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Methane hydrate dissociation in the presence of novel benign additives

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Abstract

The apparent drawbacks of the classical approaches towards dissociation of natural gas hydrates have resulted in a paradigm shift into the development of new hybrid hydrate dissociation practices combining the various basic hydrate dissociation techniques. Another approach that can be followed to maximize the efficiency of gas production from natural gas hydrate reserves is the identification of benign additives which when used even in sparingly small concentrations may enhance the kinetics of hydrate dissociation. In the present work, a class of such additives, never reported before, have been unveiled and christened as Low Dosage Hydrate Dissociation Promoters (LHDPs). The additives were first short listed from a wide potential pool using a lab scale (~250 ml) stirred tank reactor setup and then further studied using a bench scale (~2.35 l) reactor setup where they were injected in the form of a water-additive stream to dissociate hydrates. The dissociation approach followed in the case of the bench scale reactor experiments was a combination of the thermal stimulation and depressurization processes along with the element of injection of additives. For both sets of experiments (lab and bench scale), the newly identified LHDPs were found to enhance the kinetics of methane hydrate dissociation as compared to pure water. It was observed that concentration of additive and its flow rate also affect the kinetics of methane hydrate dissociation. An energy and efficiency analysis for the hydrate dissociation method in the case of bench scale reactor revealed that additive presence enhanced the energy ratio and thermal efficiency four fold as compared to pure water.

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Keywords: Methane Hydrate, LHDP, Dissociation, Kinetics, Thermal Stimulation, Depressurization, Energy Ratio, Thermal Efficiency

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1. Introduction

Gas hydrates are non-stoichiometric ice-like crystalline compounds formed when water and gas molecules interact under conditions of low temperature and high pressure. The gas or other suitable hydrocarbon (guest) molecules get trapped inside hydrogen bonded cages formed by the water (host) molecules and help stabilize these cages. The incipient low temperature and high pressure conditions required to form gas hydrates are frequently encountered in deep-ocean (marine) and permafrost settings thus resulting in the presence of highly concentrated gas hydrate deposits on the continental shelves and in permafrost, formed over a period of millions and millions of years [1], [2], [3].

Being such a large untapped source of clean energy, natural gas hydrates have been the recipient of widespread research activities around the world and have quickly scaled up the “viable energy resource” ladder to become a highly promising fuel of the future. There are currently four different types of approaches that may be employed to recover natural gas from its hydrate reserves, namely thermal stimulation, depressurization, inhibitor injection and CH₄-CO₂ exchange. However, in spite of the persistent interest in methane recovery from natural gas hydrates researchers have been unable to use any of the aforementioned processes with desired outcomes as each of these processes pose their own challenges. While the thermal stimulation process requires the use of large amount of energy, depressurization and CH₄-CO₂ exchange are both extremely time consuming and the inhibitor injection process involves the use of large concentrations of chemicals that may prove to be fatally toxic to the marine environment.

It has long been accepted that the way forward with regards to recovery of natural gas from its hydrate deposits is employing a combination of one or more of the four main techniques for hydrate dissociation mentioned above. The present work follows this model to introduce a never before used approach for the dissociation of natural gas hydrates. In addition to developing a process for hydrate dissociation combining the depressurization and thermal stimulation approaches, a new class of additives has been proposed. These have been christened as low-dosage hydrate dissociation promoters (LHDPs) – mostly bio derived benign substances posing no threat to the marine environment, and which when used in exceedingly small quantities (maximum 1 wt %), remarkably promote the dissociation rate of natural gas hydrates. Possible additives were first narrowed down from a wide potential pool (developed through a thorough literature survey) using experimental evidence obtained from a lab scale (~250 ml) stirred tank reactor setup. The additives that were found to most significantly promote hydrate dissociation kinetics were further studied using a bench scale (2.35 l) methane recovery apparatus. The effect of varying the additive concentration and flow rate of additive stream on the kinetics of methane hydrate dissociation were also investigated. An energy and efficiency analysis was performed for the hydrate dissociation process employed in the bench scale setup using the newly identified LHDPs.

2. Materials and Methods

The various additives used in the present study were obtained from HiMedia Laboratories Pvt. Ltd. India. Silica Sand and clay were obtained from Sakalchand and Co., India. Deionized water was used for all the experiments.

2.1. Preliminary identification of the additives

In addition to the environment friendly nature, the preliminary selection of additives was based on a number of criteria so as to fulfil the following three objectives: **a) substantially enhance hydrate dissociation kinetics, b) exhibit viability for scale up of operations and c) achieve desired effects even when used in small doses.**

After an extensive literature search, it was felt that for an additive to significantly enhance hydrate dissociation kinetics, it needs to work through one of the following mechanisms:

- **Should be capable of forming hydrogen bonds with water molecules** thus disrupting their ability to form cages and enclathrate guest molecules. Cage defects may be created as a result of the difference in

number of hydrogen bonds formed between the specific compound and water compared to typical water-water interactions [4].

- **May be zwitterionic.** Some additives may exist as zwitterions. It is known that around electric charges, water molecules tend to become less ice like. The electric charges present on the molecules will enable them to interact more freely with water with water molecules having a special tendency to favor the negative charge [5].
- **May change the thermodynamic phase equilibria boundary of methane or natural gas hydrates.** Some additives may change the thermodynamic phase equilibria boundary of methane or natural gas hydrates, not allowing hydrates to remain stable at their inherent equilibrium conditions [6]. [7], [8].

The various classes of identified additives that have the ability to work through the mechanisms described above and thus exhibit potential to act as hydrate dissociation promoters are: **a) hydrophilic, hydrophobic and charged amino acids, b) zwitterionic compounds such as betaines, c) polysaccharides, and d) hydrogen bond formers such as alcohols.** Table 1 given below lists the various additives (LHDPs) that have been identified for this study. The additives have been listed along with their respective class, the gas used for forming hydrates and the concentration of additive used. However not all these additives were used in both the lab scale and bench scale experimental setups owing to their rheological properties and other factors. It may be noted that a much larger set of additives was tested in the lab scale stirred tank setup but haven't been reported in this paper for the sake of brevity.

Sr. No.	Additive	Class of Compound	Gas used for forming hydrates	Conc. of additive used
1.	L-histidine	Hydrophilic Amino Acid	Pure Methane	0.1, 1 wt %
2.	L-proline	Hydrophobic Amino Acid	Pure Methane	0.1, 1 wt %
3.	Bicine	Zwitterionic Compound	Pure Methane	0.1, 1 wt %
4.	Gum Arabic	Natural gum (mixture of glycoproteins and polysaccharides)	Pure Methane	1 wt %
5.	Gellan Gum	Long Chain Polysaccharide	Pure Methane	1 wt %
6.	L-tryptophan	Hydrophobic Amino Acid	Pure Methane	0.1, 1 wt %
5.	Ethylene Glycol*	Alcohol (thermodynamic inhibitor)	Pure Methane	1 wt %

*Not part of the newly identified additives but used for the purpose of comparison.

Table 1: List of the additives identified for use as hydrate dissociation promoters in the present study

2.2. Experimental Setups

After preliminary identification, the efficacy of the potential LHDPs was tested using a dedicated reactor setup which was basically a stirred tank reactor with a volume of ~250 ml, details of which may be found elsewhere [9]. The better performing additives were then studied in a bench scale (2.35 l) circulating flow loop apparatus.

Figure A1 (Appendix A) shows the schematic diagram of the Bench Scale Methane Recovery Setup whereas Figure A2 (Appendix A) shows the physical image of the same. It consists of a 2.35 L SS-316 high pressure hydrate crystallizer (CR) having a design pressure of 200 bar and equipped with a cooling jacket connected to an external refrigerator (ER1) to maintain the CR at desired temperature. The CR is provided with a rupture disk in adherence with safety regulations. Seven RTDs Pt-100 type with range -199.9 to 600 0C and $\pm 0.25\%$, ± 1 LSD accuracy are present within the CR at various depths inside the hydrate forming sediment to measure the temperature as shown in the figures. Gas from the supply vessel (SV) which is also connected to ER1 is immersed in the crystallizer at the experimental temperature and pressure. A mass flow controller (MFC) Brooks instruments make with a maximum flow rate of 0-500ml/min at calibrated inlet pressure of 70 bar is attached to the outlet of the CR and inlet of the reservoir whose main function is to act as a back pressure regulator. The pressure inside CR at the time=0 during dissociation of gas hydrate is the set point of MFC. During dissociation, pressure of the CR rises due to decomposition of gas hydrates. As the pressure of the CR rises, the valve connected to the MFC opens up and the amount of excess gas prior to dissociation generated in the CR is collected in the reservoir tank. Flow rate and volume of gas generated during decomposition is measured and logged via a totalizer which is connected to the MFC. An ECOM make high pressure liquid circulation pump (HPLC) with flow-rate range of 0-100 ml/min is connected to the CR. The inlet of the pump is connected to a temperature controlled water tank in which additive solution is stocked and this additive solution

is injected into the crystallizer via the HPLC pump during the additive injection experiments. ER2 (the second external chiller) is connected to the water tank and the reservoir to control their respective temperatures. Any change in the pressure in the CR, reservoir and water tank is measured using a WIKA make pressure transducer with a range of 0–250 bar and accuracy of 0.075% of the span. Software based SCADA system is used to log and monitor the data obtained during experiments. The detailed operation and working of the Bench Scale Methane Recovery Setup is explained in one of the upcoming sections.

3. Result and Discussions

3.1. Testing of additives in the dedicated reactor setup for additive selection

As mentioned earlier, potential LHDPs identified were first tested in a lab scale stirred tank reactor setup (volume ~250 ml) christened “the dedicated setup for additive selection”. As a result of there being no external influence on the system, the dedicated reactor setup for additive selection is a perfect system to purely test the efficacy of the additives in enhancing hydrate dissociation kinetics. All experiments were conducted at 274 K temperature and 5.0 MPa pressure using pure methane gas. In these experiments, the additives were included in the system from the beginning of the experiments. First methane hydrates were formed in the presence of the additives and then the dissociation kinetics was studied. Dissociation was studied at two different temperatures, 283 K and 293 K. The concentration of all the additives used was kept constant at 1 wt %. 80 ml water was used for all the experiments thus leaving a volume of 172 ml for the gaseous phase.

Figure 1(a) given below plots the normalised moles of gas released during dissociation at 293 K for the fresh runs for all the different additives studied and compares them with that obtained using pure water. As can be seen from the figure, all the additives used considerably enhance the kinetics of methane hydrate dissociation at 293 K. Figure 1(b) shows the methane recovery after 18 minutes in the presence of these additives and at 293 K and compares it with that obtained from pure water. From Figures 1(a) and (b), it becomes clear that the additives selected by us indeed have a potential to enhance hydrate dissociation kinetics. Representatives of all the different classes of additives studied; “Gum Arabic” for “long chain polysaccharides”, “Bicine” for zwitterionic compounds and L-histidine for “amino acids” respectively really stand out as suitable choices even in the big picture scheme of things.

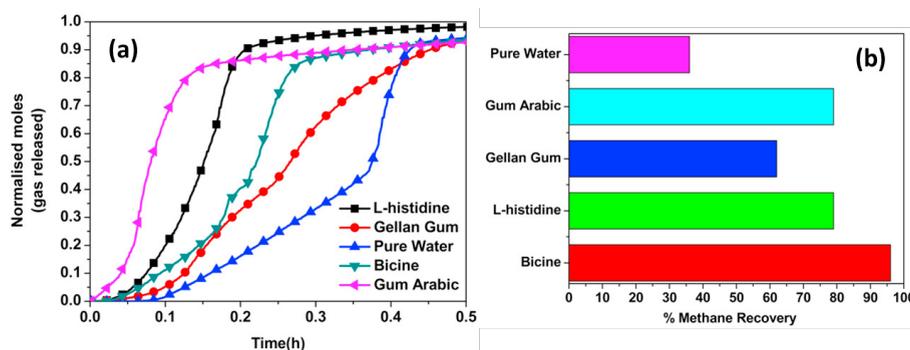


Fig. 1: Dissociation at 293 K: (a) Normalised moles of gas released vs. time (h) and (b) % methane recovery after 18 minutes for the different additives (LHDPs) studied. Concentration of additives used: 1 wt %

Figure 2(a) given below plots the normalised moles released during dissociation at 283 K for the fresh runs for all the different additives studied and compares them with that obtained using pure water at 1) 283 K and 2) 293 K. Once again, all the additives used considerably enhance the kinetics of methane hydrate dissociation at 283 K. However what is interesting is that the presence of a number of the additives such as Gum Arabic, Bicine and L-histidine in the system returns much enhanced kinetics even at 283 K when compared to that with pure water at 293 K. Figure 2(b) shows the methane recovery after 18 minutes in the presence of these additives and at 283 K and compares it with that obtained with pure water at 1) 283 K and 2) 293K. The main take away from this figure is that almost all the additives used (except the one corresponding to the dark blue bar) show higher methane recovery after 18 minutes when hydrate dissociation is carried out at 283 K as compared to that obtained with pure water at 293 K. The information garnered from Figures 2(a) and (b) is extremely important

as this can have major implications when recovering natural gas from hydrates on a commercial scale. A difference of 10 degrees achieved at lab scale can translate into a major economic advantage at field scale.

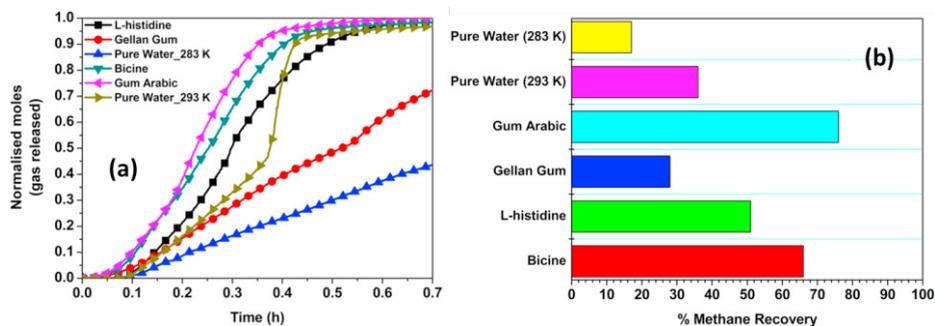


Fig. 2: Dissociation at 293 K: (a) Normalised moles of gas released vs. time (h) and (b) % methane recovery after 18 minutes for the different additives (LHDPs) studied. Concentration of additives used: 1 wt %

3.2. Injection of additives to enhance hydrate dissociation kinetics: Continuous flow loop circulating apparatus

Based on the results obtained from the experiments carried out in the dedicated reactor setup for additive selection and the feasibility of conducting the experiments on a larger scale (especially injecting the additives into the system through the water stream), a number of additives were selected for use in the continuous flow loop circulating apparatus. The experimental procedure used for these set of experiments is as follows. 700 gm of the sediment mixture was loaded into the 2.35 litre crystallizer vessel. The sediment mixture had a water saturation of 75% (~110 ml) and was made up of sand and clay mixed in a 75:25 ratio by weight. The crystallizer was then brought down to the experimental temperature (274K) with the help of an external circulating water bath. Once the desired temperature was reached, methane gas was introduced into the system at the desired experimental pressure (~50 bar) leading to the formation of pure methane gas hydrates. Methane hydrates were allowed to form overnight and dissociated after saturation was reached in the growth phase. Dissociation was achieved by injecting a water-additive mixture stream (at ambient temperature) into the system with the help of a high pressure circulating pump. Additives were used in low concentrations (0.1 wt %-1 wt %) and the water-additive mixture was injected to the system in a continuous stream for 1 hour following which the supply of water to the system was stopped. The mass flow controller attached to the crystallizer was opened at the same time at which pumping was started and the MFC was set at the initial crystallizer pressure at the beginning of the dissociation process. This ensures that only the gas released due to dissociation of methane hydrates passes through the MFC and gets collected in the reservoir. After the pumping of the water-additive mixture was stopped, the system was left as it is for thirty minutes. Following this, the temperature of the crystallizer was brought up to room temperature (298K) to finish the hydrate dissociation process.

Figure 3(a) plots the methane recovery obtained using the continuous apparatus for the pure water system and in the presence of a number of newly identified benign additives. The flow rate of the injected solution was kept constant at 10 ml/min for all the experiments conducted and all the additives were used in the same concentration (0.1 wt %). Methane recovery has been shown for the first thirty minutes of hydrate dissociation. Various hydrophilic and hydrophobic amino acids were used separately for the sake of comparison. The long chain polysaccharide Gum Arabic presented the problem of flowing freely as a result of which it wasn't used for this set of experiments. A separate approach will need to be developed in order to scale up the use of this particular LHDP. As can be seen in Figure 3(a), out of all the novel benign additives tested, L-histidine (a polar amino acid) serves our purpose the best by considerably speeding up the hydrate dissociation process as compared to pure water with Bicine (a zwitterionic molecule) not far behind. On the other hand, the hydrophobic amino acids L-proline and L-tryptophan fail to adequately enhance the kinetics of methane hydrate dissociation with L-proline in fact showing a slight inhibition. The latter two results notwithstanding, it is still extremely promising to see the superb enhancement in methane hydrate dissociation kinetics observed with an extremely low concentration (0.1 wt %) of the additives L-histidine and Bicine as compared to pure water.

The effect of varying the additive concentration and flow rate of the additive stream on the kinetics of methane hydrate dissociation was also studied and the results obtained have been shown in Figures 3(b) and 3(c). For the systems reported in Figure 3(b), the flow rate of the injected solution was maintained at 30 ml/min while the concentration of the additives used was kept constant at 0.1 wt %, whereas, for the systems reported in Figure 3(c), the flow rate of the injected solution was maintained at 30 ml/min and the concentration of the additives used was kept constant at 1 wt %. The two best LHDPs at 0.1 wt % and 10 ml/min (L-histidine and Bicine) were both chosen for the study on varying the additive concentration and flow rate of the additive stream on the kinetics of methane hydrate dissociation. While the thermodynamic inhibitor Ethylene Glycol was used when the systems with higher additive flow rates were investigated, this additive was not used when the additive concentration was increased to 1 wt % due to its obvious toxic nature. From Figure 3(b), it can be seen that all the LHDPs show a marked improvement in hydrate dissociation kinetics as compared to pure water injected at 30 ml/min. L-histidine achieves the maximum kinetic enhancement as compared to pure water and is closely followed by Bicine while both in fact, show better hydrate dissociation kinetics as compared to Ethylene Glycol, the thermodynamic inhibitor. This is a very important result from the point of view that the use of a higher injection flow rate can be seen to have a very positive effect on hydrate dissociation kinetics while also increasing the effectiveness of our novel benign additives as a result of faster delivery to the hydrate containing sediment. Figure 3(c) shows that there isn't too much of a change when the concentration of a LHDP is increased from 0.1 wt % to 1 wt %, while keeping the flow rate of the additive stream constant. For these systems, Bicine leads the pack in terms of enhancing hydrate dissociation kinetics (compared to pure water) and is closely followed by L-histidine. Though the improvement in hydrate dissociation kinetics obtained with these systems is remarkable as compared to pure water, when compared to their counterpart systems - same flow rate of additive stream but with lower concentration of LHDPs (Figure 3(b)), it can be seen that there isn't too pronounced of a change in the kinetics of methane hydrate dissociation.

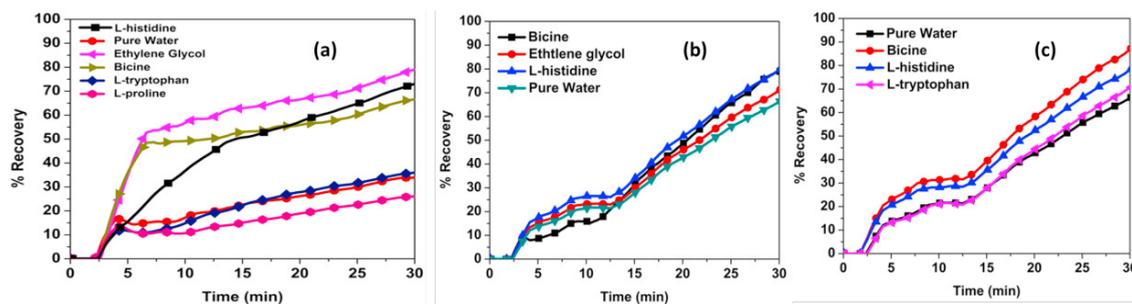


Fig. 3: % Methane recovery vs. time (min) for hydrate dissociation effected by the injection of benign LHDP-water mixtures into the large scale continuous apparatus-a) 0.1 wt % and 10 ml/min, b) 0.1 wt % and 30 ml/min and c) 1 wt % and 30 ml/min

3.3. Energy and Efficiency Analysis in the presence of low concentrations of additives (injection)

Energy ratio and thermal efficiency are the two common parameters used to evaluate the efficiency of gas production from a hydrate reservoir and the same was calculated for the hydrate dissociation process in presence of additives employed here. While energy ratio is the ratio of the total combustion heat of the produced methane gas to the total input energy, thermal efficiency is an indicator of the proportion of the total amount of heat used to dissociate the formed hydrate to the total injected heat. The procedure followed for the calculation of the energy ratio and thermal efficiency is given in Appendix A.

Energy ratio is a parameter which evaluates the effectiveness of a hydrate dissociation process from the perspective of energy output. A higher energy ratio signifies greater energy output for the same amount of input energy. Thermal efficiency however speaks from the viewpoint of energy use. A higher thermal efficiency means more amount of the injected heat is used in dissociating the hydrate, that is to say the hydrate dissociation process is more energy efficient. The energy ratios and thermal efficiencies for the various systems (different additive concentrations and injection flow rates) with respect to time were calculated for the first thirty minutes of hydrate dissociation and the maximum energy ratio and thermal efficiency obtained for each system has been reported in Table 2.

Additive concentration and Flow Rate	Additive	Maximum Energy Ratio Obtained	Maximum Thermal Efficiency Obtained
0.1 wt % and 10 ml/min	Pure Water	1.0	0.06
	L-histidine	4.7	0.28
	Ethylene Glycol	2.2	0.13
	Bicine	4.5	0.26
	L-tryptophan	2.5	0.15
	L-proline	1.5	0.08
0.1 wt % and 30 ml/min	Pure Water	3.0	0.18
	Bicine	3.2	0.20
	L-histidine	3.7	0.24
	Ethylene Glycol	3.1	0.19
1 wt % and 30 ml/min	Pure Water	2.8	0.18
	Bicine	3.5	0.23
	L-histidine	3.0	0.20
	L-tryptophan	3.0	0.20

Table 2: Energy and efficiency analysis for the various systems studied (injection of additives)

It can be seen from Table 2 that the energy and efficiency analysis in general follows the same trend as the gas release profiles that is to say that the systems which show higher methane recovery also exhibit higher values for the energy ratios and thermal efficiencies. When the flow rate of the injected additive stream is increased while keeping the concentration of injected additive constant, it can be observed that the values of energy ratio and thermal efficiency for the pure water and ethylene glycol systems increase whereas those for Bicine and L-histidine decrease. The reason for this is that when the flow rate of the additive stream is increased, the systems like pure water and ethylene glycol now receive an extra driving force to aid in the dissociation process which results in faster release of gas from the formed hydrate and hence a higher energy ratio. For the L-histidine and Bicine systems, the additives used were already providing the extra driving force (so to say) when the flow rate of the additive stream was low (10 ml/min) and hence when the flow rate of the additive stream was increased to 30 ml/min, since the concentration of the additives in the additive stream remained constant, the systems returned a lower energy ratio than the earlier case as a result of the pump doing more work to maintain the higher flow rate. There is no real improvement in the values of the energy ratios and thermal efficiencies obtained when the concentration of injected additive is increased while keeping the flow rate of the additive stream constant thus indicating that a very small amount of additive is enough to satisfactorily enhance the energy ratio and thermal efficiency of the system. For all the additive systems studied, a higher energy ratio and thermal efficiency is observed as compared to pure water which not only highlights the positive effect of the novel benign additives on methane hydrate dissociation kinetics but also goes a long way in strengthening the argument on the feasibility of the additive injection based hydrate dissociation process.

4. Conclusions

In the present study, a number of benign additives were identified which when used in low concentrations enhanced the kinetics of methane hydrate dissociation compared to pure water. The efficacy of the additives was first tested using a lab scale stirred tank reactor setup following which they were studied in a larger bench scale setup where they were injected in the form of an additive-water stream to dissociate already formed hydrates. The trend observed with regards to the effectiveness of the additives to enhance hydrate dissociation kinetics was the same for both the lab scale and bench scale reactor setups. It was theorized that the ability of additives to interact with water molecules and modify/ break hydrogen bonds is one of main reasons behind the enhancement in dissociation of methane hydrates in presence of additives. An energy and efficiency analysis revealed that all the additives used actually enhance the energy ratio and thermal efficiency of the process as compared to pure water. High flow rate is required to enhance the energy ratio and thermal efficiency for just the pure water system whereas for the systems containing L-histidine and Bicine, only a small concentration of additive in solvent stream and low flow rate of the same is required to obtain satisfactorily high energy ratio and thermal efficiency. In the latter case, higher flow rate actually decreases the energy ratio and thermal efficiency of the system as higher flow rate signifies more work done by the pump and hence higher energy input into the system. The hybrid hydrate dissociation approach developed in this study, combining the depressurization and

hot water flooding methods while also employing benign additives such as amino acids thus indeed holds great promise for the future, environmentally, economically and commercially.

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Appendix A

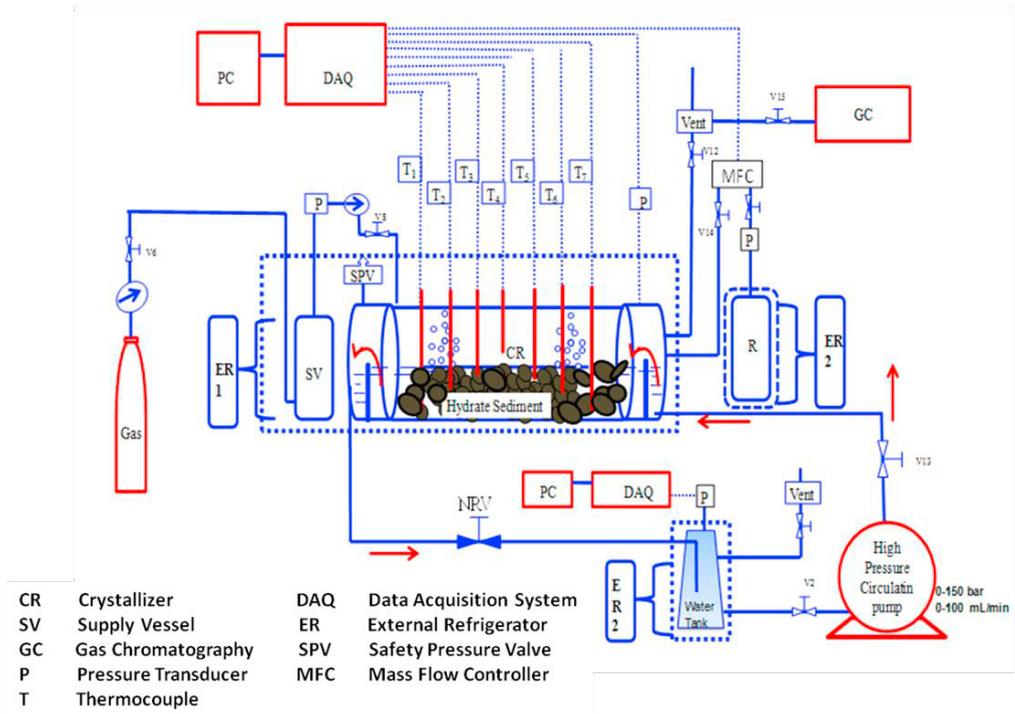


Figure A1: Schematic of the bench scale methane recovery setup.



Figure A2: Bench scale high pressure continuous setup for studying methane hydrate decomposition kinetics in sub-sea environments

Procedure followed for the calculation of Energy Ratio and Thermal Efficiency

Energy ratio is the ratio of the total combustion heat of the produced methane gas to the total input energy and is given by the following formula:

$$\eta = \frac{G_p M_{gas}}{C_w m_w (T_{inj} - T_{env}) + W_{pump}} \quad (A1)$$

G_p is the cumulative amount of the produced gas (mol), M_{gas} is the combustion heat of methane (890.3 kJ/ mol), C_w is the specific heat of water (4.2 kJ kg⁻¹ K⁻¹), m_w is the total mass of injected water, T_{inj} is the temperature of injected water (298K), T_{env} is the temperature of the reservoir during hydrate formation and W_{pump} is the total work done by the metering pump in pumping the injection solution at a particular flow rate.

The total work done by the pump can be calculated as:

$$\text{Pump Work} = \text{Shaft Power} \times \text{Time for which pump was operated} \quad (A2)$$

Shaft Power can be calculated as:

$$\text{Shaft Power} = \frac{\text{Hydraulic Power}}{\text{Efficiency of Pump}} \quad (A3)$$

where the efficiency of the pump is 70 % as specified by the manufacturer.

Hydraulic Power of the pump can be calculated as:

$$\text{Hydraulic Power} = \text{Pressure head } (\Delta P) \times \text{Flow rate of injection solution} \quad (A4)$$

The flow rate of the injection solution varies according to the experiment in question (10 ml/ min and 30 ml/ min).

The thermal efficiency on the other hand is an indicator of the proportion of the total amount of heat used to dissociate the formed hydrate to the total injected heat. Thermal efficiency can be given by the following equation:

$$\zeta = \frac{N_h \Delta H_h}{C_w m_w (T_{inj} - T_{env})} \quad (A5)$$

where N_h is the number of moles of dissociated hydrate, ΔH_h is the decomposition heat of hydrate (52.9 kJ/mol at 274.15K).