, pipeline rupture and loss of lives)

- To reduce Gas Flaring by storing the gas in hydrate form.

  (1 cuft of hydrate contains up to 182scf of gas, while, 1 cuft of dry natural gas @ 900psi and 60^{o}F will give off 66 scf of gas when depressurized. (Ellison et al., 2000))