

Article

# Improved Kinetics and Water Recovery with Propane as Co-Guest Gas on the Hydrate-Based Desalination (HyDesal) Process

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**Abstract:** Water is a key resource for sustainable development and plays a crucial role in human development. Desalination is one of the most promising technologies to mitigate the emerging water crisis. Thermal desalination and reverse osmosis are two of the most widely employed desalination technologies in the world. However, these technologies are energy intensive. Clathrate-hydrate-based desalination (HyDesal) is a potential energy-efficient desalination technology to strengthen the energy–water nexus. In our previous study, we proposed a ColdEn-HyDesal process utilizing waste Liquefied Natural Gas (LNG) cold energy based on a fixed-bed reactor configuration. In this study, we evaluated the effect of 10% propane in three different gas mixtures, namely, nitrogen (G1), argon (G2), and carbon dioxide (G3), as hydrate formers for the HyDesal process. The achieved water recovery was very low (~2%) in the presence of NaCl in the solution for gas mixtures G1 and G2. However, high water recovery and faster kinetics were achieved with the G3 mixture. To improve the water recovery and kinetics of hydrate formation for the G2 gas mixture, the effect of sodium dodecyl sulfate (SDS) was evaluated. The addition of SDS did improve the kinetics and water recovery significantly.

**Keywords:** gas hydrates; desalination; clathrate process; seawater

## 1. Introduction

Water is one of the key resources for sustainable development and plays a crucial role in human development. Due to the increasing global population, extensive urbanization, and a changing climate, access to freshwater will be a challenge. Even today, close to 1.2 billion people have no access to safe drinking water [1–3]. Freshwater accounts for only 2.5% of all the water on the planet and less than 1% is actually available, while the remaining is in the form of ice and snow cover in mountainous regions, the Antarctic, and Arctic regions [4]. By 2050, the demand for fresh water is expected to increase by 55% [5]. Hence, the water industry has become increasingly reliant upon desalinating brackish water and seawater.

Desalination is the process of removing salts and minerals from seawater or brackish water. Desalination processes are broadly categorized as thermal or membrane-based technologies [6,7]. Multistage flash (MSF) distillation, a thermal desalination technique, remains the primary technology for desalination in the Middle East due to the easy availability of fossil fuels and the poor feed water quality. The specific energy consumption and water recovery of MSF are 13.5–25.5 kWh/m<sup>3</sup> and up to 20%, respectively, depending on the operating conditions [8–10]. Reverse osmosis (RO), a membrane-based technology, is presently the state-of-the-art technology for seawater desalination and contributes to 66% of the world's installed desalination capacity. The water recovery of the RO process is up to 55% and its specific energy consumption is 3–6 kWh/m<sup>3</sup> of recovered potable water [11–13]. The major limitation of these technologies is that both are energy intensive, which in

turn results in a corresponding increase in the emission of greenhouse gases [13,14]. Hence, there is a need to develop an innovative low-energy desalination process for sustainable development.

One such technology is hydrate-based desalination (HyDesal). The HyDesal process effectively falls in the class of approaches based on freezing. In this process, water molecules form cages around a guest gas/liquid component, thereby effectively separating themselves from the brine solution even at temperatures higher than the normal freezing temperature of water. These hydrate crystals, when melted, are essentially fresh water and the guest component can be reused for the desalination. Other applications of hydrate-based technology on selective fractionation are gas separation, gas storage, natural gas storage and transport, CO<sub>2</sub> sequestration, cold storage, and refrigeration [15–22].

Although hydrate-based desalination was first proposed in 1942, major R&D efforts followed in after the 1960s. A detailed review of works on hydrate-based desalination till 1990 was presented by Englezos [17]. The initial approach that was proposed several decades ago was to pump hydrate-forming guest species directly into the ocean at depths of 1000 m, separate the crystals, and, upon dissociation, produce pure water [23,24]. This attempt failed due to the challenge of separating the hydrates from the seawater as well as the issue of the stability of hydrate crystals. Later, an improved clathrate desalination process was proposed using halogenated hydrocarbons as guests for hydrate formation [25]. However, these refrigerants have been banned due to their environmental impact [26] and cannot be used; hence, the process never received much attention. Ripmeester and McCormack [27] proposed a clathrate-hydrate-based desalination process using cyclopentane as a clathrate-forming agent. The proposed process requires an additional step of separating cyclopentane from fresh water. Our recent work employing cyclopentane for carbon dioxide capture revealed significant solvent loss and environmental impact because of its high volatility [28]. Although the HyDesal process has been studied for last 70 years, it has never been commercially viable due to slow kinetics, difficulty in separating hydrate crystals from the brine solution, and the higher energy cost involved due to refrigeration [17,29]. The state of the art of clathrate-hydrate-based desalination in the literature and development challenges for successful commercialization are presented elsewhere [29].

In our previous work, we proposed a conceptual hydrate-based desalination (ColdEn-HyDesal) process employing a fixed-bed reactor configuration utilizing waste Liquefied Natural Gas (LNG) cold energy to minimize the energy requirement based on the ability of propane as a co-guest in a gas mixture to draw dispersed water from the sand bed towards the gas phase for hydrate growth, resulting in enhanced kinetics [30]. We also reported that by utilizing waste LNG cold energy, the specific energy consumption of the HyDesal process can be lowered from 65.13 to 0.84 kWh/m<sup>3</sup> of potable water [31]. The other constituent in the gas mixture along with propane needs to be identified, as this can result in enhanced kinetics.

In this study, the effect of C<sub>3</sub>H<sub>8</sub>/N<sub>2</sub> (G1), C<sub>3</sub>H<sub>8</sub>/Ar (G2), and C<sub>3</sub>H<sub>8</sub>/CO<sub>2</sub> (G3) gas mixtures on water recovery were evaluated for hydrate-based desalination employing a fixed-bed reactor configuration. Experiments were carried out with pure water and a 3 wt% NaCl solution in a fixed-bed reactor with sand as porous media to evaluate the kinetics of hydrate formation and water recovery. In addition, the effect of the addition of sodium dodecyl sulfate (SDS) as a kinetic promoter was also evaluated.

## 2. Materials and Methods

### 2.1. Materials

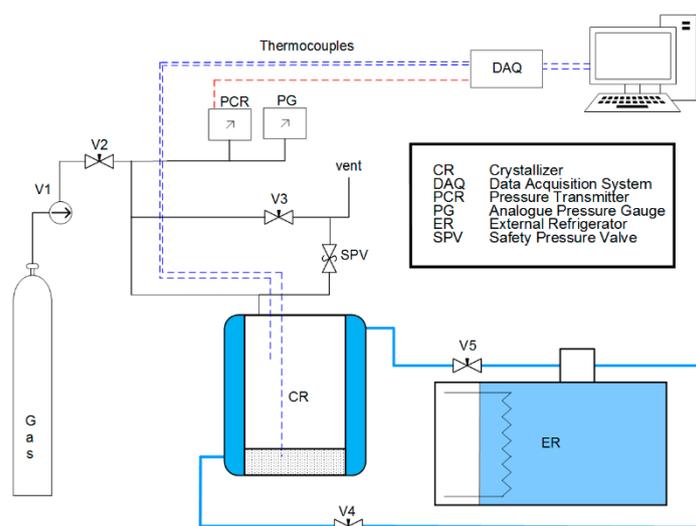
The N<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (90 mol%/10 mol%), Ar/C<sub>3</sub>H<sub>8</sub> (90 mol%/10 mol%), CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (90 mol%/10 mol%), CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (95 mol%/5 mol%), and CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> (80 mol%/20 mol%) gas mixtures employed in this study were supplied by Soxal Private Limited. Silica sand and sodium chloride (CAS 7647-14-5) of 99% purity were supplied by Sigma-Aldrich. The properties of the silica sand employed in this study, such as size, pore volume, and bulk density, are tabulated in Table 1. SDS of 99% purity was supplied by Amresco. Deionized and distilled water were used for the experiments and to prepare the different concentration solutions.

**Table 1.** Summary of silica sand properties.

	Medium Sand 1 (MS1)	Medium Sand 2 (MS2)	Coarse Sand	Granular Pebble
Size range (mm)	0.1–0.5	0.21–0.29	0.56–1.3	1.5–3.0
Bulk density (g/cm <sup>3</sup> )	1.56	1.61	1.53	1.49
Pore volume (cm <sup>3</sup> /g)	0.27	0.27	0.238	0.258

## 2.2. Apparatus

The detailed description of the apparatus can be found in our previous work [32]. The schematic of the experimental apparatus is shown in Figure 1. Briefly, the apparatus consisted of a crystallizer of volume 980 cm<sup>3</sup> and an internal diameter of 10.16 cm. A window at the top of the crystallizer allowed for viewing the crystallizer contents. The temperature of the crystallizer was controlled by the cooling jacket connected to an external refrigerated circulator. An Omega copper-constantan thermocouple with an uncertainty of 0.1 K located at 1 cm from the bottom of the crystallizer measured the bed temperature. Another Omega copper-constantan thermocouple was used to measure the gas phase temperature. The pressure of the crystallizer was measured using a Rosemount smart pressure transducer (model 3051S,  $\pm 20$  kPa). The pressure and temperature data were recorded using a National Instruments CompactRIO data acquisition system and LabView software.

**Figure 1.** Schematic of the clathrate-hydrate-based desalination apparatus.

## 2.3. Procedure

### 2.3.1. Preparation of Solution

The NaCl solution of desired concentration was prepared by adding the desired amount of sodium chloride and distilled water and mixing thoroughly. In this study, 3.0 wt% concentration of NaCl was used. SDS solution of desired concentration was prepared by adding the desired amount of SDS and distilled water and mixing thoroughly. The concentrations of SDS used in this study were 100, 500, and 1000 ppm. The SDS-salt solution was prepared by adding the desired amount of sodium chloride, SDS, and distilled water and mixing thoroughly.

### 2.3.2. Preparation of Silica and Bed

In our previous study [30], we reported a 1.5-cm bed height to be optimum. Therefore, we used a bed height of 1.5 cm in this study. The amount of silica sand and solution used to prepare the bed were 197.24 g and 53.26 mL, respectively. The bed was set up by splitting the required amount of sand and solution into three equal parts and placing each in a batch order to form a uniform bed.

### 2.3.3. Hydrate Formation Procedure

Once the bed was prepared, the crystallizer was closed and the thermocouples were connected to their respective ports. To purge the air inside the crystallizer, the system was pressurized to 300 kPa and then depressurized to 50 kPa with the gas mixture three times. The crystallizer was then cooled to the experimental temperature using the external refrigerated circulator. Once the crystallizer reached the desired temperature, the system was pressurized with the same gas mixture used in the purging step to the desired experimental pressure. The temperature and pressure were allowed to stabilize and reach the experimental conditions. The time at which the pressure and temperature of the system reached the experimental condition was recorded as time zero. The data were recorded every 20 s. The crystallizer pressure dropped due to hydrate formation and growth. The experiment was continued until no significant pressure drop in the crystallizer was observed. A schematic of the experimental procedure followed is shown in Figure 2.

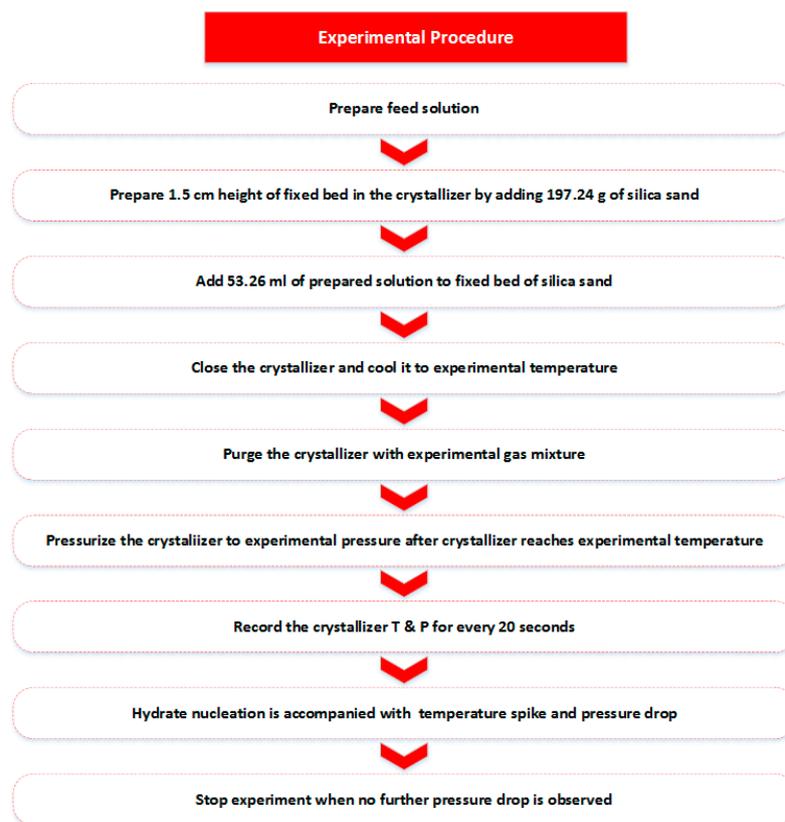


Figure 2. Schematic of the experimental procedure.

### 2.4. Calculation of Water Recovery

The moles of gas consumed for hydrate formation and growth at any time were calculated using the following equation:

$$(\Delta n_{H,\downarrow})_t = \left( \frac{PV}{zRT} \right)_{CR,0} - \left( \frac{PV}{zRT} \right)_{CR,t} \quad (1)$$

where  $P$ ,  $V$ , and  $T$  are the crystallizer pressure, volume, and temperature, respectively;  $R$  is the ideal gas constant; and  $z$  is the compressibility factor calculated by Pitzer's correlation [33].

The volume of water converted to hydrate can be determined by using the following equation:

$$\text{Volume of water converted to hydrates} = \Delta n_{H,\downarrow} \times \text{hydration number} \times 18 \text{ (cm}^3\text{)} \quad (2)$$

where  $\Delta n_{(H,\downarrow)}$  is the number of moles of gas consumed for hydrate formation at the end of the experiment determined from the gas uptake. The hydration number is the number of water molecules per guest molecule. Ar/C<sub>3</sub>H<sub>8</sub> gas mixtures formed structure II (sII) hydrate, which had 16 small cages and 8 large cages in a one-unit cell composed of 136 water molecules. The theoretical hydration number used in the above equation was 5.67. For N<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> gas mixtures, the hydration number used was 9.65 and 8.21, respectively, which were calculated using CSMGem [34].

Water recovery represents the volumetric process efficiency of the HyDesal process and can be calculated by using the following equation, as given in the literature [29]:

$$\text{Water recovery \%} = \frac{\text{Volume of water converted to hydrate} \times F_h}{\text{Volume of feed solution}} \times 100 \quad (3)$$

where  $F_h$  is the fraction of hydrate formed that is recoverable at the hydrate crystal separation step from the brine. Since, in our study, the hydrate crystals were not separated from the brine,  $F_h$  of 1 was calculated in the above equation.

The rate of water recovery ( $R_{20}$ ) was calculated by fitting the water recovery growth versus time for the first 20 min from the nucleation point using the least-squares method.

### 3. Results and Discussion

A suitable gas mixture with propane as a constituent can lower the operating conditions as well as enhance the hydrate formation rate and water recovery. We chose nitrogen, argon, and carbon dioxide as the other constituent along with 10% propane and evaluated their effect on water recovery and rate of hydrate formation. A summary of experimental results, such as induction time (IT), gas uptake at IT, gas uptake after 60 min from IT, water recovery, and rate of water recovery, is presented in Table 2.

**Table 2.** Summary of experimental conditions and results with G1 (C<sub>3</sub>H<sub>8</sub>/N<sub>2</sub> (10 mol%/90 mol%)), G2 (C<sub>3</sub>H<sub>8</sub>/Ar (10 mol%/90 mol%)), and G3 (C<sub>3</sub>H<sub>8</sub>/CO<sub>2</sub> (10 mol%/90 mol%)) gas mixtures.

System with G1 Mixture	Exp. No	Pressure (MPa)	Temperature (K)	Induction Time (IT) (min)	Gas Uptake at IT (mol/mol of Water)	Gas Uptake 60 min from IT (mol/mol of Water)	Water Recovery at 60 min from IT (%)	R <sub>20</sub> (cm <sup>3</sup> /min)
Pure Water	N1	5.0	275.5	250.33	0.0062	0.0438	36.34	0.21
	N2	5.0	275.5	41.67	0.0065	0.0603	51.96	0.22
	N3	5.0	275.5	160.33	0.0051	0.0519	45.21	0.22
3.0 wt% NaCl solution	N4	5.0	274.2	1600	0.0035	0.0037	0.13	0.02
	N5	5.0	274.2	117.33	0.0001	0.0014	1.24	0.00
System with G2 mixture	Exp. No	Pressure (MPa)	Temperature (K)	Induction Time (IT) (min)	Gas Uptake at IT (mol/mol of Water)	Gas Uptake 60 min from IT (mol/mol of Water)	Water Recovery at 60 min from IT (%)	R <sub>20</sub> (cm <sup>3</sup> /min)
Pure Water	A1	5.0	274.2	91.67	0.0037	0.1017	53.41	0.29
	A2	5.0	274.2	1867.00	0.0046	0.1222	64.73	0.35
	A3	5.0	274.2	429.67	0.0021	0.1060	58.90	0.92
Pure water with 100 ppm SDS	A4	5.0	274.2	0.67	0.0002	0.1025	57.99	1.00
Pure water with 500 ppm SDS	A5	5.0	274.2	0.33	0.0005	0.1102	62.16	1.16
Pure water with 1000 ppm SDS	A6	5.0	274.2	53.33	0.0017	0.0992	55.26	1.14
3.0 wt% NaCl solution	A7	5.0	274.2	24.00	0.0005	0.0971	54.75	1.20
	A8	5.0	274.2	90.67	0.0004	0.1016	57.38	1.18
3.0 wt% NaCl solution with 100 ppm SDS	A9	5.0	274.2	1864.33	0.0021	0.1053	58.52	1.23
	A10	5.5	274.2	46.00	0.0015	0.0036	1.21	0.02
	A11	5.5	274.2	3.67	0.0012	0.0032	1.10	0.02
3.0 wt% NaCl solution with 500 ppm SDS	A12	5.5	274.2	4307.00	0.0028	0.0047	1.10	0.02
	A13	5.5	274.2	42.67	0.0017	0.0132	6.50	0.17
	A14	5.5	274.2	187.67	0.0021	0.0157	7.72	0.19
3.0 wt% NaCl solution with 1000 ppm SDS	A15	5.5	274.2	10.00	0.0008	0.0217	11.83	0.26
	A16	5.5	274.2	0.33	0.0001	0.0193	10.95	0.31
3.0 wt% NaCl solution with 500 ppm SDS	A17	5.5	274.2	168.33	0.0050	0.0679	35.67	0.69
	A18	5.5	274.2	844.67	0.0020	0.0583	31.94	0.55
3.0 wt% NaCl solution with 1000 ppm SDS	A19	5.5	274.2	1.67	0.0001	0.0632	36.12	0.66
	A20	5.5	274.2	7.33	0.0009	0.0662	37.05	0.52

Table 2. Cont.

System with G3 mixture	Exp. No	Pressure (MPa)	Temperature (K)	Induction Time (IT) (min)	Gas Uptake at IT (mol/mol of Water)	Gas Uptake 60 min from IT (mol/mol of Water)	Water Recovery at 60 min from IT (%)	R <sub>20</sub> (cm <sup>3</sup> /min)
Pure Water	C1	2.5	274.2	1004.67	0.0164	0.0728	46.28	0.73
	C2	2.5	274.2	87.67	0.0042	0.0590	44.99	1.09
	C3	2.6	274.2	0.33	0.0003	0.0444	36.18	0.78
3.0 wt% NaCl solution	C4	2.6	274.2	0.00	0.0000	0.0607	49.83	0.88
	C5	2.6	274.2	0.00	0.0000	0.0464	38.12	0.84

### 3.1. Effect of 10% Propane in Nitrogen Gas Mixture (G1)

Our HyDesal approach is based on our finding that propane as a co-guest can draw dispersed water present between the interstitial pore spaces between the sand particles towards the gas phase to form hydrates [30]. Capillary action plays an important role in the migration of water through the pores of a fixed-bed medium. Sand grain size plays an important role in capillary action and hence will have a profound effect on the kinetics of hydrate formation and water recovery. Therefore, the effect of grain size on the kinetics of N<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> hydrate formation was studied. Our previous study was conducted with sand of particle size 0.21–0.29 mm only [30]. Hence, we chose four different sands with different particles size for this study. The particle sizes chosen were 0.1–0.5 mm (medium sand MS1), 0.21–0.29 mm (medium sand MS2), 0.56–1.3 mm (coarse), and 1.5–3.0 mm (granules), which were investigated for their effect on hydrate formation kinetics and water recovery.

With the above different sands, experiments were carried out at 1.5-cm bed height, 5.0 MPa, and 275.7 K with 10% propane in nitrogen and pure water. A summary of the experimental condition and results is presented in Table 2. Figure 3 shows the effect of different particle sizes on water recovery with 10% propane in nitrogen and pure water. As can be seen, MS2 sand of particle size 0.21–0.297 mm performed better compared with the other sand particles. Water recovery of 9.1% ( $\pm 2.9\%$ ), 44.5% ( $\pm 7.8\%$ ), 1.7% ( $\pm 0.6\%$ ), and 4.2% ( $\pm 1.6\%$ ) was achieved in 1 h with MS1, MS2, coarse, and granules, respectively. Water recovery within 1 h in the MS2 sand bed was 4.9, 26.2, and 10.6 times higher than MS1, coarse, and granules, respectively. Hence, MS2 of particle size 0.21–0.297 mm was chosen for subsequent investigations.

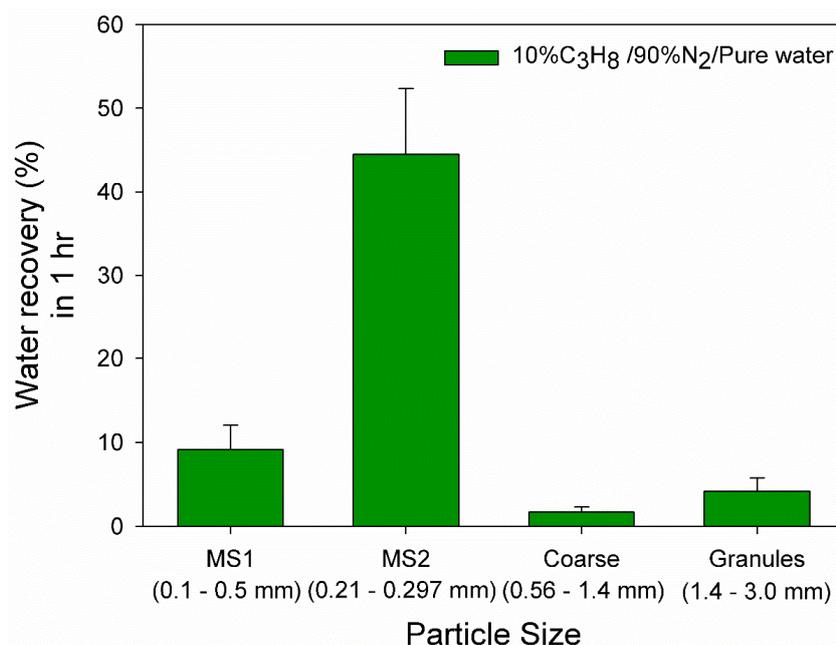
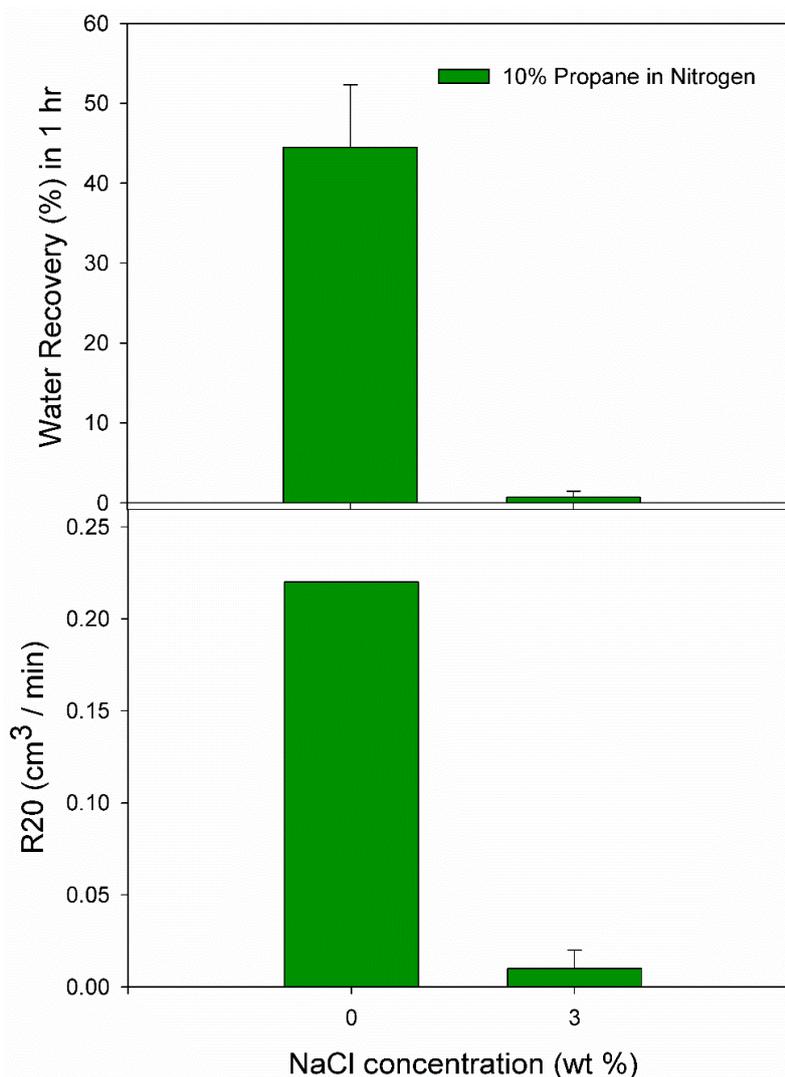


Figure 3. Effect of silica sand particle size on water recovery for 10% propane in nitrogen in pure water.

To understand the effect of the 10% propane in nitrogen (G1) gas mixture on the HyDesal process in a fixed-bed configuration, experiments were performed with pure water and 3.0 wt% NaCl solutions. The experimental temperature employed to study the effect of NaCl on water recovery experiments with pure water and 3.0 wt% NaCl solution with the G1 gas mixture were 274.2 and 275.5 K, respectively. The experimental pressure at the start of the HyDesal process was 5.0 MPa.

For experiments with pure water, the average water recovery and rate of water recovery ( $R_{20}$ ) achieved were 44.50% ( $\pm 7.83\%$ ) and 0.22 ( $\pm 0.00$ )  $\text{cm}^3/\text{s}$ , respectively. Figure 4 shows that the presence of NaCl salt drastically reduced the average water recovery and rate of water recovery ( $R_{20}$ ) to 0.68% ( $\pm 0.79\%$ ) and 0.01 ( $\pm 0.01$ )  $\text{cm}^3/\text{s}$ , respectively. Thus, it is clear that NaCl salt has a strong kinetic inhibition effect on  $\text{C}_3\text{H}_8/\text{N}_2$  hydrate formation in fixed-bed media and, hence, the gas mixture G1 is not suitable for the HyDesal process.

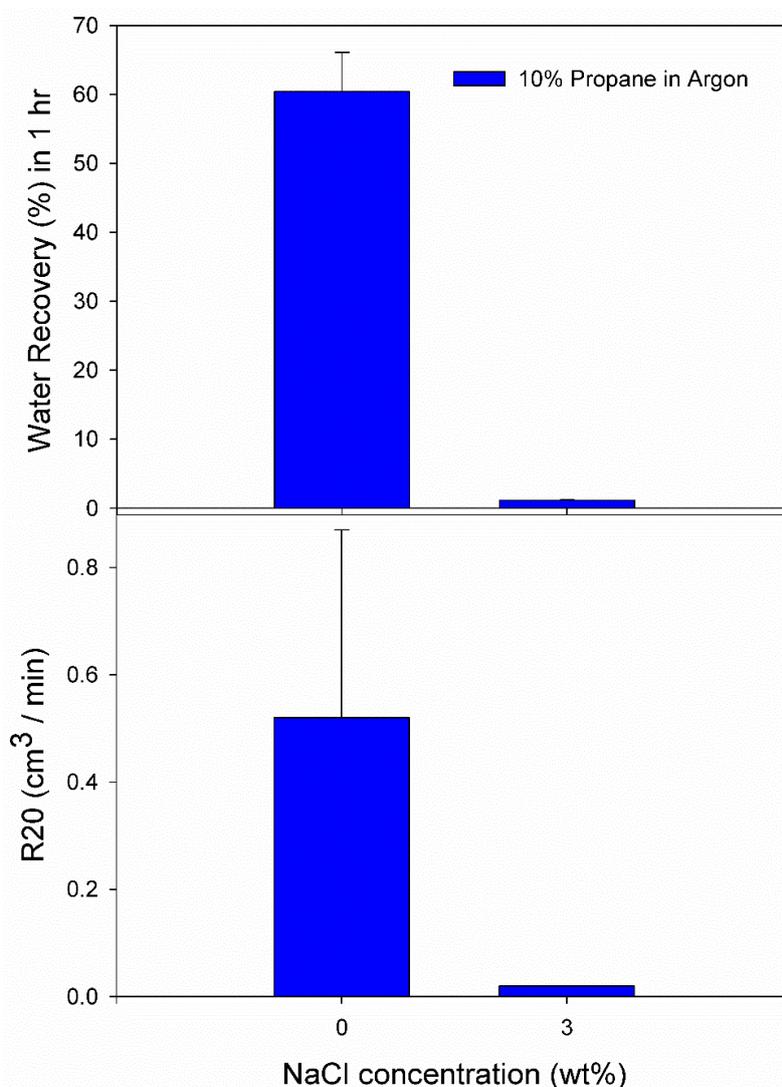


**Figure 4.** Effect of NaCl concentration on water recovery for the 10% propane in nitrogen gas mixture.

### 3.2. Effect of 10% Propane in Argon Gas Mixture (G2)

Argon gas was employed as a co-guest gas with propane to study the effect of NaCl concentration on water recovery. The hydrate phase equilibrium data for the 10% propane in argon gas mixture were generated using PVT-analysis-based Multiflash (version 4.4). Experiments were carried out with the 10% propane in argon gas mixture with pure water and 3.0 wt% NaCl at 5.0 and 5.5 MPa and 274.2 K, respectively. A summary of the experimental condition and results is presented in Table 2.

For experiments with pure water, the average water recovery and rate of water recovery ( $R_{20}$ ) achieved were 59.01% ( $\pm 5.66\%$ ) and  $0.52 (\pm 0.35) \text{ cm}^3/\text{s}$ , respectively. Figure 5 shows the impact of the addition of salt on water recovery and the rate of hydrate formation. With the increase in salt concentration, the average water recovery decreased drastically. Water recovery decreased 51.76 times for 3.0 wt% NaCl solution, respectively, when compared with experiments with pure water. For experiments with 3.0 wt%, the average water recovery in 1 h was 1.14% ( $\pm 0.07\%$ ).



**Figure 5.** Effect of NaCl concentration on water recovery for the 10% propane in argon gas mixture.

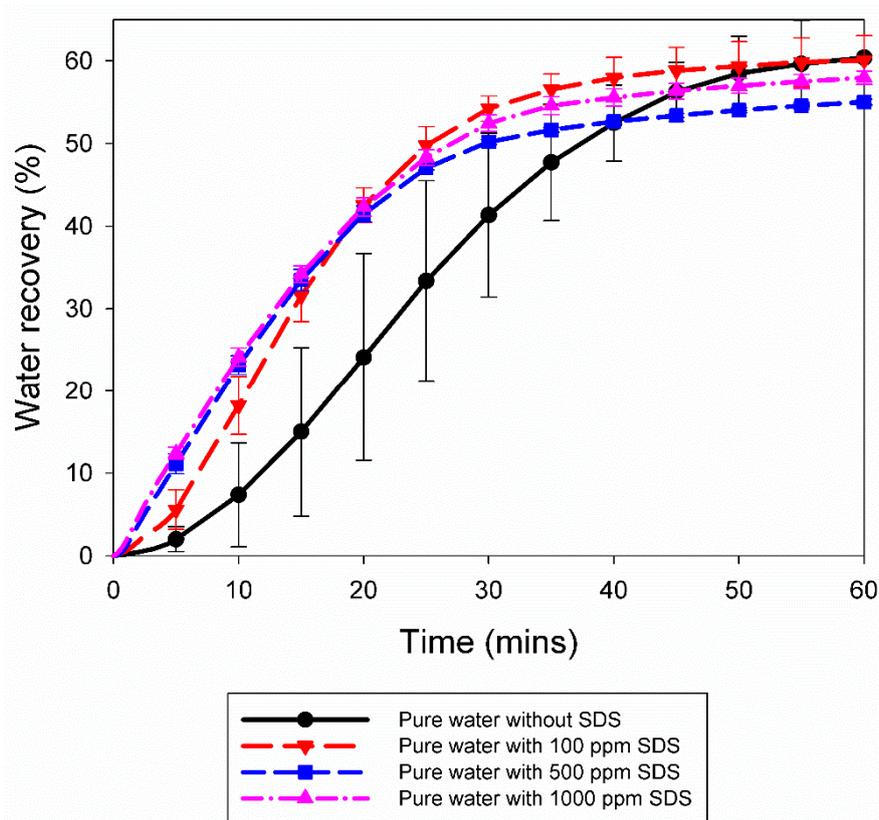
Our results show that NaCl acts as a kinetic inhibitor at 3.0 wt%, resulting in low water recovery compared with pure water. This behavior of NaCl as an inhibitor has been reported in the literature for different hydrate-forming systems [35–39]. In order to achieve better water recovery, there were two steps available: either employ a different co-guest gas with propane or use a kinetic promoter.

Kinetic promoters are compounds which can enhance the gas uptake rate for hydrate formation without affecting the thermodynamic phase equilibrium [40]. Surfactants are one such kinetic promoter which change the morphology of the formed hydrate crystals, resulting in better gas-water contact and thereby sustaining faster hydrate growth kinetics and better water recovery.

In order to improve the kinetics of hydrate formation and water recovery, we investigated the effect of SDS on water recovery in the presence of a NaCl solution of 3.0 wt% concentration. SDS, an anionic surfactant, is a well-known kinetic promoter, reported to be the best among surfactants in the

literature for different hydrate-forming systems and different reactor configurations. To understand the effect of SDS on the kinetics of hydrate formation and water recovery, the concentration of SDS was varied from 100 to 1000 ppm. The water recovery experiments were carried out with pure water and 3.0 wt% NaCl solution at the experimental conditions given in Table 2. The summary of the SDS experiments are also presented in Table 2.

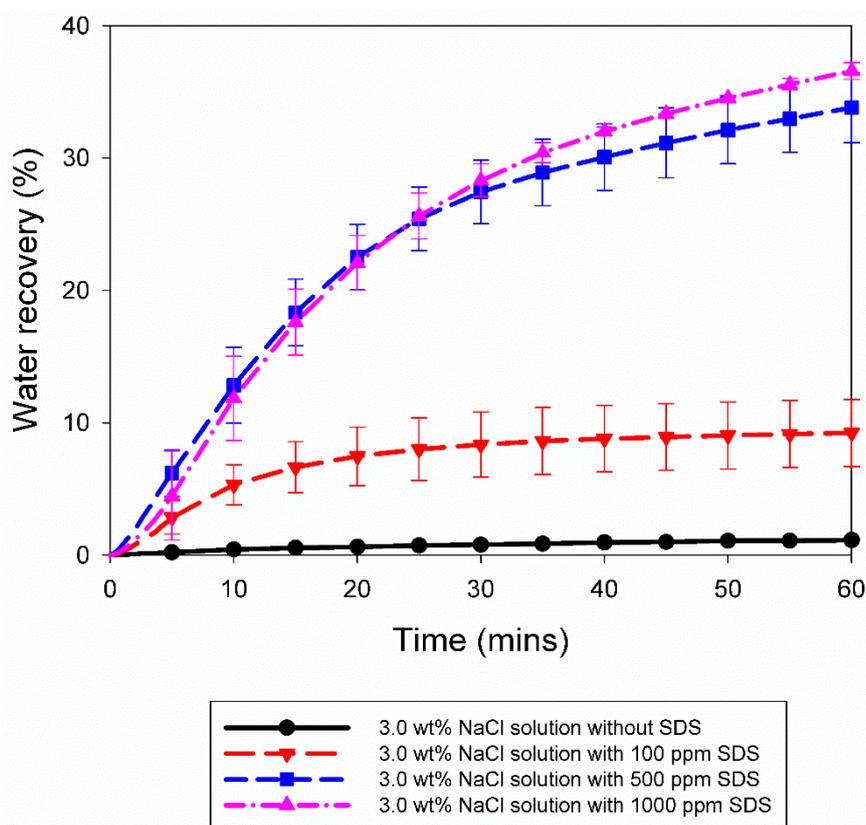
Figure 6 shows the effect of various SDS concentrations on the kinetics of hydrate formation and water recovery with the 10% propane in argon gas mixture in pure water. This graph shows the water recovered by the hydrate formation process after nucleation and, hence, time zero in the figure corresponds to the induction time. The figure shows the average water recovery with the standard deviation for every 5 min. As can be seen from the figure, with an increase in SDS concentration, the water recovery increased initially for the first 20 min from IT. At the end of 1 h from IT, the water recovery was almost the same for experiments with various concentrations of SDS in pure water and the experiment without SDS in pure water. The rate of hydrate formation ( $R_{20}$ ) for experiments with 100, 500, and 1000 ppm of SDS in pure water was 2.1, 2.25, and 2.31 times higher than that of the experiment without SDS in pure water, respectively. The rate of hydrate formation for experiments without SDS, 100, 500, and 1000 ppm of SDS were  $0.52 (\pm 0.35)$ ,  $1.08 (\pm 0.12)$ ,  $1.17 (\pm 0.05)$ , and  $1.20 (\pm 0.04) \text{ cm}^3/\text{s}$ , respectively. Experiments with further increased concentrations of SDS were not carried out since the improvement in kinetics were minimal when the SDS concentration was increased from 500 to 1000 ppm.



**Figure 6.** Effect of sodium dodecyl sulfate (SDS) concentration on water recovery in pure water with the 10% propane in argon gas mixture.

Figure 7 shows the effect of various SDS concentrations on the kinetics of hydrate formation and water recovery with the 10% propane in argon gas mixture in 3.0 wt% NaCl solution. The average water recovery increased with the increase in the concentration of SDS. The average water recovered at the end of 1 h from IT for experiments without SDS, 100, 500, and 1000 ppm SDS in 3.0 wt% NaCl solution

was 1.14% ( $\pm 0.07\%$ ), 9.25% ( $\pm 2.54\%$ ), 33.80% ( $\pm 0.62\%$ ), and 36.58% ( $\pm 0.66\%$ ), respectively. Although the water recovery for the 1000 ppm of SDS experiment at the end of 1 h was higher compared with the 500 ppm of SDS experiment, the initial rate of hydrate formation was slow. The rate of hydrate formation ( $R_{20}$ ) for 100, 500, and 1000 ppm of SDS in 3.0 wt% NaCl solution were 0.23 ( $\pm 0.07$ ), 0.62 ( $\pm 0.10$ ), and 0.59 ( $\pm 0.10$ )  $\text{cm}^3/\text{s}$ , respectively.



**Figure 7.** Effect of SDS concentration on water recovery in 3.0 wt% NaCl solution with the 10% propane in argon gas mixture.

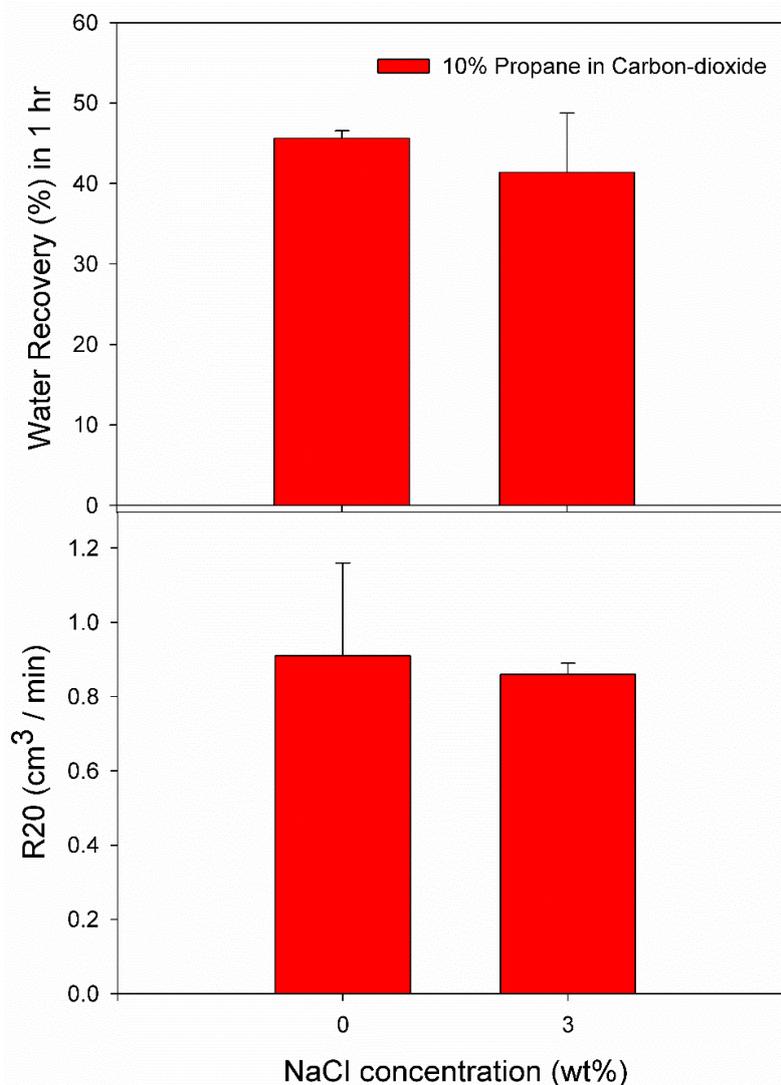
Kinetic experiments with the 10% propane in argon gas mixture show that NaCl acts as a kinetic inhibitor, resulting in low water recovery. The addition of SDS, a kinetic promoter, improves the water recovery and rate of hydrate formation. SDS present in the solution may be adsorbed onto the hydrate crystals. Hence, after removal of hydrate crystals and dissociation, the produced water samples need to be tested for the presence of SDS and its quantity. If present, it needs to be removed via a secondary treatment step, since surfactants such as SDS are known to significantly contribute to the toxicity of some effluents and are harmful to humans, marine life, and the environment. It would be desirable to identify suitable eco-friendly kinetic promoters such as amino acids [41–43], starch [44,45], biosurfactants [46], or a different co-guest gas with propane in the future for the HyDesal process.

### 3.3. Effect of 10% Propane in Carbon Dioxide Gas Mixture (G3)

It has been reported earlier that the presence of salts in porous media has no impact on the kinetics of  $\text{CO}_2$  gas hydrate formation [47]. Hence, propane in a carbon dioxide gas mixture was employed in this study. The experimental conditions employed in this study with pure water and 3.0 wt% NaCl solution with the 10% propane in carbon dioxide gas mixture were 274.2 K and 2.5 MPa, and 274.2 K and 2.6 MPa, respectively. A summary of the experimental condition and results is presented in Table 2.

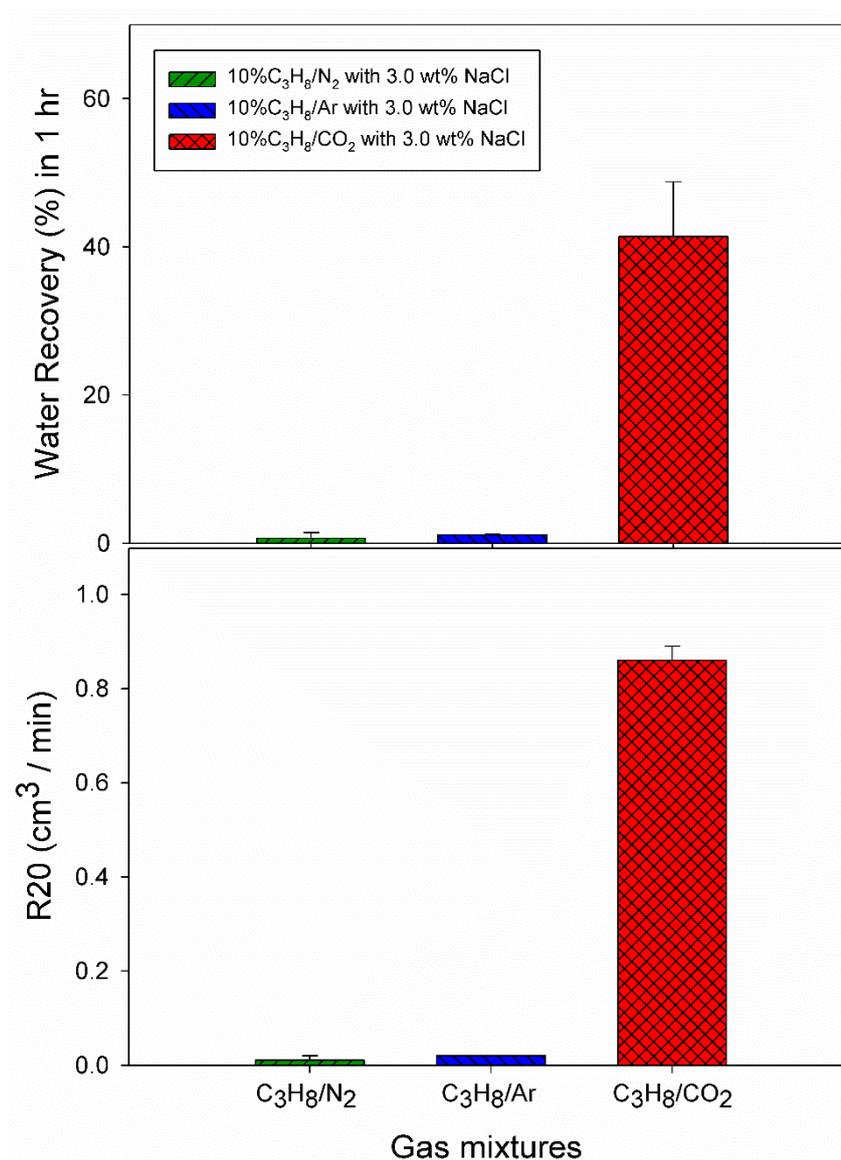
Figure 8 shows the effect of salt on water recovery with the 10% propane in carbon dioxide gas mixture. In pure water, the average water recovery and rate of hydrate formation ( $R_{20}$ ) achieved were

45.63% ( $\pm 0.91\%$ ) and  $0.91 (\pm 0.25) \text{ cm}^3/\text{s}$ . In the presence of 3.0 wt% NaCl, the average water recovery and rate of hydrate formation ( $R_{20}$ ) achieved were 41.38% ( $\pm 7.39\%$ ) and  $0.83 (\pm 0.05) \text{ cm}^3/\text{s}$ . Water recovery only reduced by 10% in the presence of NaCl salt, suggesting reduced or no kinetic inhibition effect on hydrate formation and water recovery.



**Figure 8.** Effect of NaCl concentration on water recovery for 10% propane in carbon dioxide.

A comparison of water recovery from 3.0 wt% NaCl solution with G1, G2, and G3 gas mixtures is presented in Figure 9. Water recovery with the  $\text{C}_3\text{H}_8/\text{CO}_2$  gas mixture in 1 h was 60 and 36.39 times faster compared with  $\text{C}_3\text{H}_8/\text{N}_2$  and  $\text{C}_3\text{H}_8/\text{Ar}$ , respectively. The 10% propane in carbon dioxide gas mixture showed the highest water recovery of 41.38% ( $\pm 7.39\%$ ). Similarly, the rate of hydrate formation ( $R_{20}$ ) from 3.0 wt% NaCl solution for the G3 gas mixture was 83 and 41.5 times that of the G1 and G2 gas mixtures, respectively. The G1, G2, and G3 gas mixtures had an average rate of hydrate formation ( $R_{20}$ ) of  $0.01 (\pm 0.01)$ ,  $0.02 (\pm 0.00)$ , and  $0.86 (\pm 0.03) \text{ cm}^3/\text{min}$ , respectively. From experiments conducted with pure water and 3 wt% NaCl solution with different gas mixtures, it is clear that propane in carbon dioxide yielded higher water recovery compared with the other gas mixtures employed. Hence, propane/carbon dioxide was chosen as the preferred gas mixture.



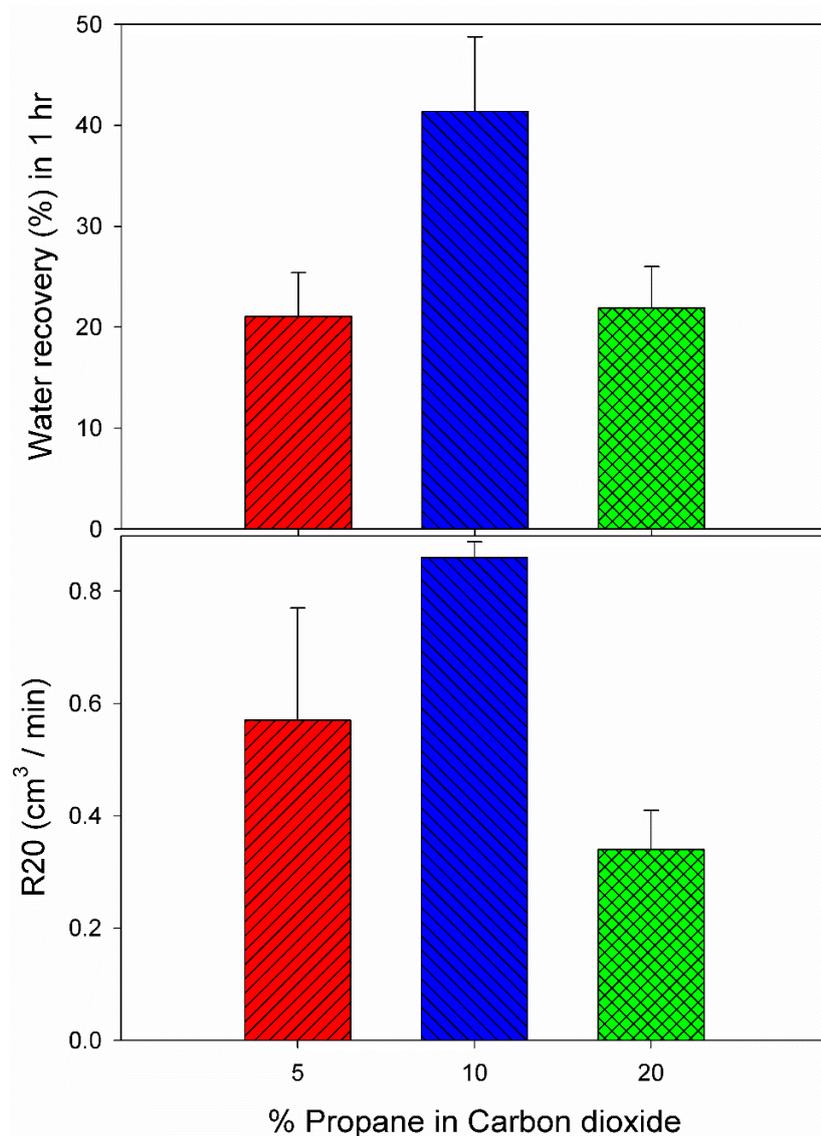
**Figure 9.** Comparison of water recovery with different gas mixtures and 3.0 wt% NaCl aqueous solution.

Further studies were carried out to optimize the concentration of propane in carbon dioxide to maximize water recovery from salt water. In this study, four different propane concentrations in carbon dioxide were employed, namely, 2.5%, 5%, 10%, and 20%. Experiments were carried out at a constant temperature of 274.2 K and a driving force  $\Delta P$  of 1.97 MPa with the gas mixture with different concentrations of propane and 3 wt% NaCl solution. Experimental conditions employed for this investigation, such as the composition of the gas mixture, pressure, temperature, and results, are presented in Table 3. Multiple experiments with 2.5% propane in carbon dioxide gas did not nucleate for several days. Figure 10 shows the effect of varying concentrations of propane in carbon dioxide on water recovery from 3.0 wt% NaCl solution. Water recovery with 3.0 wt% NaCl solution increased as the propane concentration increased from 5% to 10%. However, water recovery reduced when the concentration of propane was further increased to 20%. Hence, we did not study the higher concentration of propane gas mixtures with carbon dioxide. Water recovery with 10% propane in carbon dioxide was about two times higher than water recovery with 5% and 20% propane in carbon dioxide gas mixtures. Figure 10 shows that water recovery with 3.0 wt% NaCl solution obtained in this study was 21.06% ( $\pm 4.34\%$ ), 41.38% ( $\pm 7.39\%$ ), and 21.89% ( $\pm 4.13\%$ ) for 5%, 10%, and 20% propane in carbon dioxide, respectively. Also, 10% propane in carbon dioxide showed the highest rate of hydrate

formation ( $R_{20}$ ). Hence, 10% propane in carbon dioxide was chosen as the hydrate for further studies of the HyDesal process.

**Table 3.** Summary of experimental conditions and results with different concentrations of propane in carbon dioxide.

System with (%) Propane in Carbon Dioxide	Exp. No	Pressure (MPa)	Temperature (K)	Induction Time (IT) (min)	Gas Uptake at IT (mol/mol of Water)	Gas Uptake 60 min from IT (mol/mol of Water)	Water Recovery at 60 min from IT (%)	$R_{20}$ ( $\text{cm}^3/\text{min}$ )
5	C6	2.85	274.2	85.00	0.0064	0.0391	24.13	0.54
5	C7	2.85	274.2	1042.00	0.0147	0.0391	18	0.39
20	C8	2.0	274.2	2171.00	0.0142	0.0359	18.97	0.29
20	C9	2.0	274.2	105.67	0.0051	0.0335	24.82	0.39



**Figure 10.** Effect of propane composition in carbon dioxide with 3.0 wt% NaCl aqueous solution.

#### 4. Conclusions

Water is a key resource for sustainable development and plays a crucial role in human development. Desalination is one of the most promising technologies to mitigate the emerging water crisis. MSF and reverse osmosis are two of the most widely employed desalination technologies

in the world; however, they are energy intensive. HyDesal is a potential energy-efficient desalination technology that could strengthen the energy–water nexus. In this study, we evaluated the effect of 10% propane in three different gas mixtures as hydrate formers for the HyDesal process based on the fixed-bed approach. With the 10% propane in nitrogen and 10% propane in argon gas mixtures, the water recovery achieved was very low (~2%) in the presence of 3 wt% NaCl in the solution. To improve the water recovery and kinetics of hydrate formation, SDS, a kinetic promoter, was added and its effect was evaluated at different concentrations in the 10% propane in argon gas mixture. The addition of SDS improved the kinetics and water recovery significantly. With the 10% propane in carbon dioxide gas mixture, the reduction in water recovery due to the presence of salt was found to be less than 10%. Hence, the 10% propane in carbon dioxide gas mixture is suitable for the HyDesal process. However, further studies to evaluate the salt rejection rate and process scalability need to be carried out. The current experimental setup used in this study does not have any provision to extract the hydrate crystals. We are currently developing a new system that will enable us to extract the produced water to be characterized for composition analysis and subjected to post-treatment for the removal of surfactants.

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