Prediction of Methane, Water and Ice Properties for Numerical Gas Hydrate Simulations

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Abstract

Gas hydrates are considered as near-future potential energy resources. Due to the lack of gas production data from gas hydrate reservoirs, numerical simulations are very important to make production predictions for both experimental studies and field production trials. Methane and water flow together when gas hydrates dissociate inside the sediments. Hence, many parameters of methane and water such as density, viscosity, enthalpy, internal energy and thermal conductivity should be calculated at different pressure and temperature values during non-isothermal numerical gas production simulations from gas hydrate reservoirs. As a solid phase, ice might exist in the pores due to the endothermic dissociation of gas hydrates. For this reason, water, methane, ice properties as a function of temperature and pressure are estimated by the Matlab codes written in this study: waterprop.m, gasprop.m, and iceprop.m. Density, viscosity, enthalpy, internal energy and thermal conductivity of water and methane calculated with the Matlab codes in this study, National Institute of Standards and Technology were compared, and the reliability of waterprop.m, gasprop.m and iceprop.m was proved.

Keywords: Gas hydrates, methane hydrate, methane, water, ice, numerical simulation, equations of states.

1. Introduction

Unconventional gas reserves such as shale gas, coalbed methane and gas hydrates have become very important with the decline of conventional gas reserves. Among these reservoirs, the amount of gas in gas hydrate reservoirs is the highest. Since 1970s, many gas hydrate reserve calculations have been made for gas hydrates in marine and permafrost environments by using gas hydrate stability zone thickness, pressure gradient, temperature gradient, salinity, porosity, hydrate saturation, etc. It is considered that even with the conservative estimates, gas hydrate reserves are at least 2 times greater than all conventional gas reservoirs [1].

Figure 1 shows the gas hydrate distribution in the world both in permafrost environment and marine environment. Approximately 99 % of gas hydrates are found in marine sediments and other 1 % of gas hydrates is found in permafrost region. In the last decades, many gas hydrate experimental, numerical, exploration studies and field production trials were conducted [1].
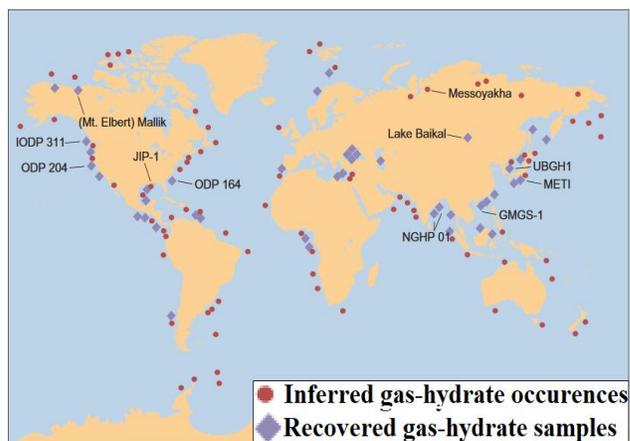
Figure 1. Distribution of gas hydrates in the world [2].

Gas hydrates are ice-like structures that form at low temperature and high pressure conditions. At these conditions, water and gas molecules form gas hydrates with the effect of hydrogen bonds between water molecules and van der Waals forces between gas molecules and water molecules. Thus, gas molecules are trapped inside the cages formed by water molecules [2].

Methane (CH_4), ethane (C_2H_6), propane (C_3H_8), i-butane (i-C_4H_{10}), carbon dioxide (CO_2), hydrogen sulfide (H_2S) and other molecules form gas hydrates when these molecules interact with water molecules at high pressures and low temperatures. In nature, although there are mixed gas hydrates formed from gas mixtures including CH_4, C_2H_6, C_3H_8, etc., it is considered that nearly 99 % of gas hydrates include approximately 100 % of CH_4 (biogenic gas) [1]. Figure 2 shows CH_4 hydrate equilibrium curve calculated by HEP.m software, predicting gas hydrate properties written by Merey and Sinayuc [3]. Generally, the temperature of CH_4 hydrate reservoirs in marine sediments is less than 30ºC [1].
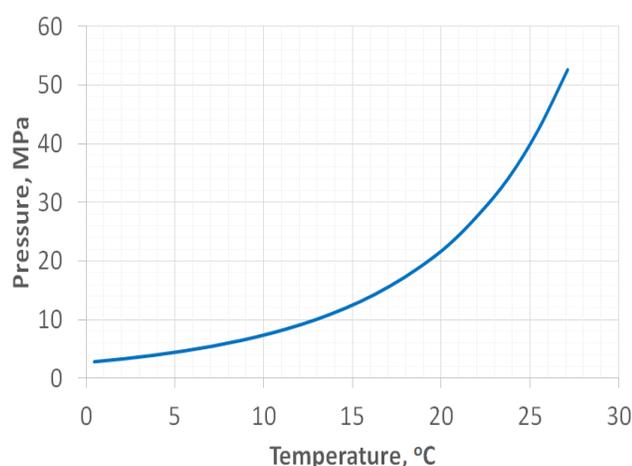
Figure 2. CH_4 hydrate equilibrium curve calculated by HEP software [3].

Recently, a few gas production test trials were conducted in Nankai Through Field, Japan (marine sediments), Mallik Field, Canada (permafrost), and Ignik Sikumi Field, Alaska (permafrost). The first depressurization production method in marine sediments was conducted in Nankai Trough, 2013 and 120,000 m^3 CH_4 was produced in 6 days from gas hydrate sections in this field. Depressurization method is basically to decrease reservoir pressure below gas hydrate equilibrium pressure and after gas hydrate dissociation, free gas and free water are produced via wellbore. In Mallik Field, depressurization method, thermal injection method and combination of these methods were applied [1]. Basically, the aim of thermal injection is to increase temperature by an injection of hot water, steam or microwave heating and destabilize gas hydrates in sediments [2]. As shown in Figure 2, if temperature and pressure of a gas (CH_4) hydrate reservoir are above CH_4 hydrate equilibrium curve, gas hydrates are stable. However, if the chemicals such as methanol, ethylene glycol, etc. are injected into gas hydrate reservoirs, CH_4 hydrate equilibrium curve is shifted to left and gas hydrates dissociate. This method is called chemical injection

method. Different from these three production methods, CH_4-CO_2 swapping method was suggested. Below 10.3ºC, pure CO_2 hydrate is much more stable compared to pure CH_4 hydrate. Hence, when CO_2 is injected into CH_4 hydrate reservoirs, CH_4 and CO_2 gas molecules swap and CO_2 is stored in hydrate cages while some CH_4 molecules are pushed outside and then they are produced. For better CH_4 recovery, 77 % N_2/ 23 % CO_2 gas mixture was injected into CH_4 hydrate reservoir at 5.6ºC in Ignik Sikumi Field, Alaska (permafrost) and CH_4-CO_2/N_2 swapping was observed for the first time in this field trial in 2012 [1].

Currently, all available gas hydrate production methods have some advantages and handicaps. For instance, depressurization is considered as the most promising production method because no extra heat inserted since its handicaps are high water production rate, low gas production rate and geomechanical stability problems. Thermal injection is an effective way to dissociate gas hydrates but heat loss, feasibility problems, injection problems and geomechanical stability problems of sediments are the main handicaps of this method. Chemical injection method is not preferred commonly since it is harmful for the environment and expensive. Although CH_4-CO_2 swapping is advantageous for both CO_2 sequestration and geomechanical stability of sediments, this method has injection problems, low replacement rate and risk of pure CO_2 hydrate formation [2].

Numerical simulation of gas production from gas hydrates is quite important as in conventional oil and gas reservoirs. One of the handicaps of gas hydrate numerical studies is that there is almost no long term field gas production data from gas hydrate reservoirs and it is difficult to test the success of numerical codes. With gas hydrate experimental data and field-trial project data such as Mallik Field, these gas hydrate numerical codes were improved and tested. Table 1 shows the numerical simulators for gas hydrate production by depressurization, thermal injection and chemical injection. Some of these simulators have ability to model CH_4-CO_2/N_2 swapping such as Mix3HydrateResSim, STOMP-HYD-KE, and CMG-Stars [4].

The numerical simulators in Table 1 can model the non-isothermal gas release, phase behavior and flow of fluids and heat under conditions typical of common natural CH_4 hydrate deposits in complex geological media at any scale at which Darcy's law is valid by solving the coupled equations of mass and heat balance [5].

Table 1. Reservoir Simulation codes used for hydrate reservoirs [4].

Name	Owner	Capabilities	Source Availability
HydrateRes Sim	Lawrence Berkeley, National Laboratory, National Energy Technology Laboratory	Kinetics and Equilibrium Model (CH_4 hydrate)	Free Open Source Code
CMG Starts	Computer Modelling Group Ltd.	Kinetics and Equilibrium Model (CH_4/CO_2 hydrates)	Commercial Code
MH-21 HYDRES	National Institute of advanced Industrial Sciences and Technology, Japan	Kinetics and Equilibrium Model (CH_4 hydrate)	Only MH-21 consortium
TOUGH+HY DRATE	Lawrence Berkeley National Laboratory	Equilibrium and Kinetics Model (CH_4 hydrate)	Free for U.S. Government, Collaborator and Available for purchase
Code from University of Houston	University of Houston	Kinetic Model (CH_4 hydrate)	Not Available
HYRES	German Sugar, Umsicht	Kinetic Model (CH_4 hydrate)	Not Available
STOMP-HYD-KE	Pacific Northwest National Laboratory	Kinetics and Equilibrium Model (CH_4-CO_2 mixed hydrate)	Free for U.S. Government, Collaborator and Available for purchase
Mix3Hydrate ResSim	National Energy Technology Laboratories (NETL)	Kinetics and Equilibrium Model (CH_4-CO_2-N_2 mixed hydrate)	Not Available

During the simulation of gas and water flow after gas hydrate dissociation, many parameters such as viscosity, density, thermal conductivity, enthalpy, etc. of water, gas and ice should be calculated at different temperatures and pressures. This is because the pressure of gas hydrate reservoir changes with production and also the reservoir temperature changes with the endothermic dissociation of gas hydrates [5]. Even if reservoir temperature is above freezing point of water, during production with depressurization method, reservoir temperature might decrease below freezing point of water with the endothermic dissociation of gas hydrates and ice might form in the pores. For this case, the prediction of ice properties become important.

Formation of ice might increase gas production rate with the latent heat released with ice formation or ice might decrease effective permeability and gas production rate. Hence, the prediction of ice properties is crucial as the prediction of water and CH_4 properties. Mostly, the numerical simulators of gas hydrates include four components (hydrate, methane, water, and inhibitor) and four phases (hydrate, gas, aqueous, ice) [5]. Hence, I proposed HEP.m Matlab code predicting gas hydrate properties at different pressures and temperatures and I proved the success of HEP.m code with the article of Merey and Sinayuc [3]. In order to develop numerical gas hydrate simulator for depressurization, thermal and chemical injection, as well as hydrate properties, the properties of water, CH_4 and ice at different temperatures and pressures should be calculated. For this reason, in this study, several Matlab codes were written for predicting water, ice and CH_4 properties and these codes were integrated with HEP.m [3]. The reliability of these codes were proven in this study.

2. Materials and Methods
2.1 Numerical Simulation of Gas Hydrate Reservoirs
In order to simulate gas and water production from gas hydrate reservoirs, mass balance equations and Darcy flux equations should be constructed but if the simulation occurs in non-isothermal environment, additionally, heat balance equations should be written for each phases. Dissociation of gas hydrate is endothermic so it should include all mass equations, Darcy flux equations, heat balance equations for each component. The equations used in the hydrate simulators in Table 1 are mostly similar. In order to show the importance of CH_4, water and ice properties for these equations, the following formulas used in HydrateResSim simulator from Equation (2.1) to (2.10) are listed [5]:

The continuity equation for component CH_4 (m) can be written as [5]

$$\frac{\partial(\varphi S_A \rho_A X_A^m)}{\partial t} + \frac{\partial(\varphi S_G \rho_G X_G^m)}{\partial t} + \nabla(X_A^m \vec{F_A}) + \nabla(X_G^m \vec{F_G}) + \nabla(\vec{J_G^m}) = X_A^m q_A + X_G^m q_G + \dot{n} M_{weight}^m \quad \textbf{(2.1)}$$

The continuity equation for component water (w) can be written as [5]:

$$\frac{\partial(\varphi S_A \rho_A X_A^w)}{\partial t} + \frac{\partial(\varphi S_G \rho_G X_G^w)}{\partial t} + \nabla(X_A^w \vec{F_A}) + \nabla(X_G^w \vec{F_G}) + \nabla(\vec{J_G^w}) = X_A^w q_A + X_G^w q_G + \dot{n} M_{weight}^w \quad \textbf{(2.2)}$$

The continuity equation for component hydrate (h) can be written as [5]

$$\frac{\partial(\varphi S_H \rho_H)}{\partial t} = -\dot{n} M_{weight}^h \quad \textbf{(2.3)}$$

The energy balance equation can be written based on the summation of the enthalpy over all phases as [5]:

$$\frac{\partial((1-\varphi)\rho_R H_R)}{\partial t} + \frac{\partial(\varphi S_A \rho_A H_A)}{\partial t} + \frac{\partial(\varphi S_G \rho_G H_G)}{\partial t} + \frac{\partial(\varphi S_H \rho_H H_H)}{\partial t} +$$
$$\frac{\partial(\varphi S_I \rho_I H_I)}{\partial t} - \nabla(K_{ave}\nabla T) + \nabla(f_\sigma \sigma_o \nabla T^4) + \nabla(H_A \overrightarrow{F_A}) +$$
$$\nabla(H_G \overrightarrow{F_G}) = H_A q_A + H_G q_G + \dot{n}\Delta H_H^o \qquad \textbf{(2.4)}$$

For fluid flow in porous media, the aqueous and gas velocities are assumed to obey the multiphase Darcy's law in Equations (2.1), (2.2), (2.4) [5]:

$$\overrightarrow{F_A} = -K_{abs}\frac{K_{rA}\rho_A}{\mu_A}(\nabla P_A - \rho_A \overrightarrow{g}) \qquad \textbf{(2.5)}$$

$$\overrightarrow{F_G} = -K_{abs}\left(1 + \frac{b}{P_G}\right)\frac{K_{rG}\rho_G}{\mu_G}X_G^\kappa(\nabla P_G - \rho_G g) \qquad \textbf{(2.6)}$$

In Equation (2.4), the enthalpies [5]:

$$H_A = X_A^w H_A^w + X_A^m(H_A^m + H_{sol}^m) \qquad \textbf{(2.7)}$$
$$H_G = X_G^w H_G^w + X_G^m H_G^m + H_{departure} \qquad \textbf{(2.8)}$$
$$H_H = X_H^w H_H^w + X_H^m H_H^m + \Delta H_H^0 \qquad \textbf{(2.9)}$$
$$H_I = H_I^w + \Delta H_I^0 \qquad \textbf{(2.10)}$$

Where A: aqueous phase; G: gas phase; I: ice phase; H: hydrate; φ: porosity; ρ_R: rock density [kg m^{-3}]; ρ_β: density of phase β (A, G, H, I) [kg m^{-3}]; S_β: saturation of phase β (A, G, H, I); X_β^κ: mass fraction of component κ: w (water),m (methane),c (hydrate) in phase β (A, G, H ,I) [kg/kg]; $\overrightarrow{J_G^\kappa}$ the diffusive mass flux of component κ in the gas phase [kg m^{-2} s^{-1}]; M_{weight}^m : molecular weight of CH$_4$; M_{weight}^h : molecular weight of CH$_4$ hydrate; F^κ : Darcy flux vector of component [kg m^{-2}s^{-1}]; J_β^κ:diffusion of component κ in phase β: G; q$^\kappa$: source/sink term of component κ: w (water),m (methane),c (hydrate) [kg m^{-3} s^{-1}]; t: time, second; K_{abs}: rock instrinsic permeability [m^2]; K_{rA}: relative permeability of the aqueous phase; μ_A: viscosity of the aqueous phase [Pa s]; P$_\beta$: Pressure of β phase: A, G, [Pa]; g: gravitational accaleration vector [m s^{-2}]; b: Klinkenberg b-factor; K_{rG}: relative permeability of the gaseous phase, μ_G: viscosity of the gaseous phase [Pa s]; K_R: thermal conductivity of the rock [W m^{-1} K^{-1}]; K_β: thermal conductivity of phase β: A, G, H, I [W m^{-1} K^{-1}]; H$_\beta$: specific enthalpy of phase β: A, G, H, I [J kg^{-1}]; fσ: radiance emittance factor; σ_o: Stefan-Boltmann Constant [5.6687x10-8 J m^{-2} K^{-4}]; U$_\beta$: specific internal energy of phase β [J/kg]; ΔH_H^0: latent heat of hydrate formation or dissociation (J kg-1); ΔH_I^0: latent heat of ice formation or dissociation (J kg^{-1}).

During the numerical simulation, the mass balance, flow equations and heat balance equations are solved in a non-isothermal system because with hydrate formation or dissociation, the temperature of the system is not constant. Moreover, phases (hydrate, gas, aqueous, ice) change with hydrate formation or dissociation. This phase changes are tracked by using the primary switching method and with the changes of phases, the primary variables in the mass and heat equations also change. Primary variables for kinetic model are shown in Table 2. Finite difference method is used to solve differential equations implicitly. For every grids, the equations from Equation (2.1) to Equation (2.10) are solved for kinetic model [5].

Almost all of the numerical simulators in Table 1 are not free and some of them are private and only used in their research group. Therefore, it is important to write the codes of your own and make it freely available with the tutorials in details. For this purpose, initially, HEP software was written with Matlab to predict gas hydrate properties [3]. As seen from Equation (2.1) to (2.10), many properties of water, ice and CH$_4$ such as mainly density, their dissolutions in different phases, viscosity, thermal conductivity, enthalpy and internal energy are essential in order to run gas production simulations for gas hydrate reservoirs. Only CH$_4$ is selected as guest molecules in gas hydrates because in nature, biogenic CH$_4$ hydrate is common [1-3]. For this reason, waterprop.m, iceprop.m and gasprop.m codes were written with Matlab to predict these parameters.

Table 2. Primary Variables in Kinetic Hydrate Simulations without Inhibitor [5]*.

| Phase	State Identifier	Primary Variable 1	Primary Variable 2	Primary Variable 3	Primary Variable 4
1-Phase: Aqu	**Aqu**	P	X_m_A	S_hyd	T
2-Phase: AqG	**AqG**	P_gas	S_aqu	S_hyd	T
2-Phase: AqH	**AqH**	P	S_aqu	X_m_A	T
3-Phase: AGH	**AGH**	P_gas	S_aqu	S_gas	T
3-Phase: AIG	**AIG**	P_gas	S_aqu	S_hyd	S_gas
Quadruple Point: QuP	**QuP**	P_gas	S_aqu	S_gas	S_ice

* Where the possible primary variables are: P, pressure [Pa]; P_gas, gas pressure [Pa]; T, temperature [C]; X_m_A, mass fraction of CH$_4$ dissolved in the aqueous phase; Y_m_G, mass fraction of CH$_4$ dissolved in the gas phase; S_aqu, liquid saturation; S_gas, gas saturation; S_hyd, hydrate saturation; X_i_A, mass fraction of inhibitor dissolved in the aqueous phase. If the system including an inhibitor, the variables are updated as: X_iA becomes the 4th primary variable, and the 4th primary variable (as listed in Table 2) becomes the 5th primary variable

Ş. Merey

3. Results and Discussion
3.1 Prediction of Water Properties
During gas hydrate production simulations, water properties at different pressure and temperature values are essential. Even though some of water properties such as density and viscosity were assumed constant in some of the gas hydrate simulation studies [4], water properties change with temperature and pressure. For accurate simulations, these changes should be in consideration. In order to account for the changes in water properties such as density of water or aqueous phase (if it includes dissolved gas), specific internal energy, specific isobaric heat capacity, specific enthalpy, thermal conductivity, thermal diffusivity, surface tension and vapor pressure at different temperature and pressure, waterprop.m code was written in Matlab. To analyze the reliability of this code, the calculated data with waterprop.m were compared with those data in National Institute of Standards and Technology (NIST) [6]. If CH_4 dissolved in water, it changes water properties such as density and viscosity. By entering dissolved gas composition and CH_4 gas density, the properties of aqueous phase are easily calculated with waterprop.m.

In a project of the DOE (Department of Energy, USA)/NETL (National Energy Technology Laboratory), the code comparison studies were conducted for seven case problems of gas hydrate simulations by five different reservoir simulators: CMG STARS, HydrateResSim, MH-21 HYDRES, STOMP-HYD, and TOUGH+HYDRATE. For instance, a 10 m hydrate zone (80 % gas hydrate saturation) in bounded vertically by two 25 m shale zones (the length and height of the domain is 1000 m x 60 m) were selected as a case study. Then, gas production for this case was simulated with different size of grids by depressurization method [4]. Figure 3 shows the cumulative gas and water production for the selected case problem.
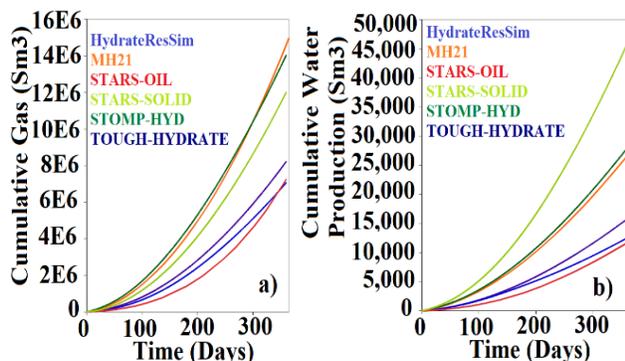
Figure 3. a) Cumulative Gas Production **b)** Cumulative Water Production [4].

As seen in Figure 3, the simulation results are quite different because every gas hydrate reservoir simulator has its own numerical method, assumptions, relative permeability formulas, gas properties, water properties and ice properties. Unfortunately, the tutorials of these simulators are not very informative. Hence, in this study and Merey and Sinayuc [3], it is aimed to describe all the methods used one by one and propose a new gas hydrate simulator to predict gas production by especially depressurization because it is the most commonly preferred gas production method [1]. Thus, the codes predicting water properties, CH_4 properties and ice properties are proposed in this study.

As shown in Equations (2.1) to (2.10), many properties of water should be calculated at different temperature and pressure values for each time step of numerical gas production simulation from gas hydrates. These water properties are:

- ➢ Density
- ➢ Viscosity
- ➢ Enthalpy
- ➢ Internal Energy
- ➢ Thermal Conductivity

Figure 4 shows the algorithm of waterprop.m code written in this study in Matlab [7-10] Mainly, in Equations (2.1), (2.2), (2.4) and (2.5), water density is essential at different temperatures and pressures. In order provide water density to these equations, the formulas of IAPWS-IF97 [7] were used and these formulas are valid when pressure is less than 100 MPa and temperature is between 273.15 K and 1073.15 K. Similarly, the formulas proposed in IAPWS-IF97 [7] were used to calculate internal energy and enthalpy. The temperature and pressure conditions of marine gas hydrate reservoirs are in the pressure-temperature ranges of the formulas of IAPWS-IF97 [1, 3].

Gas production from gas hydrates is non-isothermal so the prediction of energy parameters is quite important for accurate numerical studies as seen in Equation (2.4) and Equations (2.7) to (2.10). During gas production with gas hydrate dissociation, water and gas exist together and multiphase flow occurs. Especially for the calculation of flux parameters in Equations (2.5) and (2.6), viscosity should be estimated at different temperature and pressure values. By using the method of Sengers and Parsi [8], water viscosity is predicted at different pressures and temperatures. Thermal conductivities are also important as shown in Equation (2.4) and it is predicted in waterprop.m by using the method of IAPWS [9].
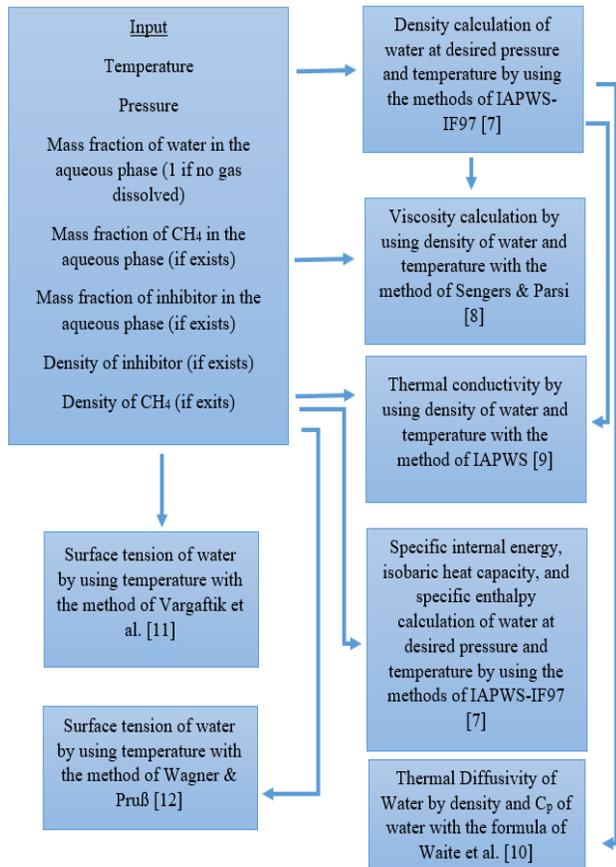
Figure 4. Algorithm of waterprop.m code.

The water properties calculated by waterprop.m and NIST [6] at 5ºC, 10ºC, 15ºC, 20ºC and 25ºC when pressure is between 0 and 24 MPa are shown in Figure 5. The reason of the selection of these temperature ranges (5 to 25ºC) and pressure ranges (0 to 24 MPa) is that the temperature and pressure of gas hydrates in nature are within these ranges [1, 3]. During gas production from gas hydrate reservoirs, both temperature and pressure vary. For example, while applying depressurization method, pressure and temperature decrease. The reason of temperature reduction is due to the endothermic dissociation of gas hydrates. For this reason, for numerical simulators, the prediction of gas and water properties at different pressure and temperature values is quite important. The range selected in this study is appropriate for marine gas hydrate reservoirs.

As seen in Figure 5, there are good agreements between density, viscosity enthalpy, internal energy and thermal conductivity of water calculated by NIST [6] and waterprop.m. Moreover, R^2 error analysis were done between these values estimated with NIST [6] and waterprop.m. Table 3 lists these R^2 values and it is obvious that the accuracies of the results are higher than 99 % (R^2).

Table 3. Error Analysis between NIST [6] and waterprop.m (Figure 5).

Condition	R^2 (%)				
	Density	Viscosity	Enthalpy	Internal Energy	Thermal Conductivity
At 25ºC	99.99	100	100	99.99	99.04
At 20ºC	100	100	100	100	99.07
At 15ºC	100	99.99	100	100	99.41
At 10ºC	99.99	100	100	100	99.28
At 5ºC	99.99	100	100	100	99.36
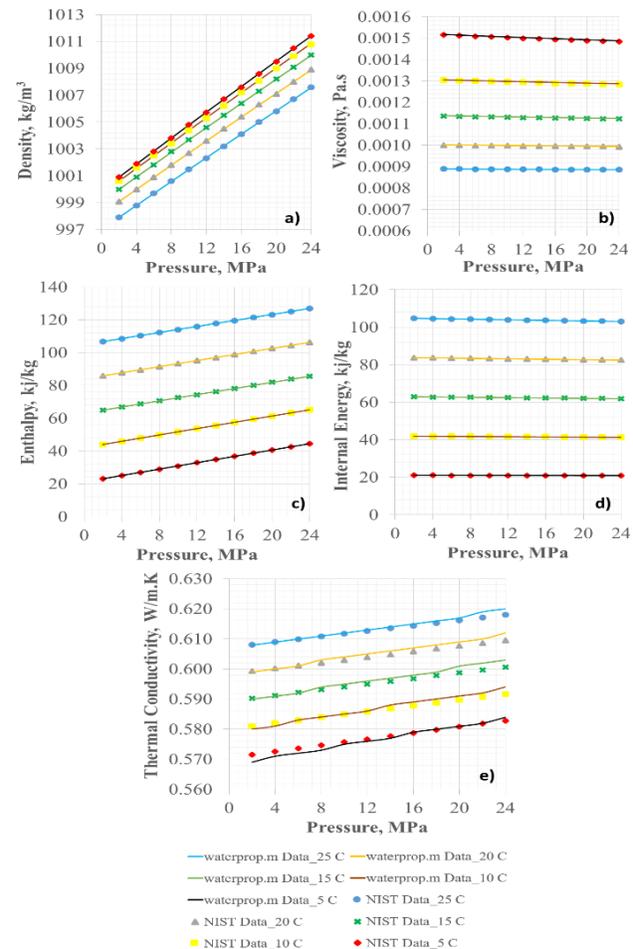
Figure 5. Variations of (**a**) density (**b**) viscosity **c**) enthalpy **d**) internal energy (**e**) thermal conductivity of water with increasing pressure and temperature.

For this reason, waterprop.m has ability to estimate water properties and these values can be used during numerical gas production from gas hydrates. As seen in Figure 5-a, as pressure increases or temperature decreases, the density of water increases. This is the expected behavior of water molecules. Figure 5-b indicates the viscosity of water varying with pressure and temperature. As expected, the viscosity of water decreases with increasing temperature but the effect of pressure on the viscosity of water is almost negligible. The enthalpy, internal energy and thermal conductivity of water increases with increasing pressure and increasing temperature as seen in Figure 5-c, Figure 5-d and Figure 5-e, respectively. The calculated data with waterprop.m and NIST data fit very well as indicated in Figure 5 so this shows the reliability of waterprop.m code.

3.2 Prediction of CH$_4$ Properties

While simulating gas production from gas hydrates in porous sediments, different phases can appear and disappear. For example, Table 2 lists the possible phases in HydrateResSim numerical simulator. Aqueous (Aqu), Aqueous and Gas (AqG), Aqueous and Hydrate (AqH), Aqueous, Hydrate and Gas (AGH), Aqueous, Ice and Gas (AIG), and 4 phases (Aqueous, Ice, Gas, Hydrate, QuP) might occur in porous sediments [5]. Hence, the estimation of gas (CH$_4$) properties at different temperature and pressure values is crucial for numerical simulation at each time step. Most of gas hydrates in nature include approximately 100 % of CH$_4$ [1] so in this study, it was aimed to calculate only CH$_4$ properties instead of calculating the properties of other gases such C$_2$H$_6$ and C$_3$H$_8$, etc. Simulation of gas mixtures in gas hydrates increases the run time therefore most of the simulators only predict gas production from CH$_4$ hydrates [4]. In order to estimate CH$_4$ properties at different temperature and pressure conditions, gasprop.m Matlab code was written in this study. As seen in Equations (2.1) to (2.10), many properties of CH$_4$ should be estimated at different temperatures and pressures at each time step of numerical gas production simulation from gas hydrates. These CH$_4$ properties are [10-18]:

➢ Density
➢ Viscosity
➢ Enthalpy
➢ Internal Energy
➢ Thermal Conductivity
➢ Gas heat capacity (Cp)
➢ Solubility in water

Figure 6 shows the algorithm of gasprop.m code written in this study in Matlab [10-18]. CH$_4$ density is quite important as in mainly Equations (2.1), (2.2), (2.4), and (2.5), which is a function of pressure and temperature. Modified Peng-Robinson Equations of States (EOS) was chosen to

calculate CH$_4$ density and it is valid in wide range of pressure and temperature values. As well as the density of CH$_4$, the viscosity of CH$_4$ is an important factor determining gas flux in the pores (Equation (2.6)) while producing gas from gas hydrates. In gasprop.m code, the method of Hanley et al. [13] for CH$_4$ viscosity calculation at different pressures and temperatures was preferred in this study. Different from conventional oil and gas reservoirs, gas hydrates are sensitive to temperature changes because its dissociation is endothermic and its formation is exothermic [2]. The energy parameters should be estimated and they are mostly function of pressure and temperature. For this purpose, the enthalpy and internal energy of CH$_4$ are calculated with the formulas proposed by Kylie [18] in gasprop.m Matlab code. The formulas of Hanley et al. [13] and Younglove & Elly [14] were integrated and used in gasprop.m to calculate thermal conductivity. Before using gasprop.m in numerical simulations, it is important to prove the reliability of this code. NIST (National Institute of Standards and Technology) [6] is a viable online program to calculate CH$_4$ properties as a function of pressure and temperature.
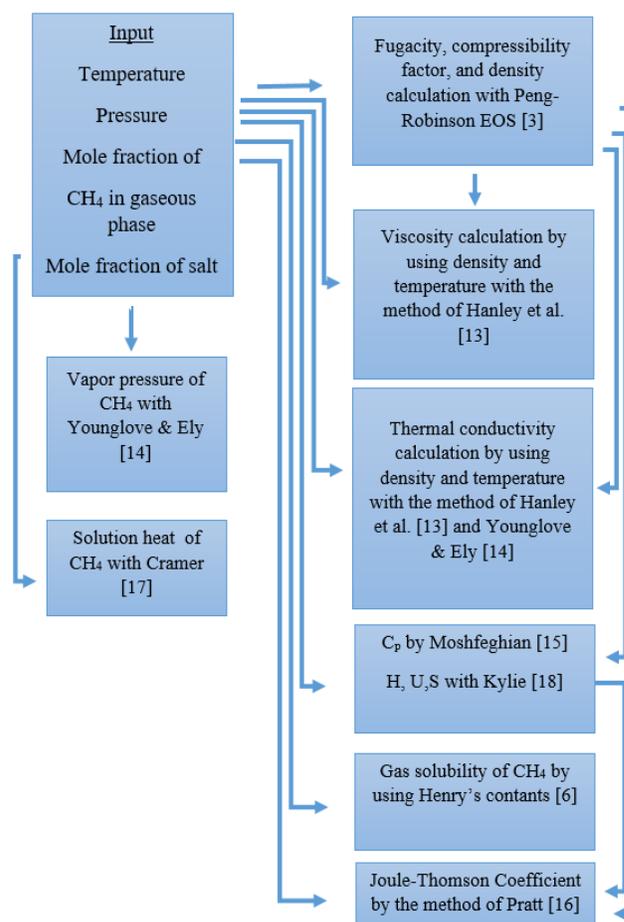

Figure 6. Algorithm of gasprop.m code.

In this study, CH$_4$ properties such as density, viscosity, thermal conductivity, enthalpy and internal energy estimated by NIST [6] and gasprop.m were compared in this study and the comparisons are shown in Figure 7. In Figure 7-a, Figure 7-b, Figure 7-c, Figure 7-d and Figure 7-e, the density, viscosity, enthalpy, internal energy and thermal conductivity of CH$_4$ calculated by gasprop.m and NIST [6] are shown respectively at 5°C, 10°C, 15°C, 20°C and 25°C with varying pressure from 0 to 24 MPa. These temperature and pressure conditions are commonly observed in marine gas hydrate reservoirs [1, 3] so these values were selected to test the reliability of gasprop.m.
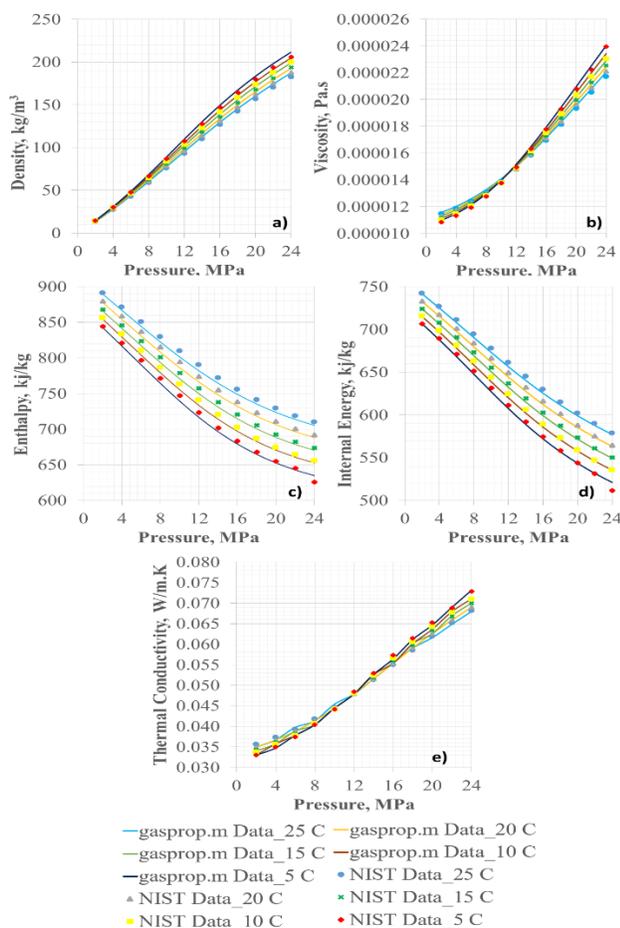
Figure 7. Variations of (**a**) density (**b**) viscosity (**c**) enthalpy (**d**) internal energy (**e**) thermal conductivity of CH$_4$ with increasing pressure and temperature.

As shown in Figure 7, there are good agreements between the density, viscosity enthalpy, internal energy and thermal conductivity of CH$_4$ calculated by NIST [6]. Moreover, R^2 error analysis were done between these values estimated with NIST [6] and gasprop.m. Table 4 lists these R^2 values and it is obvious that the accuracies of the results are higher

than 99 % (R^2). Therefore, gasprop.m has ability to estimate CH$_4$ properties and these values can be used during numerical gas production from gas hydrates.

Table 4. Error Analysis between NIST [6] and gasprop.m (Figure 7).

Condition	R^2 (%)				
	Density	Viscosity	Enthalpy	Internal Energy	Thermal Conductivity
At 25°C	100	99.99	99.84	99.87	99.74
At 20°C	100	99.98	99.85	99.88	100
At 15°C	100	99.98	99.85	99.88	99.81
At 10°C	99.99	99.97	99.85	99.88	99.83
At 5°C	100	99.97	99.49	99.54	99.87

As seen in Figure 7-a, as pressure increases or temperature decreases, the density of CH$_4$ increases. The effect of pressure on gas properties is high. Figure 7-b indicates the viscosity of CH$_4$ varying with pressure and temperature. As expected, the viscosity of CH$_4$ increases with increasing pressure. The enthalpy and internal energy of CH$_4$ decreases with increasing pressure and decreasing temperature as seen in Figure 7-c and Figure 7-d. The calculation of thermal conductivity of all fluids in the porous media is quite important for numerical gas production simulations from gas hydrate reservoirs since heat transfer is dominant in these systems. Therefore, by using gasprop.m, the thermal conductivity values of CH$_4$ were calculated and compared with NIST data in Figure 7-e. Compared to temperature, the effect of pressure on CH$_4$ thermal conductivity is very high. The calculated data with gasprop.m and NIST data fit very well in Figure 7 so this indicates the reliability of gasprop.m.

3.3 Prediction of Ice Properties
Mostly gas hydrates in nature are stable at temperatures above 0°C (freezing point of water) and 99 % of CH$_4$ hydrates are thought to exist in marine sediments [1, 2]. However, even the temperature of CH$_4$ hydrate reservoir is above 0°C, the reservoir temperature decreases below 0°C with endothermic dissociation of gas hydrates and ice forms inside the pores. In some studies, the exothermic ice formation adds additional heat to the reservoir and increases gas production but in other studies [3, 5], ice plugs the pores and decreases gas production. Therefore, ice properties mainly, density, thermal conductivity, specific enthalpy and specific internal energy should be calculated at different pressure and temperature values. For this purpose, iceprop.m Matlab code was developed in this study to be used during the gas hydrate simulations [19, 20]. Figure 8 illustrates the algorithm of iceprop.m Matlab code.
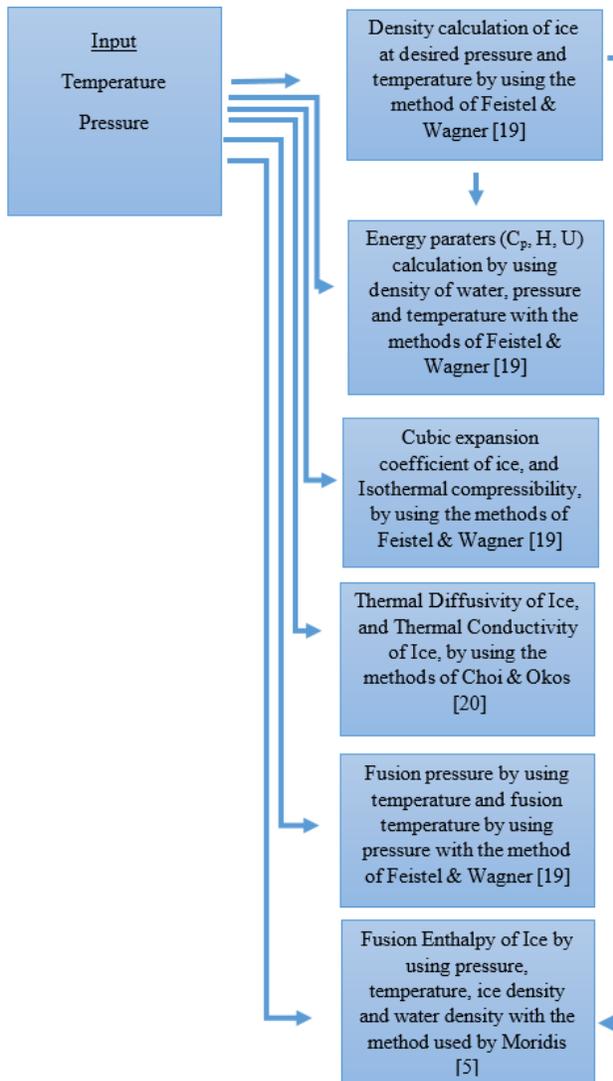
Figure 8. Algorithm of iceprop.m code.

Ice is in solid form so it is assumed stable in the pores and flux terms in Equations (2.5) and (2.6) are only valid for aqueous and gaseous phase flows. As seen in Equation (5.1), ice saturation decreases effective permeability and effective porosity. Thus, during numerical simulation, the determination of ice properties accurately is essential.

$$K = K_o(1 - S_h - S_i)^N \qquad \text{(5.1)}$$

Where K: Effective permeability; K_o: Absolute permeability; S_h: gas hydrate saturation; S_i: ice saturation; N: fitting parameter between 2 and 15 depending on gas hydrate morphology in the pores [1]

Feistel and Wagner [19] proposed a set of formulas to estimate ice properties (ice density, specific enthalpy and specific internal energy of ice). These methods were used in iceprop.m code. For the calculation of thermal

conductivity of ice, the method of Choi and Okos was chosen [20]. The results at different pressures and temperatures at -2ºC, -5ºC, and -10ºC and 0-24 MPa were shown in Figure 9. Online program of NIST (National Institute of Standards and Technology) [6] cannot predict ice properties at different temperature and pressure values so iceprop.m data were not compared with it. However, Feistel and Wagner [19] and Choi and Okos [20] obtained good results with their models therefore their methods were used in iceprop.m. Hence, iceprop.m code is aimed to be used in the numerical study of gas production from gas hydrates if ice exists in the pores.
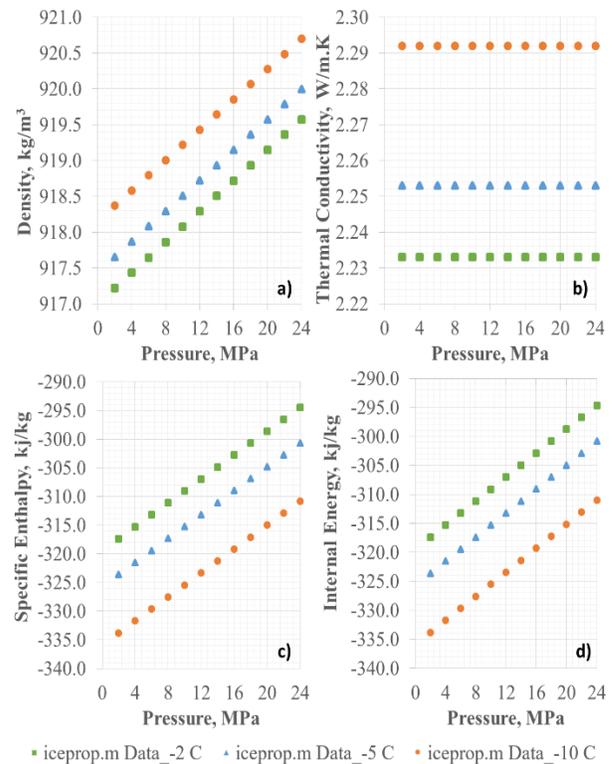
Figure 9. Variations of **(a)** density and **(b)** thermal conductivity **(c)** enthalpy **(d)** internal energy of ice with increasing pressure and temperature.

4. Conclusion
Numerical simulation of gas production from gas hydrate reservoirs requires non-isothermal multiphase calculations at each time step. This is because during gas production both pressure and temperature values in the system changes quickly. For this reason, the prediction of water properties, CH_4 properties (density, viscosity, enthalpy, internal energy, thermal conductivity), and ice properties (density, enthalpy, internal energy, thermal conductivity) at different pressure (0 to 24 MPa) and temperature (5 to 25ºC) values is quite important. These pressure and temperature ranges

were selected according to the ranges of natural gas hydrate reservoirs in marine environment.

In this study, the Matlab codes written: waterprop.m and gasprop.m to predict water and CH_4 properties, which are necessary to simulate gas production from gas hydrate reservoirs. These codes will be the core of future numerical gas hydrate codes planned to be developed. For this reason, it was important to prove the reliability of the Matlab codes written in this study. The reliability of these codes was proved by comparing with NIST [6] data. Due to the possibility of ice formation in the pores during gas production especially with depressurization method, ice properties (density, enthalpy, internal energy and thermal conductivity) are predicted with iceprop.m Matlab code written in this study.

In this study, gas hydrates in permafrost region were ignored because it is known that most of gas hydrates in the world are located in marine environment. Therefore, waterprop.m, gasprop.m and iceprop.m can be used for marine gas hydrate reservoirs instead of permafrost gas hydrate reservoirs.

Acknowledgements

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