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Gas Hydrate Formation by using Propane and Methane Mixture and the Effect of Additives

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ABSTRACT
The current study investigates the effect of some additives such as isopentane and sodium dodecyl sulfate (SDS) on Prepone/Methane mixture for hydrate formation rate with distilled water and seawater. A stirred tank with 600 RPM has been used to evaluate the gas hydrate formation in terms of water recovery and gas uptake. The experimental pressure is set up at 650 PSI for methane. The lowest recovery ratio was obtained for seawater without using any additives. The highest was obtained for seawater and using isopentane additives by 644.74% with a pressure cycle duration of 120 minutes. Adding isopentane additives significantly improves the hydrate water recovery ratio for seawater. The seawater recover increased by 8690 %, and higher hydrate yields can be observed. Isopentane enhances the induction time for both distilled water and seawater.
Keywords - Hydrate, Gas hydrate, hydrate additives, Guest Gas C3H8, seawater desalination.

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I. INTRODUCTION

Gas hydrate desalination is an emerging technology to produce pure water. It can be categorized under freezing-based desalination methods where the hydrate formation process, in which water molecules create cages to entrap a gust gas to forms ice-like hydrate crystals under low temperature and high-pressure state, results in separation of water molecules from the saline solution. Pure water can be collected after melting the hydrate crystals. However, this technology did not gain attention commercially due to its drawbacks, such as high energy requirement for refrigeration [1]. Based on some environmental constrains, related regulation and environmental impacts through brain rejection to seawater which harming the marine life, only few desalination technologies such as membrane distillation (MD) and gas hydrate desalination (G. Hyd) have been an interesting subject to recent researchers based on their limited impact on the environment [2, 3].

Gas Hydrates such as methane (CH4) hydrates are formed of water molecules in ice-like crystals (lattice shape) with cavities in which the methane gas (gust gas) molecules are engaged in. Gas hydrate formation occurs at specific conditions, mainly low temperature, and high pressure. Gas Hydrate desalination produces no carbon dioxide emission which makes it an environmentally friendly process, while the methane gas fuel can be completely recovered by low energy such as waste heat stream. Gas hydrate can be regarded as an energy storage method with high content per unit volume which makes it a cost-effective process and gas hydrate is non-flammable and can be stored and transferred without harming the surroundings which make it a safe process [4].

During hydrate dissociation process for methane gas, self-preservation effect is performed below water freezing temperature, which creates the potential for natural gas storage and transportation [5]. At atmospheric pressure, Methane hydrates can be stable at a temperature of 193.2 K, and this requires extra energy to control the temperature during hydrate storing. In order to achieve effective kinetic energy and getting hydrate with a structure I (sI) the temperature need to be lower as 274.2 K and pressure need to be between 8 to 15 MPa [6] (Asheesh Kumar et al., 2019), moreover, for mixture gases such as methane/propane, structure II (sII) formed first followed structure I (sI) of methane hydrate. Methane (CH4) is the most used gas in hydrate formation, and it forms the (sI) structural form in a stable condition. [7]. It was reported that methane hydrate could increase the storage capacity, in which a single volume of methane hydrate is capable of storing around 180 volumes of methane in the gas phase [8]. Natural Gas (NG) is a valuable source of energy, and it is one of the cleanest fossil fuel with low carbon dioxide emission comparing to coal and crude oil, and it has been utilized as the main source of energy in many countries around the world, which raise the market share to 25% (BP Statistical Review, 2018), and in the USA, the most popular NG is the underground inventory such as natural gas reservoirs [5].

Generally, NG can be found faraway from industrial and residential sectors or in a different land, which makes transferring this energy to the demand location is required. Thus; it can be transferred through high-pressure pipelines, transfer to liquid and stored in tanks as liquefied natural gas (LNG) or compressing the gas to be stored in tanks as compressed natural gas (CNG) however, each method has different constraints. For transportation through pipelines, it requires free lands to lay down or parry the pipes. The installation cost is quite high, for LNG, the process requires to decrease the temperature up to 191 K which need extra cost for the cooling process, and in some cases, the gas can't be stored for a long time. This process has around two-third of gasoline in terms of volumetric energy storage density, however, the storage for a long time is not applicable for some condition. [4]. Propane is used as a guest gas for gas hydrate desalination of seawater and showed a unique ability to enhance the kinetics of gas hydrate formation when employed for separation of hydrates from residual brine in a fixed bed reactor. The hydrate dissociation occurs at 0.4 MPa and 279.65 K. [9]. Babu et al., [10] noted through hydrate formation morphology mapping that in the presence of propane gas in the system, hydrate formation propagates entirely in the gaseous phase resulting in significant hydrate formation. Utilizing mixed guest gases for hydrate formation has shown good results with silica sand bed and water [11], it was reported that an enhancement in hydrate formation kinetics for sand bed was accrued, and high rate of hydrate formation for gas mixture including propane was performed. Also, it was reported that fuel gas mixture with 2.5 mol% of propane decrease operation condition from 9 to 6 MPa with remarkable improving hydrate formation kinetics and increasing the gas uptake [12]. Linga and others indicated that significantly higher formation rates for the gas mixtures containing could be performed with a pressure up to 46 bar [11]. Babu [10] revealed a significantly higher rate of hydrate formation could be attributed due to the presence of propane and reported that in the case of using methane gas mixture, a higher rate of formation could be obtained at 50 bar. This study investigates some options for improving the gas hydrate formation rate during seawater desalination. Hailu [13] reported that a mixture of methane and propane (ch4:c3h8) provides an essential parameter for sII hydrate growth kinetics. Linga [11] indicated that significantly higher formation rates for the gas mixtures could be performed with a pressure up to 46 bar. Babu [10] revealed a significantly higher rate of hydrate formation can be attributed due to the presence of propane. Tianbiao et al., [9] reported that in the case of using a methane-propane gas mixture, a higher rate of formation could be obtained when the propane partial pressure is between 4.5 and 7.9 bar.

Additives are mainly added to a gas-water system in order to promote the hydrate formation process and are categorized based on the promoters' objective into thermodynamic promoters and kinetic promoters [14]. Adding surfactants such as sodium dodecyl sulfate (SDS) to methane improved surface tension between methane and water, thus promoted the hydrate formation process up to the highest hydrate formation limit with the stable rate [15]. Thermodynamic promoters are additives utilized to perform hydrate formation in easier operation conditions and mainly by low pressure and higher temperature to minimize the operation cost. Therefore, the selection of thermodynamic promoters is subjected to forming hydrate in moderate conditions. Thermodynamic promoters are mainly affecting the phase changes, they fill the large spaces in hydrate structure cages, and the gas fills the small cages. Therefore, they enable the hydrate to form in milder conditions and easily achievable low pressure and high temperature [4].

The current work compares the gas hydrate formation process for gas mixture (methane–propane mixture) water system with additives namely; SDS, isopentane and a mixture from both.

II. MATERIALS AND METHOD

2.1 Materials

stainless-steel reactor with an internal volume of 1760 ml, an internal diameter of 100 mm and a height of 250 mm was utilized. The reactor top cover contained two sight windows fitted with acrylic glasses to allow visual observation while conducting the experiments. Two rod-type E- type thermocouples, omega inc., were fixed on the top cover to measure the temperature of the water sample. A high-pressure transmitter and an analogue pressure gauge (range 0-100 bar) were also connected directly to the reactor. Fig. 1. Illustrates the schematic diagram for the experiment procedure.

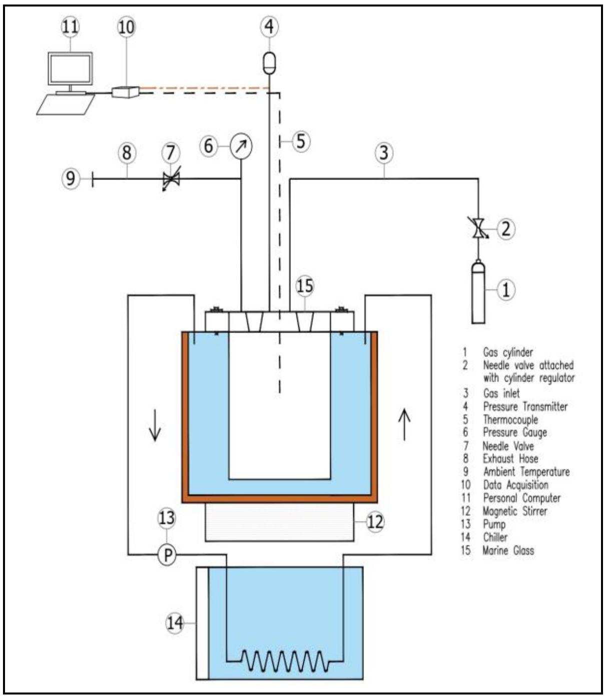

Fig.1 Schematic diagram for the experiment procedure.

The reactor is submerged in a thermal basin with a volume of 0.04 m^3 filled with glycol for cooling the reactor. The glycol is circulated through a pump and spiral heat exchanger submerged in a cooling circulator. The thermal basin is placed on a holder under which a magnetic stirrer, from Fisher Scientific, was placed. A gas pipeline connects the reactor with the gas cylinder. A digital camera was installed above the reactor pointed on one of the glass windows located on the cover of the reactor. Fig. 2 shows a photo of the reactor tank used in the current investigations.

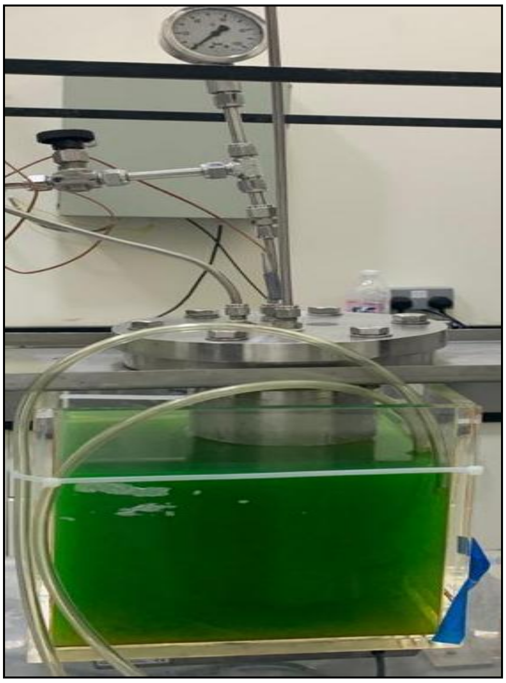

Fig. 2 Rector Tank used in the current experiments.

2.2 Method

2.2.1 Preparation of solutions

The water solutions of the desired concentration were prepared by adding the desired amount of additives to the water samples. The solutions were mixed for one hour using a magnetic stirrer. In this study additive added to water samples were 0.5% and 1% by weight. Seawater was collected form a seawater desalination plant from the pretreated seawater feed to RO units.

2.2.2 Experiment procedure

The prepared solution is poured inside the reactor; then the reactor is closed and tightened and placed in the thermal basin at 10C. Then the reactor is flushed with the selected gas for 15 seconds to remove air. The needle valve is closed, and the reactor is pressurized with C3H8CH4 450 psi, then the gas cylinder valve is closed. A pressure drop was observed inside the reactor in the first 15 minutes due to the cooling of gas to the reactor temperature. Hence, the gas cylinder valve was opened to adjust the gas pressure to 450 psi and then closed again. The gas pressure pattern with time inside the reactor depends on the occurrence of gas hydrate formation and its development. During this period a pressure drop occurs due to depletion of gas for hydrate formation. The occurrence of hydrate formation can be observed from the glass windows and by watching the magnetic bar movement. The magnetic bar will stop moving as a result of increased resistance inside the solution due to hydrate formation. Table 1 presents the parameters of the study.

Table 1 Parameters of the study

Parameters	Name
Type of solutions	• Distilled Water • Sea Water
Type of Gases	• Propane C3H8 • Mixture Methane/Propane (CH4:C3H8) (90.5:9.5%)
Durations	24 hr
Gas Pressures	45 bar
Additives	• A1: Isopentane • A2: (SDS) sodium dodecyl sulfate • A3: A1 + A2
Stirring (RPM)	600
Temperature (C)	1.5

2.2.3 Gas hydrate calculation

The amount of gas hydrate formed was calculated using the equation of state of the gas system. the Pressure and Temperature between the number of moles/grams of the gas at time t and the number of moles/grams at time zero the number of moles of methane gas released from hydrate dissociation can be found by using the following equation [12]:

$$(\Delta n_{H\uparrow}) = V_R\left(\frac{P}{zRT}\right)_0 - V_R\left(\frac{P}{zRT}\right)_t \qquad (1)$$

Where $\Delta n_{H\uparrow}$ amount of methane gas consumed, V_R reactor volume, P and T are the pressure and temperature of the reactor at any time, z is the compressibility factor calculated by Pitzer's correlations, and R is the universal gas constant. For hydrate water recovery ratio (hydrate yield) was computed by using Eq (3) [16]:

$$\text{hydrate yield (\%)} = \frac{\Delta n_{H\uparrow} \times \text{Hydrate Rate}}{\Delta n_{H2O}} \times 100 \quad (2)$$

Where the mass of water formed in the hydrate (g)= $\Delta n_{H\uparrow} \times$ Hydrate Rate.The hydration number is the number of water molecules required per gas molecule to form the hydrate structure. 6.73 was used as the theoretical minimum water to gas ratio 6 mole water/ 1 mole methane.

2.2.4 Plan of experiments

A total of eight experimental runs were carried out to determine the effect of gas-water system pressure, concentration and type of additives and water sample type on the amount of hydrate formed. Table 2 shows the parameters of each experiment.

Table 2 Parameters of experimental runs for gas-water system

Exp	System	Additives	Stirring rate rpm	Gas Pressure psi	Temp (^{0}C)	Duration (hr)
1	DW - CH_4: C_3H_8	None	600	650	1.5	24
2	DW - CH_4: C_3H_8	IsoCP/DW (1:3.3)	600	650	1.5	24
3	DW - CH_4: C_3H_8	SDS	600	650	1.5	24
4	DW - CH_4: C_3H_8	SDS + IsoCP/DW (1:30)	600	650	1.5	24
5	SW - CH_4: C_3H_8	None	600	650	1.5	24
6	SW - CH_4: C_3H_8	IsoCP/DW (1:3.3)	600	650	1.5	24
7	SW - CH_4: C_3H_8	SDS	600	650	1.5	24
8	SW - CH_4: C_3H_8	SDS + IsoCP/DW (1:30)	600	650	1.5	24

III. RESULTS AND DISCUSSIONS

A 600 RPM The stirred tank was used to investigate the effect of SDS and isopentane additives on Propane/Methane mixture hydrate formation. The gas consumption and hydrate water recovery ratio have been calculated as explained in the previous section. Table 3 summarizes the experiments with distilled water and seawater under the Propane/Methane mixture pressure of 650 PSI. The table presents the induction time for hydrate formation, the gas uptake, the water volume to hydrate, the percentage of water recovery and the final gas consumption.

As shown in the table, the induction times were between 1.50 and 6.97 min. For distilled water samples, the induction time has been decreased with isopentane and SDS additives by 20% and 3% respectively. Isopentane showed remarkable enhancement in the induction time. The additive mixture (A3) has better induction time than SDS.

For seawater samples, the induction time has been decreased by isopentane additives. The induction time was enhanced by 151% with isopentane, and it shows better results than SDS and the additive mixture (A3). The gas uptake has been increased with additives; however, isopentane shows higher results than SDS. The changes in gas uptakes for all experiments for 120 min are presented in Fig. 2.

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Table 3 Summary of the experimental trials.

Exp.	System	Pressure (PSI)	Induction Time (min)	Gas Uptake (mol)	Vol. H2O (ml)	Water Recovery (%)	Gas Cons. (mol / mol)
1	Distilled Water	650	1.80	0.0223	24.09	18.46%	0.0309
2	Distilled Water-with A1: Isopantane	650	1.50	0.0896	60.07	46.42%	0.0769
3	Distilled water with A2: SDS	650	1.76	0.0285	60.87	35.94%	0.0885
4	Distilled water with A3: (SDS + Isopentane)	650	1.72	0.0639	69.06	44.73%	0.0780
5	Seawater	650	6.97	0.0705	7.62	5.70%	0.0083
6	Seawater- with A1: Isopantane	650	2.77	0.1877	19.2142	17.74%	0.0246
7	Seawater with A2: SDS	650	6.10	0.0596	9.48	7.42%	0.0098
8	Seawater with A3: (SDS + Isopentane)	650	5.31	0.1778	6.45	14.88%	0.0121

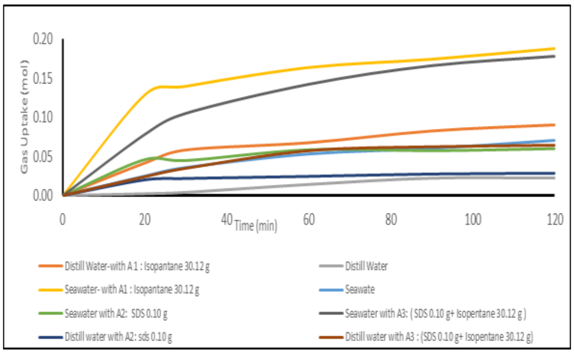
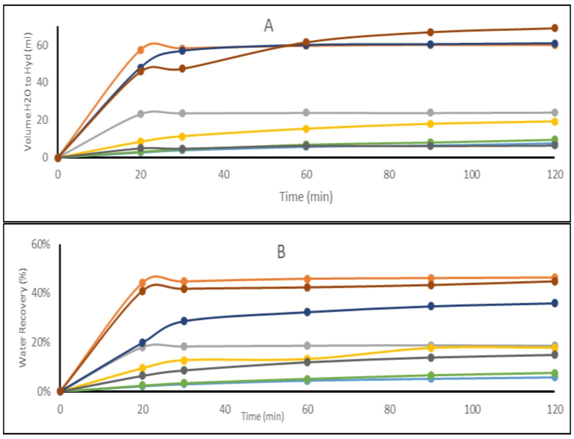


Fig. 2 Gas uptake for all Experiments.

Pure isopentane (A2) shows better performance than the mixture additives (A3). Water recovery rate has increased with a mixture of additives for distilled water, and it has been significantly increased by using isopentane with seawater by 210%. In addition, the changes in H_2O volume have been increased by 153%. Fig. 3 illustrates the changes in H_2O volume, water recovery and final gas consumption during 120 min for all experiments.



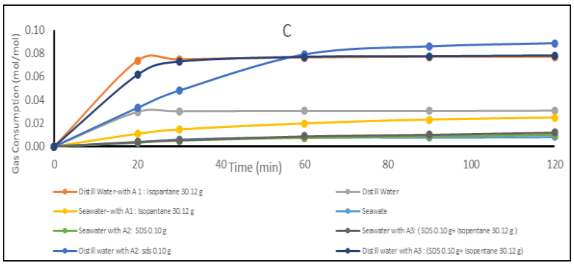


Fig. 3 Experiments results: A) H_2O volume, B) water recovery and C) final gas consumption.

Fig. 4 shows a comparison with other's experimental study [15]. As illustrated in the figure, the highest gas uptake for isopentane additives in the current investigation, followed by the current investigation with SDS and isopentane additives. The present results for distilled water without any additives have around 3 % deviation, which might be due to experimental error; thus, the results can be validated with their work. The current investigation showed higher gas uptake for distilled water than others [15].

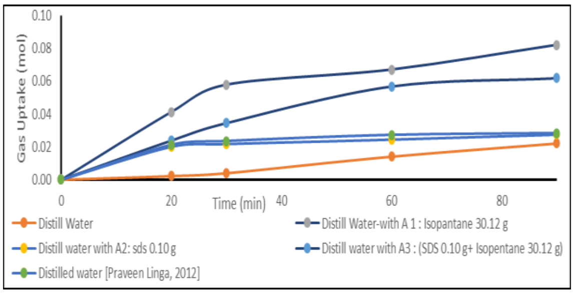


Fig. 4 Comparison of Gas uptake with other's experiments.

The hydrate behavior and growth can be explained by profile in the stirred reactor tank with 600 RPM. Fig. 5 illustrates these relations for all experiments.

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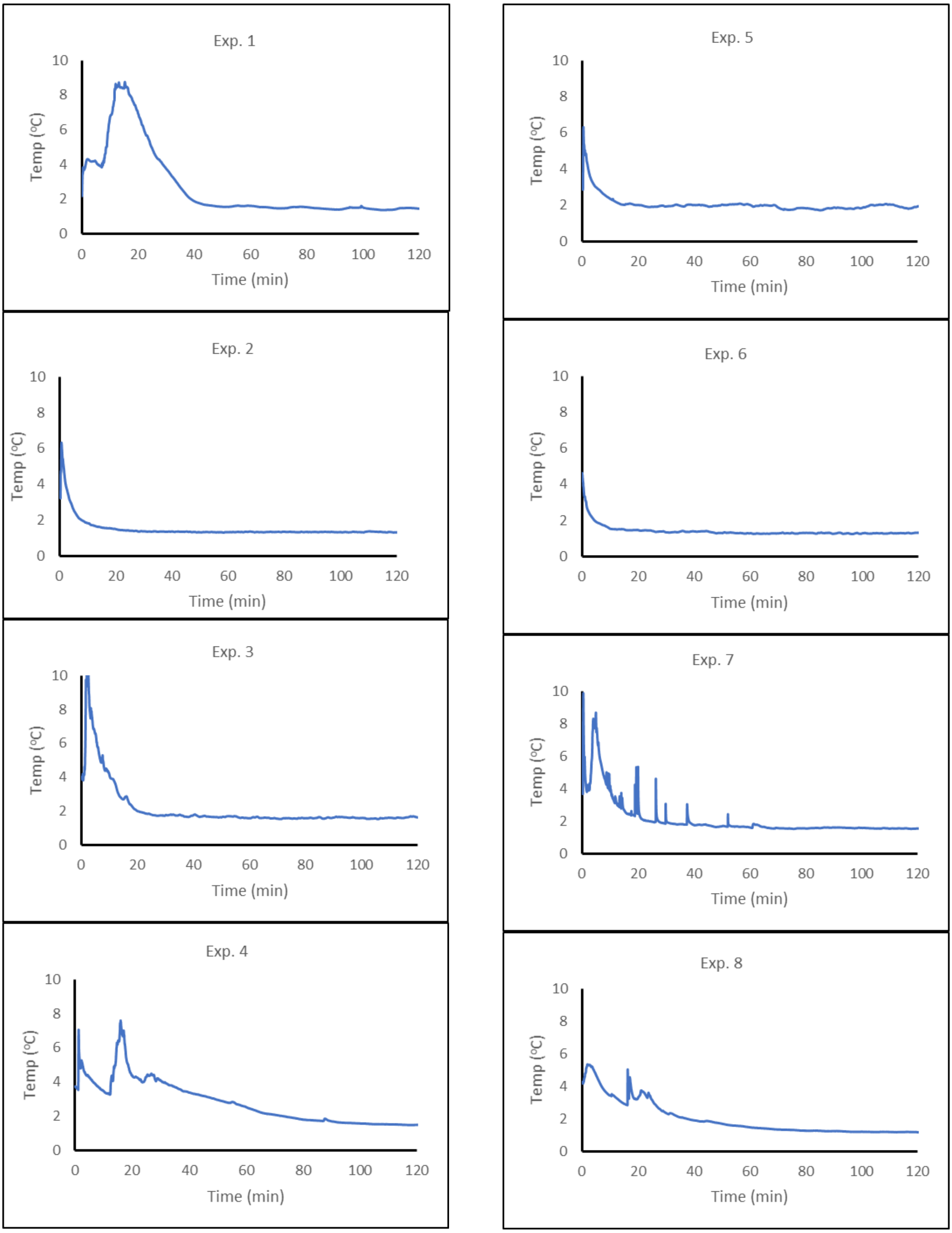

Fig. 5 Temperature profiles for all experiments.

The temperature profile was obtained using a thermocouple inserted in the stirred tank, and they were utilized during all eight experiments (each experiment is 120 min duration). As shown in the figure for Exp.1 for distilled water, a peak was observed at 1.07 min, and the temperature was increased up to 8.3°C. However, the temperature spike has been performed due to hydrate nucleation and releasing exothermic heat. The set experimental temperature was reached after 40 min.

For Exp. 2 with distilled water and isopentane mixture, a peak was observed at 0.60 min, the temperature was increased up to 6.5°C, and the induction time was faster. The set experimental temperature was reached after 8 min.

The profiles for distilled water and SDS additives (Exp. 3) showed a high-temperature spike at 10.2°C, and the set experimental temperature was reached after 20 min. The profiles for distilled water and mixture additives (Exp.4) showed more than two peaks and the first one was performed based on the first hydrate nucleation followed by a second nucleation phase (20 min between the two nucleation phases).

For seawater system, Exp. 5 and 6 showed similar temperature profiles. The seawater temperature profile (Exp. No. 7 and 8) showed multiple peaks In Exp. No. 7, the first peak was observed at 10.09 min, the temperature was increased up to 8.4°C. The set experimental temperature was reached after 65 min. In Exp. No. 8, the first peak was observed at 8.92 min, and the temperature was increased up to 5.3°C. The set experimental temperature was reached after 35 min. The water recovery reached 14.88% with 0.024 mol final gas consumption.

The lowest recovery ratio was about 7.42 % obtained from Exp. 5 for seawater without using additives, and the highest was 644.74% from Exp. 6 for seawater and using isopentane additives with a pressure cycle duration of 120 minutes. Therefore, adding isopentane additives, significant improvement in the hydrate water recovery ratio can be obtained with seawater and seawater by about 8690 %, and higher hydrate yields can be observed.

IV. CONCLUSION

This work investigates some options for improving the gas hydrate formation rate during seawater desalination. The main research objectives are to investigate Isopentane and SDS additives' effect in a stirred tank to assess the propane/methane hydrate formation in terms of water recovery and gas uptake. The experimental pressure is set up at 650 PSI for the gas mixture. It was concluded that isopentane additives improve the recovery rate for water in the presence of propane/methane mixture. Isopentane enhances the induction time for both distilled water and seawater. Additional factors can be considered to enhance the hydrate formation process such as improving the heat and mass transfer mechanism and overcomes the thermal resistance through modifying the reactor tank design.

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