Preventing Gas Hydrate Agglomeration with Polymer Hydrogels

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ABSTRACT: This study investigates the potential to use hydrogel particles for simultaneously inhibiting the formation of gas hydrates and preventing their agglomeration after they form. The particles were synthesized specifically for this application and swell to a controlled degree in water and remain discrete. A stirred autoclave was used to determine the hydrate onset time, subcooling temperature, initial growth rate, and torque changes during hydrate formation with the water absorbed in the hydrogel particles. The system also included a liquid decane phase which simulates a condensate. In comparison to water (with no particles) + decane mixture, the hydrate onset time was delayed and the subcooling temperature increases. In addition, both the initial growth rate and hydrate fraction were lower for polymer hydrogels. Stable torque is observed for polymer hydrogels while there are sharp increases in torque before the stirrer stops for water + decane mixture, suggesting that the hydrogel particles (and hence hydrate particles) are well-dispersed in the decane phase. Experimental observations show that the hydrates form as a surface shell on the hydrogel particles and grow inward. The hydrate shell-covered hydrogel particles do not agglomerate or deposit under stirring because the particles remain discrete due to the polymer network. In order to further investigate the ability of the hydrogel particles to prevent agglomeration, the stirring was stopped after confirming the formation of hydrate was complete. After 4 h, additional hydrate formation was negligible, and no serious torque increase or stirrer blockage was observed when the stirring was restarted. These results suggest that the synthesized polymer in this work has the potential to prevent hydrate agglomeration without using surfactants, which is a new concept.

INTRODUCTION

Gas hydrates are nonstoichiometric crystalline compounds that are classified into three structural families of cubic structure I, cubic structure II, and hexagonal structure H.1 Gas hydrate formation is a serious concern in the oil and gas industry because it can block flow lines upon hydrate formation.1,2 Offshore flow lines transporting hydrocarbons have to be operated very carefully to avoid the formation of gas hydrates. For many years, the industrial practice to prevent hydrate-related risks has been to inject thermodynamic hydrate inhibitors (THIs) at the wellhead, commonly methanol or monoethylene glycol (MEG).3,4 However, hydrate prevention strategies are now moving toward hydrate risk management, where the hydrates are allowed to form, but the formation is either delayed or the agglomeration is prevented to avoid pipeline blockage.1–4

Alternative materials exist for hydrate prevention including kinetic hydrate inhibitors (KHIs) and anti agglomerants (AAs). KHIs are water-soluble polymers that delay the formation of hydrate crystals.1,5 These include homo- and copolymers of the N-vinylpyrrolidone and N-vinyl caprolactam.5–8 KHIs have been applied in field operation successfully; however, from an industry point of view, they are considered to be effective at subcoolings only up to approximately 14 °C. Laboratory evaluation of KHIs presents subcoolings as high as 17 to 19 °C, but it depends on the fluid characteristics, ambient temperature, cooling process, among others. There have been many literature examples that suggest the relevant procedure for evaluating the performance of KHIs. The ability to delay the hydrate onset in the presence of KHIs can be evaluated by measuring the onset time. However, due to the stochastic nature of hydrate formation, the measurement need to be carried out multiple times. In addition, their performance can be affected by the presence of other chemicals such as corrosion inhibitors.4,9,10 Anti agglomerants (AAs) are surfactants which suspend the water phase as small droplets, ensuring that the droplets are converted to small hydrate particles when the temperature decreases below hydrate equilibrium condition. The hydrate particles are well-dispersed in the liquid phase, thus preventing hydrate blockage in subsea flowlines.4,5,11,12 The polar headgroup of the surfactant is hydrate-phillic and disrupts the hydrate growth. The hydrophobic tails assist with dispersing the hydrate crystals in the liquid hydrocarbon phase. Quaternary ammonium groups are effective for the hydrate-phillic heads, and AAs based on quaternary ammonium surfactant have been deployed in a number of fields.5,10,12 The technical drawbacks of using AAs is their environmental impact—they are ineffective at low condensate levels, and their performance is dependent on the composition of the fluids. For example, field application of diester quaternary AA has been canceled due to its insufficient biodegradation.5 Efforts have focused on reducing the environmental impact of quaternary AAs by adding inorganic salts to the produced water in combination with anionic polymers, which might induce other chemical compatibility issues with other production chemicals.13–15 In general, the water-cut for AAs should be below 50

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to 75%; otherwise, the liquid hydrocarbon phase becomes too viscous to transport. However, the use of AAs is an effective way of managing the risk of hydrate plug formation because they can be used for both steady-state and transient operation, but there is a need for new AA or strategies to prevent agglomeration of hydrates.

AAs do not prevent hydrate formation but are effective in pipelines because the hydrate remains as a transportable slurry of particles dispersed in the liquid hydrocarbon phase. The water droplets are well-dispersed in the presence of AAs and are converted to hydrate particles readily as AAs increase the surface-to-volume ratio of the water phase that reduce mass transfer limitation. Recently, there have been attempts to use superabsorbent polymer networks, such as poly(acrylic acid) sodium salt (PSA) for improving the kinetics of H₂ enclathration within gas hydrates. The PSA particles are swelled by absorbing aqueous THF solution, and particulate gel materials are produced that do not agglomerate during hydrate formation. The same authors also reported that water-swellable polymers can be effective in accelerating the formation of methane hydrates. However, the application of water-swellable polymers to hydrate inhibition has not been investigated and could offer a surfactant-free approach that overcome many of the issues associated with surfactant-based AAs.

Here we investigate the possibility of using hydrogel particles as a method for preventing agglomeration of hydrate particles due to the discrete nature of the particles. As such, the mechanism for this is different than conventional anti-agglomerants which utilize surface active species, and this term is avoided herein. In addition, the particles are held together by a polymer network, and this backbone may also influence the hydrate formation. Figure 1 illustrates schematically the formation of the hydrogel particles from water-swellable polymer networks (Figure 1A,B) and their conversion into a transportable hydrate slurry (Figure 1C) that does not agglomerate when the stirring is stopped (Figure 1D). The dried polymer particles (structure shown in Figure 1E and microscopy image in Figure 1F) contact the aqueous phase and swell to a controlled degree to form hydrogel particles. It is worth noting that this is fully reversible, and the particles can be deswollen using a water-miscible solvent that cannot dissolve the polymers (e.g., ethanol).

The commercially available water-swellable polymers (e.g., PSA) that have been reported previously can also be used for forming the hydrogel particles. However, we found that these superabsorbent polymers (SAPs) continue to swell in the presence of water, have limited ability to suspend in a liquid hydrocarbon phase, and could not retain water through multiple cycles. Therefore, we synthesized hydrogel particles based on polyacrylamide (PAM), where the swelling capacity was accurately controlled by controlling the structure of the polymer. The ability of the particles to prevent agglomeration of hydrates is explored by exposing them to synthetic natural gas and a liquid hydrocarbon at high pressures and low temperatures. The hydrate onset time, subcooling temperature, and gas consumption rates in the presence for hydrogel particles from the measurements of temperature and pressure changes during hydrate formation are included. The torque was also monitored and used to discuss the ability of the hydrogels to prevent agglomeration of hydrates.

### SYNTHESIS OF WATER-SWELLABLE POLYMER NETWORK

#### Materials. All of the chemicals for the hydrogel particle synthesis were purchased from Sigma-Aldrich and were used as received. These chemicals are the following: polyacrylamide-co-acrylic acid partial sodium salt (PAM-co-AA), $M_w$ 520 000, $M_n$ 150 000, typical acrylamide level 80%; N-(3-(dimethylamino)-propyl)-N’-ethylenediamino hydrochloride (EDC, commercial grade); N-hydroxysuccinimide (NHS, 98%); and 1,2-diamino ethane (EDA >99%).
Synthesis of the Hydrogel Particles. The synthesis of hydrogel particles has been described previously and involves the carbodiimide-mediated cross-linking (CMC) reaction of PAM-co-AA in an inverse suspension.19 The particles are referred to as CMC-PAM-co-AA. Briefly, EDC (0.3993g) was dissolved in 0.5 mL of distilled water and added to 5 mL of an aqueous solution of PAM-co-AA (15 wt %, weight of polymer to water), and the resulting highly viscous solution was mixed. After 3 min, 0.24 g of NHS dissolved in 0.5 mL of distilled water was added, and at this stage, the viscosity of the solution decreased. This activated polymer solution was then added dropwise over a 5 min period to 95 mL of heptane containing 5 wt % Span 60 in a 250 mL round-bottom flask heated to 50 °C. The solution was continuously stirred at 1000 rpm using a magnetic stir bar (egg-shaped; 32 × 16 mm) to provoke droplet generation. This mixture was termed an inverse suspension of activated polymer and consisted of an aqueous polymer phase suspended as droplets in heptane. After 5 min, the cross-linker (0.063g EDA), dissolved in 0.5 mL of water, was added dropwise to the inverse suspension which initiates the CMC reaction. The reaction was complete after only 40 min at 50 °C, and the resulting hydrogel microspheres were denoted CMC-PAM-co-AA. They were isolated by filtering through a filter funnel that was heated to 60 °C. The particles were washed with heptane and were swelled further by mixing in excess water (250 mL) for 2 h. They were filtered to remove any free water, the amount of polymer in particles was 5% (w/v, polymer/water), and at this concentration, there was no free dispersed in the hydrocarbon phase. However, in the system without hydrogels (Figure 2B), the hydrate is deposited on the walls of the vessel, but with hydrogels, the hydrate is dispersed in the hydrocarbon phase.

Hydrate inhibition experiments were carried out in a high-pressure autoclave system shown in Figure 3. The cell is made of 316 SUS and has an inner diameter of 75 mm, height of 125 mm, and total volume for fluids of 460 cm³. The maximum working pressure of the cell is 150 bar. Pressure transducers and pressure gauges are mounted to measure the pressure (accuracy was 0.1 bar). The temperature of the liquid phase is measured using a thermocouple with an accuracy of 0.1 °C. The cell is located in a refrigerator to control and maintain the temperature of the cell. Video and snapshot recordings were collected during the experiment using a CCD camera coupled with a borscope when using a magnet stir bar; however, the phase behavior could not be observed when the overhead stirrer was used to measure torque changes. Temperature, pressure, images, and torque data were recorded using a data acquisition system.

An initial experiment was carried out with a magnet stir bar, which allowed for the phase behavior to be observed during the hydrate formation in the presence of hydrogel particles and to study their effect on the hydrate equilibrium. A continuous cooling/heating technique was used with a rate of 0.1 °C/h to avoid excessive dissociation of the hydrates. The details of hydrate equilibrium measurements were discussed in our previous work.21,22

The ability of the hydrogel particles to prevent agglomeration of the hydrates was carried out with an autoclave equipped with an overhead stirrer. The aqueous mixture of decane and polymer hydrogels was transferred into the cell and the cell was pressurized to around 100 bar at 20.0 °C while stirring the liquid phase at 400 rpm for at least 2 h to saturate the decane with synthetic natural gas. When the cell pressure reached steady-state conditions, the valves between the cell and gas cylinders were closed. All experiments were conducted under isochoric conditions using constant cooling. The experiments under isochoric conditions have been widely used to investigate the hydrate formation characteristics with or without hydrate inhibitors.23 The temperature was decreased from 20.0 to 4.0 °C continuously with 400 rpm stirring. For all experiments, the time required for the cell to reach 4.0 °C was set to 60 min.

Measurement of hydrate onset conditions needs to be repeated to obtain the averaged value due to the stochastic nature of hydrate formation. In this work, a total of five experiments were carried out in the presence of hydrogel particles and decane. Other experiments were performed for water + decane mixture at a water cut of 20% to investigate the hydrate formation characteristics without any added particles. Figure 4 shows an example of pressure, temperature, and torque changes during the experiment with water + decane mixture. Hydrate formation was accompanied by a sharp decrease in pressure due to consumption of gas while forming hydrates as shown in Figure 4b. The performance of the hydrogel particles in preventing agglomeration of the hydrate was evaluated using torque changes. When hydrate particles in the slurry agglomerate and form a plug, the torque rises sharply and then drops due to stoppage of overhead stirrer as shown in Figure 4c. The synthesized hydrogel particles were compared against a commercial superabsorbent polymer hydrogel (SAP). The hydrate formation was also experimentally investigated for both systems. The hydrogels used in this study were swelled to 5% (w/v, polymer/water), and at this concentration, there was no free water present. The water cut in each experiment was 20%, and when

Table 1. Composition of Synthetic Natural Gas

<table>
<thead>
<tr>
<th>components</th>
<th>composition (mol %)</th>
</tr>
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<tbody>
<tr>
<td>CH₄</td>
<td>84.22</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>6.79</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>3.12</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>0.41</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>0.59</td>
</tr>
<tr>
<td>i-C₅H₁₂</td>
<td>0.04</td>
</tr>
<tr>
<td>n-C₅H₁₂</td>
<td>0.02</td>
</tr>
<tr>
<td>C₆+</td>
<td>0.01</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.19</td>
</tr>
<tr>
<td>N₂</td>
<td>5.29</td>
</tr>
</tbody>
</table>

The aqueous phase was deionized water, and the liquid hydrocarbon phase was decane (Sigma-Aldrich). Cross-linked poly(acrylic acid) sodium salt was used as a commercial super absorbent polymer (SAP) without further purification. The water cut was typically 20% in all experiments,12 and the total volume of the liquid phase in the cell was 200 mL. The procedure for synthesizing and swelling the hydrogel to be tested is outlined above. The concentration of the polymer in the hydrogel was 5.0 wt % (5 wt % of polymer to 95% water) as determined gravimetrically. The hydrogel particles were then transferred into the autoclave cell to the desired water cut, which was 20% in this work, and mixed with decane. The polymer network and particulate nature of the hydrogels limits the swelling capacity and allows for dispersion in the liquid hydrocarbon phase. The diameter of each hydrogel particle was approximately 993 μm and was measured from optical images as described above. Figure 2 shows top-down images of experiments with water only (no hydrogels, Figure 2A,B) and polymer hydrogels both dispersed in liquid hydrocarbon phase. Figure 2A,C are before commencing hydrate formation experiment and after formation (Figure 2B,D). As can be seen before hydrate formation, both systems look similar to the water (Figure 2A) or hydrogels (Figure 2C) being dispersed in the hydrocarbon phase.
the commercial SAP was used, the amount of polymer required to absorb the same amount of water (without free water) was much lower (0.5%; w/v, polymer/water), which was clear from visual observations. Commercial SAPs are designed to have superior swelling capacity, whereas the swelling capacity of the hydrogels in this study were limited. For example, the maximum uptake for the synthesized polymer was 32 g/g (water/dry polymer), and the commercial SAP was >160 g/g under the same conditions. Controlled swelling which is limited will benefit the application of such materials because it will prevent plugging due to overswelling. As such, the concentration of SAP to disperse the water as hydrogel particles in decane was 0.5 wt %.

■ RESULTS AND DISCUSSION

Hydrate Formation for Aqueous PAM-co-AA Solutions. Polyacrylamide (PAM)-based hydrogels are one of the most widespread synthetic hydrogel analogues, and we selected PAM-co-AA as a base polymer for synthesizing the cross-linked hydrogel particles in this work. However, we first investigated the effects that the linear base polymer (not in particle format) had on the formation of gas hydrates using the above-described

Figure 2. Images of water (A and B) or polymer hydrogels (C and D) dispersed in decane (A and C) before hydrate formation and (B and D) after hydrate formation. All of the systems contain a magnetic stir bar, which can be observed, and the bright rings at the center are the light reflections from the boroscope.

Figure 3. Schematic diagram of the high-pressure autoclave system.

Figure 4. Representative example of temperature, pressure, and torque changes during the cooling of water, decane, and a natural gas mixture: (upper panel) temperature changes, (middle panel) pressure changes, and (lower panel) torque changes.
constant cooling method. Hydrate onset time, subcooling temperature, and initial growth rate are presented in Table 2. Figure 5 shows the moles of gas consumed after hydrate onset for pure water and both 0.5 and 5.0 wt % PAM-co-AA solutions.

The hydrate onset time was 15.7 min when 0.5 wt % of linear PAM-co-AA was added; however, it decreased to 11.1 min when the concentration of PAM-co-AA was increased to 5.0 wt %. It is worth noting that the viscosity of the higher concentration PAM-co-AA solutions is much higher. In this study, we decided to focus on the initial growth stage of hydrate particles in the presence of hydrogel particles, where the gas consumption rate was observed as a linear curve with a slope of the initial growth rate, \( r_{\text{init}} \), as the mass transfer is the limiting step for hydrate formation. The initial gas consumption rates are very close for pure water, 0.5 wt %, and 5.0 wt % PAM-co-AA solutions, which indicates that the PAM-co-AA has no significant effect on the growth of hydrate particles in aqueous phase. The hydrate fraction in the aqueous phase was calculated from the moles of gas consumed during the formation of hydrate and will be discussed in detail later. The hydrate fraction for pure water is 0.72, and it slightly decreases to 0.59 when adding 5.0 wt % of PAM-co-AA. These results clearly indicate that the PAM-co-AA, the base polymer, has no significant effect on the onset and growth of gas hydrates in aqueous phase particularly at higher concentrations. The hydrate particles are free to grow and deposit on reactor wall in the PAM-co-AA solution just as in pure water. It is worth noting that in this study the polymer network has not been optimized as a KHI and will be investigated further. PAM was selected because it can be used to form hydrogel particles and is one of the most common synthetic hydrogels. The formation of hydrates with hydrogel particles formed by cross-linking the PAM-co-AA was also investigated.

<table>
<thead>
<tr>
<th>System</th>
<th>( t_{\text{init}} ) (min)</th>
<th>( T_{\text{subcool}} ) (°C)</th>
<th>( r_{\text{init}} ) (mmol/min)</th>
<th>Hydrate fraction ( \Phi_{\text{hydr}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>11.4 (±3.5)</td>
<td>5.8 (±1.5)</td>
<td>0.6 (±0.2)</td>
<td>0.68 (±0.07)</td>
</tr>
<tr>
<td>0.5 wt % PAM-co-AA solution</td>
<td>15.7 (±1.5)</td>
<td>7.6 (±0.6)</td>
<td>0.7 (±0.1)</td>
<td>0.74 (±0.01)</td>
</tr>
<tr>
<td>5.0 wt % PAM-co-AA solution</td>
<td>11.1 (±0.5)</td>
<td>5.4 (±0.3)</td>
<td>0.7 (±0.1)</td>
<td>0.53 (±0.02)</td>
</tr>
</tbody>
</table>

*Standard deviation of each value is shown in parentheses.

Hydrate Formation for Hydrogel Particles and Decane Mixture. To the best of our knowledge, the effect of hydrogel particles on hydrate equilibrium conditions has not been investigated, especially in the presence of liquid hydrocarbons. To experimentally investigate this effect, pressure and temperature profiles were generated while performing continuous cooling and heating cycles.

Figure 6 shows the pressure—temperature (P–T) profile indicating the formation and dissociation of hydrates within the hydrogel particles. Hydrate decomposition was complete at 90.7 bar and 15.4 °C where the heating curve meets the cooling curve. The temperature and pressure at this condition was defined as the hydrate equilibrium condition for hydrogel particles. The hydrate equilibrium curve was also calculated for a water, decane, and synthetic natural gas mixture (without hydrogel particles) using MultiFlash software\(^\text{23}\) (version 4.4) and is included in Figure 5 with the obtained P–T conditions. The Cubic Plus Association (CPA) equation of state is used along with the transport property models: Lohrenz–Bray–Clark (LBC) model for viscosity, Chung–Lee–Starling model for thermal conductivity, and McLeod–Sugden model for interfacial tension.\(^\text{24–27}\) The calculated equilibrium temperature at 90.7 bar was 15.3 °C for the water + decane + synthetic natural gas system, which is only 0.1 °C lower than the measured equilibrium temperature for the hydrogel particles. Hydrate equilibrium measurements were carried out again by increasing the initial pressure, and the measured equilibrium temperature at 104.1 bar was 16.2 °C, which is also in good agreement with the calculated equilibrium conditions. Therefore, the hydrogel particles synthesized for this work do not affect the hydrate equilibrium conditions in the temperature range.
and pressure range used in this study. Further data will be collected on the hydrate equilibrium conditions for the hydrogel particles in the near future.

The hydrogel particles were tested as a kinetic hydrate inhibitor and as a method to prevent agglomeration of the hydrates using the standard cooling method. The initial pressure and temperature were set to 100 bar and 20 °C. Five experiments were carried out to obtain the average hydrate onset conditions for the hydrogel particles in decane. The water cut was 20%, and the dried polymer was added to this water (5% w/w based on water). Figure 7a shows pressure profiles with time during hydrate formation for hydrogel particles, decane, and the synthetic natural gas mixture. The hydrate onset conditions were clearly detected from a sharp decrease in pressure. The corresponding temperature was recorded as the hydrate onset temperature. The subcooling temperature is defined by the difference between the hydrate onset temperature and the hydrate equilibrium temperature, which is indicative of the subcooling temperature before hydrate formation in the presence of the hydrogel particles. The hydrate onset time is a hydrate-free period for the hydrogel particles because the temperature becomes lower than hydrate equilibrium temperature. Table 3 shows that the average hydrate onset time was 38.4 min, and the average subcooling temperature was 9.5 °C.

The moles of gas consumed during hydrate formation was calculated from the pressure difference between the measurement moment and calculated pressure with the assumption that no hydrate was formed. This procedure has been suggested in the literature as a method to study hydrate formation in a flow wheel apparatus as well as an autoclave systems. Thus

\[ \Delta n_{H,t} = \left( \frac{P_{\text{cal}}V_{\text{cell}}}{zRT} \right)_t - \left( \frac{P_{\exp}V_{\text{cell}}}{zRT} \right)_t \]

where \( \Delta n_{H,t} \) is the moles of gas consumed for hydrate formation at a given time, \( P_{\text{cal}} \) is the calculated pressure assuming no hydrate, \( P_{\exp} \) is the measured pressure, \( V_{\text{cell}} \) is the volume of gas phase, \( z \) is the compressibility factor calculated using Cubic Plus Association equation of state, and \( T \) is the temperature of the gas phase. A typical gas consumption curve shows linear gas consumption during initial growth stage, as the hydrate formation is mainly controlled by mass transfer. Figure 7b shows gas consumption profiles for the polymer hydrogels, decane, and synthetic natural gas system we studied. It is noted that the initial growth rates of each experiment are close, and an average value of the growth rates is 0.26 mmol/min with a standard deviation of 0.03. The hydrate fraction, \( \phi_{\text{hyd}} \) in the liquid phase at the end of each experiment is calculated using the hydration number of 6.5 and the following equation:

\[ \phi_{\text{hyd}} = \frac{V_{\text{hyd}}}{V_{\text{hyd}} + (V_w - V_{w,\text{conv}})} \]

where \( V_w \) is the volume of water, \( V_{w,\text{conv}} \) is the volume of the water converted to hydrate, and \( V_{\text{hyd}} \) is the volume of hydrate calculated from the molecular weight and density of hydrates calculated at a given time. These equations can be used to describe the hydrate plugging potential using the relationship between the hydrate fraction and the pressure drop in a flowloop. The hydrate number, 6.5, was calculated and averaged from cage occupancies of gas molecules in 512 and 51264 cages of structure II formed from pure water and

![Figure 7](dx.doi.org/10.1021/ef500613m | Energy Fuels 2014, 28, 4409–4420)
The final hydrate fractions were in the range between 0.21 and 0.25, leading to an average value of 0.23 (standard deviation of 0.02). These results indicate that hydrates form in a well-controlled manner on the surface of each hydrogel particle, possibly as a hydrate shell. Inside the hydrate-shell-covered hydrogel particles, the hydrate film would continue to grow inward until the mass transfer of gas molecules through the hydrate shell becomes limited. This will depend on the particle size which can be controlled depending on the synthesis method employed for the polymer hydrogels. These hydrate particles may agglomerate or deposit on the wall, and therefore, torque measurements were carried out to investigate the hydrate plugging potential of hydrate-shell-covered hydrogel particles.

To avoid formation of a hydrate plug, extensive research efforts have focused on developing AAs. Rocking cells or autoclaves have been used to evaluate AAs, and in particular, torque measurements can be used with a stirred autoclave. For a good AA, the torque remains constant after hydrate formation. Conversely, an ineffective AA would result in sharp torque increases followed by hydrate plug formation and severe agglomeration of the hydrate particles.\textsuperscript{15} Motor current can be also monitored to evaluate the effectiveness of AAs and the degree of agglomeration of hydrate particles. The motor current rises sharply when the hydrate particles start to agglomerate and to form the plug.\textsuperscript{31} Figure 8 shows torque changes with time during each experiment using hydrogel particles. A slight increase in torque was observed upon hydrate onset; however, this quickly returned to the initial value. When a blockage was formed (eg., bulk water without additive), the torque or motor current rose sharply at the onset of hydrate formation, and the stirrer stopped rotating. A typical surfactant-based AA that is effective would prevent this from occurring, and the torque would remain stable even after hydrate formation.\textsuperscript{12,20,31} As summarized in Table 3, the hydrogel particles show little difference between the initial torque and the maximum torque during hydrate formation, which provides strong evidence that they are effective at preventing hydrate agglomeration. This mechanism is different than surfactant-based AAs because the effect is due to the sufficient rigidity of hydrogel particles that prevents the particles from agglomerat-

The hydrate formation characteristics in bulk water + decane mixtures were also studied at the same water cut (20%) for comparison. Figure 9a shows the pressure profiles with time during hydrate formation in water, decane, and a natural gas mixture: (a) pressure, (b) gas consumption profiles.

Figure 8. Torque changes with time during hydrate formation in hydrogels, decane, and a natural gas mixture.

Figure 9. Pressure and gas consumption profiles over time during hydrate formation in water, decane, and a natural gas mixture: (a) pressure, (b) gas consumption profiles.
rate was around 0.55 mmol/min, resulting in an average growth rate of 0.43 mmol/min. In this work, the hydrate fraction varied from 0.18 to 0.52 and appears to be related to initial growth rate. When the initial growth rate was 0.20 mmol/min, the final hydrate fraction was only 0.18; however, the fraction reached 0.52 when the initial growth rate was 0.51 mol/min. In this case, when pure water is used, the hydrate onset occurs slightly earlier than with the hydrogel particles, and the growth rate is also higher. However, dramatic differences were observed in torque changes during the hydrate growth period for pure water when compared to the case with hydrogel particles.

Figure 10 shows torque changes with time during hydrate formation from water, decane, and a natural gas mixture. Unlike

rate is worth noting that the initial growth rate and the final hydrate fraction was higher than that for hydrogel particles.2,39,40 However, the water droplets keep colliding with each other and the wall, causing agglomeration and deposition of these hydrate-shell-covered water droplets. Again it is worth noting that the initial growth rate and the final hydrate fraction was higher than that for hydrogel particles.

Previous studies40,41 have suggested that hydrate agglomeration is dominated by capillary attractive force between hydrate particles, which is caused by a liquid hydrocarbon phase (decane in this case). As a result, wet hydrate lumps can occur due to capillary adhesion forces between hydrate particles, and these lumps are prone to deposit on the wall of offshore flow lines. This agglomeration and deposition of hydrate particles and their conversion to wet hydrate lumps can be avoided by removing the free liquid phase (which is not always possible) or injecting an anti agglomerant. It is believed that if hydrate particles float freely in a liquid phase in the presence of an effective AA, the measured torque remains stable without the stirrer stopping. In our experiments, when the hydrate particles agglomerated and deposited on the wall, the stirrer could no longer rotate, and the system became blocked (experiment no. 6 and 8). Alternatively, the hydrate particles can partially block the stirrer leading to higher torque values compared to the initial values. This was the case with experiment no. 9 where the stirrer keeps rotating at 40.5 N cm. The water cut in these experiments is 20%, and the hydrate particles can become free floating agglomerates in the decane phase (experiment no. 7 and 10). From experiments in Table 4, the water, decane, and a natural gas mixture shows complex behavior for hydrate agglomeration and deposition. The system can be described as blocked, partially blocked, or no blockage on the basis of torque measurements. The fluid can remain flowing even with the formation of large hydrate pieces. However, there is a high probability that the hydrates would be deposited on the wall over time, which would lead to flow restriction and eventually plug formation as seen in subsea pipelines. Once this happens in subsea flow lines, costly production stoppage and remediation of the hydrate plug is required.

It is clear that the synthesized hydrogel particles can prevent agglomeration of hydrate particles, and therefore, we also investigated using a commercial SAP. Figure 11 shows hydrate formation characteristics when a commercial SAP is added to a decane + water mixture. Subcooling temperatures were measured between 10.6 and 12.1 °C with an average value of 11.3 °C, whereas hydrate onset time were measured in between 14.7 and 19.7 min with an average value of 16.6 min, as represented in Table 5. An average value of initial gas consumption rate is 0.21 mmol/min, which is slightly lower than that of synthesized polymer. However, for every experiment, inflection points were observed when the gas consumption reached 0.013 and 0.017 mol, and the gas consumption rate decreased to 0.05 mmol/min. For the synthesized hydrogel particles developed for this study, the gas consumption curves continuously increased until they reached between 0.027 and 0.037 mol before reaching a plateau. The hydrate fraction for the commercial SAP was 16.8% and is slightly lower than that of synthesized polymer.
Figure 12 shows torque changes with time during hydrate formation with the SAP, and there is no significant change for all experiments. Once again, it is confirmed that the SAP particles prevent serious agglomeration and deposition issues when hydrates form on the surface of the SAP particles. However, the use of commercial SAP for this purpose suffers from several limitations such as broad particle size distribution, excessive swelling in water, and they undergo significant interpenetration before hydrate formation. Moreover, after five cycles of hydrate formation and dissociation, free water was observed in the SAP particles due to phase separation, which indicates there are issues in terms of long-term stability; this was not the case with synthesized hydrogel particles. These results suggest that the structure of the commercial SAP would need to be modified for use as a hydrate inhibition strategy. SAPs are designed to maximize swelling potential, which is advantageous in terms of the absolute amount of SAP that can be minimized. However, in this study, SAP-type swelling is detrimental, and the presence of the ionic groups (sodium salt) on the polymer backbone would make the polymer performance sensitive to salts. The hydrogel particles that were synthesized were optimized in terms the desired gel strength, modulus, swellability, and the cross-linking is covalent in nature and minimizes ionic groups (they are consumed in the cross-linking reaction). The synthesis allows for other functionality to be incorporated into the particles so they can be further optimized in terms of hydrate inhibition. In addition, it is also possible to optimize the initial size of hydrogels and to limit the final size by controlling the structure of polymer network to match the conditions within the offshore flow lines.

In this study hydrogel particles were investigated as a new method to prevent hydrate agglomeration, which we have investigated experimentally. These data were compared to systems with no additive present (water only) and also a commercial SAP. For water + decane mixtures, the hydrate formation can cause stirrer stoppage due to agglomeration and deposition of hydrate particles, although water droplets are dispersed well in continuous decane phase at high Reynolds number. Adding commercial SAP may effectively avoid hydrate blockage by forming hydrogel particles; however, the structure of the polymer needs to be modified to optimize swellability when hydrate formation occurs. From the experimental results of torque changes, initial growth rate, and hydrate fraction, the

![Figure 11. Pressure and gas consumption profiles with time during hydrate formation with a commercial SAP, decane, and a natural gas mixture: (a) pressure, (b) gas consumption profiles.](image)

![Figure 12. Torque changes with time during hydrate formation with SAP, decane, and a natural gas mixture.](image)

| Table 5. Hydrate Onset Time, Subcooling, and AA Effect for a Commercial SAP, decane, and a Natural Gas Mixture |
|---|---|---|---|---|---|
| expt no. | \( t_{\text{onset}} \) (min) | \( T_{\text{subcool}} \) (°C) | \( r_{\text{ini}} \) (mmol/min) | \( \Phi \text{_{tot}} \) | \( \tau_{\text{onset}} \) (N cm) | \( \tau_{\text{max}} \) (N cm) | note |
| 11 | 19.7 | 12.1 | 0.26 | 0.17 | 6.0 | 6.0 | no blockage |
| 12 | 16.1 | 11.4 | 0.20 | 0.16 | 6.0 | 6.2 | no blockage |
| 13 | 15.9 | 10.7 | 0.20 | 0.18 | 6.0 | 6.1 | no blockage |
| 14 | 14.7 | 10.6 | 0.15 | 0.15 | 6.0 | 6.1 | no blockage |
| 15 | 16.7 | 11.9 | 0.20 | 0.18 | 6.1 | 6.2 | no blockage |
| average | 16.6 | 11.3 | 0.21 | 0.17 | 6.1 | 6.2 | no blockage |
| standard deviation | 1.3 | 0.6 | 0.03 | 0.01 | | | |
particles can be used for cold restart in offshore flow lines transporting hydrocarbon fluids.

In order to further investigate the performance of the hydrogel particles, a shut-in and restart experiment was conducted. Hydrate onset was detected at around 10 °C, and the formation continued until 120 min. The stirring was then stopped and the temperature was maintained at 4 °C to allow more hydrate to form in the shut-in period; however, the amount of additional hydrate formed in this period was negligible considering the pressure difference of 0.2 bar during the shut-in period. Stirring was resumed after 4 h to simulate a cold restart (Figure 13), and the stirrer could be restarted without blockage and no sign of severe agglomeration of hydrate particles. At 450 min, the temperature was increased from 4 to 20 °C, and the fluids could be easily stirred during this hydrate melting process. This result suggests that hydrogel particles can be used for cold restart in offshore flow lines.

The synthesized hydrogel particles are stable under vigorous mixing and maintain their shape and properties. When the temperature and pressure fall into hydrate stability zone, a hydrate shell grows and covers the surface of hydrogel particles, and grows inward. However, due to mass transfer limitations, this growth ceases when hydrate formation reaches about 24%. The hydrogel particles with a hydrate shell are dispersed well in a decane phase and do not agglomerate or deposit as evidenced by the torque measurement, which remained stable throughout the whole process of hydrate formation. The important physical property for using the hydrogels in the field is the swelling ratio.

As we observed in the results with the commercial SAP, the polymer absorbs large quantities of water (>160 g/g water/polymer) after which it becomes unstable at these high swelling ratios. In this work, the synthesized polymer swells up to the controlled maximum upon their exposure to free water phase, thus the size of hydrogel particles can be effectively controlled. The concept of using the hydrogels is injecting dry particles into a pipeline where they will swell to a controlled size when mixed with free water. Subsequently they will be transported along the pipeline without agglomerating. Therefore, we believe that hydrate formation occurs in a well-controlled manner on the surface of hydrogel particles, which are dispersed in continuous decane phase. The hydrogel particles prevent hydrate agglomeration and are a promising alternative to typical surfactant-based AAs. Additional laboratory experiments will be carried out with increased water cut, in the presence of salt, and with other optimized structures for the hydrogel particles.

■ CONCLUSIONS

Hydrate formation characteristics including onset time, subcooling temperature, initial growth rate, hydrate fraction, and torque changes were studied for hydrogel particles. The average hydrate onset time and subcooling was 38.4 min and 9.5 °C. For pure water (without the hydrogel particles), the average hydrate onset time was 23 min, and the average subcooling temperature was 6.1 °C. This indicates that the hydrogel particles have a weak kinetic hydrate inhibition effect. The initial hydrate growth rate was 0.27 mmol/min, and hydrate fraction in the liquid phase at the end of experiments was 0.24 for the hydrogel particles. The hydrate formation occurs on the surface of the particles in a well-controlled manner, and the shell and polymer network help to prevent agglomeration and deposition of these hydrate shell-covered particles. Stable torque measurements during the formation of hydrates provide evidence for this mechanism. In contrast, for the water + decane mixture, when hydrate formation occurs in the water/decane interface, a sharp increase in torque is observed followed by stirrer stoppage due to the agglomeration and deposition of hydrate particles. The average hydrate fraction in the liquid phase was 0.24 with a standard deviation of 0.02. However, hydrate formation in the water + decane mixture varied depending on the agglomeration and deposition process of the hydrate particles. The average hydrate fraction in these cases was 0.41 (standard deviation of 0.16). A commercial SAP (cross-linked poly(acrylic acid) sodium salt) was also studied as a potential material for preventing hydrate agglomeration, and the hydrate formation characteristics are similar to those of the synthesized polymer in this work. However, the swelling is difficult to control because these polymers are designed to absorb significant quantities of water. In addition, the swelling ability is diminished after repeating times of hydrate formation and dissociation. These results suggest that the modification of polymer structure of the commercial material is required for use in hydrate inhibition. However, the synthesized polymer in this work shows promising performance as a method to prevent agglomeration of hydrates via a surfactant free route, which is an entirely new method.

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**REFERENCES**


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