Storage of Methane Gas in the Form of Clathrates in the Presence of Natural Bioadditives

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ABSTRACT: Methane (CH₄) and carbon dioxide (CO₂), the important greenhouse gases, are capable of forming clathrate hydrates under some suitable thermodynamic conditions. The gas storage capacity of these materials is high, and therefore they are often useful in gas storage applications. Certain expensive and toxic chemicals are employed to accelerate/decelerate the process. In this study, we report rapid (∼30–50 min) and effective (∼80%) methane hydrate conversion in the presence of three naturally occurring additives such as dry powders from Nelumbo nucifera (Indian lotus), Piper betle (betel), and Azadirachta indica (neem), at lower concentrations (0.5 wt %). Obtained results were carefully compared with the well-known kinetic promoter (sodium dodecyl sulfate). All the biomaterials are equally good kinetic promoters for methane hydrates, although the required subcooling is significantly large. However, nohydrate formation is observed with CO₂ gas. As promoters and the rate of gas uptake is faster. Therefore, the research on diﬀerent experimental conﬁgurations such as spray-type reactor cells and various matrix materials such as silica powders and activated carbons are being used to confine the water molecules in the pore spaces. Interestingly, the matrix materials do not directly take part in actual hydrate cage formation, but they help in accelerating the hydrate growth process.

INTRODUCTION

The clathrate hydrates, also known as gas hydrates where the host cages are constituted with the water molecules alone. These materials are attractive globally, and many research groups are working to exploit their potential for various causes, such as they are an essential energy source with natural fuel gas molecules encased as guests. Substantial hydrate deposits, both under permafrost and marine sedimentary strata, are remained unexploited and suitable technology for gas recovery is at an infant stage. The size selectivity and larger storage capacity of guest molecules opened up many attractive applications for natural gas separation, storage, and transportation applications. Additionally, the gas hydrate-based approach is useful in the carbon-dioxide capture and storage, and desalination technology.

The research on gas hydrates, to begin with, started purely as a scientiﬁc inquisitiveness, but later, it was recognized as one of the leading causes of blockages in a petroleum/gas-carrying pipeline network. Later on, research efforts were deepened to find a solution for the purpose. Noticeable drawbacks for utilizing the gas hydrate-based technology for gas storage and transportation are sluggish rate formation and freeable water to hydrate conversions. Some additives, in addition to the constituents necessary in the hydrate process, are used to decelerate/accelerate the structural transformation. Conventionally, three types of inhibiting materials, viz. thermodynamic (THI), kinetic (KHI), and antiagglomerates (AAs) are being tried for preventing the formation of such blockages. The THI materials such as alcohols and glycols, when used along with hydrate-forming systems, alter the formation/dissociation conditions to lower temperatures and high pressures, compared to the pure systems. Noticeable drawbacks, however, are that they ought to be used in large quantities and majority of them are toxic and cost ineﬃcient. The second type of materials namely KHI signiﬁcantly retard the onset of hydrate formation, and thus the phase conversion to hydrates can be delayed. Commonly, water-soluble polymers such as polyvinylpyrrolidone and polyvinyl caprolactam are used as KHI. The third class of materials AAs avoids the accumulation of hydrate particulates into larger chunks. Thus, the ﬂow-related issues can be curtailed to a more signiﬁcant extent with small-sized hydrate particulates. The study on AAs is still at an infant stage for gas hydrate systems, and some proteins and bioextracts from living organisms are being tested in the hydrate formation process. Usage of inhibitors is essential to prevent the hydrate nucleation and growth. On the contrary, rapid and eﬃcient hydrate conversion is often preferred in speciﬁc gas hydrate-based applications such as gas storage and transportation. It has been shown that well-known THIs, such as methanol, in low dosages can serve as promoters and the rate of gas uptake is faster. Therefore, the research on diﬀerent experimental conﬁgurations such as spray-type reactor cells and various matrix materials such as silica powders and activated carbons are being used to confine the water molecules in the pore spaces. Interestingly, the matrix materials do not directly take part in actual hydrate cage formation, but they help in accelerating the hydrate growth process.

All the materials used as promoters/inhibitors in the hydrate-based technology are chemical-based polymers, and
are non-ecofriendly and also costly. Particularly, if one needs to use them at larger concentrations, the process becomes more expensive. It would certainly be attractive to achieve similar results using some naturally occurring materials, involving less preparation.

Wang et al. have inspected the “bioclathrate” hydrate formation of both CH₄ and CO₂ gases. They demonstrated the formation of natural and renewable biosorbents in enhancing the gas storage (up to 120 v/v) in the form of bioclathrates in nonstirred configuration. The porous structure of certain plants and fungi such as mushrooms and eggplants was responsible for higher “sorption” of greenhouse gas molecules. On the other hand, extracts of tomato were showing significantly lesser clathrate conversion, similar to the pure water system. Fakharian et al. and Babakhani and Alamdari have also investigated the methane storage capacity and the stability of methane hydrates using water-soluble starch from potato and maize. They inferred that these systems are capable of forming hydrates in a way similar to sodium dodecyl sulfate (SDS). Wang et al. have also studied methane storage capacity in the form of hydrates using tea extracts in an unstirred reactor using an initial methane pressure of 10.5 MPa (p=293 K). They reported higher volumetric storage capacity (172 v/v or 95% hydrate conversion) in green tea (Longjing) and oolong tea (Tieguanyin), whereas the storage capacity in black tea (Yunnan) was meagre and was comparable to the bulk water system under similar conditions. Because the commercial value for such teas are high and are not advantageous to use them for storage applications, and therefore the authors have examined two other bioadditives namely extracts from dry leaves of Bauhinia purpurea and Mallotus apelta. Further, the CO₂ hydrate formation was also tested in the presence of sugar (trehalose) and also in freshly cut radishes and eggplants, whole grape, and bean samples. The presence of CO₂ hydrates in these biosamples was assessed by the spectroscopic methods and also the self-preservation phenomena, ascribed to CO₂ hydrates, is found extremely useful for storage applications in the food and beverage industry.

This study reports the use of fine powders, prepared from the dry leaves of three commonly found trees, such as Nelumbo nucifera (Indian lotus), Piper betle (betel), and Azadirachta indica (neem), in the clathrate hydrate process. We carried out all the experiments in isochoric geometry without any stirring. We observed that these powders are helpful in accelerating the methane hydrates even at lower concentrations (0.5 wt %), whereas no such effect has been found in CO₂ hydrates.

**RESULTS AND DISCUSSION**

Representative pressure–temperature (p, T) trajectories for all the hydrate-forming systems are depicted in Figure 1, and the measurements were carried two to three times to ensure the repeatability of experimental data. The experiments were conducted in the isochoric and unstirred geometry. As shown in Figure 1A, the pressure variation in the quiescent water system is linear, and no abrupt drop is observed in the hydrate stable region, whereas an abrupt pressure decrease in the 0.5 wt % SDS-containing system indicates the existence of methane hydrates. Similarly, the addition of 0.5 wt % of leaf powders, such as lotus (Figure 1B), betel, (Figure 1C) and neem (Figure 1D), as additives to water, also induced the pressure change, which leads to the hydrate formation. The black and red symbols in all these graphs represent the variations during freezing and thawing cycles, respectively, whereas the blue line is the computed phase boundary curve for the H₂O–CH₄ system using CSMGem. The process of hydrate conversion in these systems with SDS (a), lotus leaf (LL) (b), betel leaf (BL) (c), and neem leaf (NL) (d) powders as additives to the H₂O–CH₄ system is further illustrated in Figure 2 by following the temporal variations in the local temperature and the amount of methane gas in the reactor vessel. The process of hydrate conversion from gas–water is an exothermic change and is often associated with heat release, which causes an increase in the local temperature (shown as inset-1 for all the samples in Figure 2). It may not always be possible to have measurable temperature change because it will depend on factors such as the quantum of the exothermic heat, conductivity of hydrate-bearing medium, and the placement of the temperature probe. Therefore, the local temperature measurements at multiple locations within the hydrate crystalliser could be handy in assessing the spatial position of hydrate nucleation. Nevertheless, a sharp decrease in the gas pressure also indicates the hydrate nucleation and growth of the hydrate phase. As shown in Figure 2, a sharp reduction in the amount of methane gas and even temperature increase (shown as inset—1) is observed in the presence of all the additives. As shown in Figure 1, an increase in the gas pressure, due to hydrate dissociation, often follows the computed phase–boundary curve if the dissociation process is conducted at slow rates.

However, a rapid dissociation of the hydrate system could induce measurable deviations from the calculated behavior. The inset (2) in Figure 2, shows measured temperature in the time interval during hydrate dissociation. Observed faster gas release in this time zone is because of gas hydrate dissociation. The rate of heating in these systems with bioadditives is less than 1.0 K/h, whereas it is ~2.2 K/h in the case of SDS. Thus, the heating rate is not a predominant factor for the deviation from the phase boundary curve. As said earlier, placement of the thermal probe or some unknown constituents of the bioadditives could be contributing to this deviation.
The micro-Raman spectroscopic method was used to characterize the hydrate samples. The hydrate reactor was precooled to 150 K by keeping it in liquid nitrogen, and the residual gas pressure was purged out. The hydrate samples were preserved for the spectroscopic analysis. Figure 3 shows characteristic features of CH₄ molecules encased in the hydrates synthesized in the presence of SDS and other bioadditives. Observed Raman modes around 2905 and 2915 cm⁻¹ are because of CH₄ molecules occupying the cages of sI hydrates. The characteristic methane stretching mode at 2905 cm⁻¹ is because of the guest encased in the $\delta^{12}$ cage of sI, whereas the one at 2915 cm⁻¹ is because of the CH₄ molecule trapped in the $\delta^{12}$ cage.²³,²⁴

The LL shows outstanding water repellency. The reasons for these superior properties can be recognized to the combination of micro- and nano-structures with an optimized geometry and the unique chemical composition of the epicuticular waxes. The chemical analyzes of the isolated waxes show that the wax of the upper side of the leaf contains ca. 65% of various nonacosanediols and only 22% of nonacosan-10-ol, whereas the wax of the underside contains predominantly nonacosan-10-ol (53%) and only 15% of diols, together with 18% of alkanes. The remaining 13 and 14% could not be identified.²⁵ Phytochemical analysis on leaves (P. betle) revealed the presence of alkaloids, tannins, carbohydrate, amino acids, and steroidal components. The main constituent of the leaves is a volatile oil, called betel oil, and contains two phenols, betel phenol (chavibetol and chavicol). Codinene has also been found.²⁶ The principal constituents of neem (A. indica) leaves include protein (7.1%), carbohydrates (22.9%), minerals, calcium, phosphorus, vitamin C, carotene, and so forth. However, they also contain glutamic acid, tyrosine, aspartic acid, alanine, praline, glutamine- and cystine-like amino acids, and several fatty acids (dodecanoic, tetradecanoic, elcosanic, and so forth.).²⁷

Some constituents present in these bioadditives, particularly amino acids are well-known kinetic promoters for both CH₄ and CO₂ gases, even when they are present in low concentrations.²⁸–³² However, as noticed by Wang et al.,¹⁹ it may not be possible to isolate all the constituents of bioadditives and study their impact on the formation of hydrates. The characteristic methane stretching mode at 2905 cm⁻¹ is because of the guest encased in the $\delta^{12}$ cage of sI, whereas the one at 2915 cm⁻¹ is because of the CH₄ molecule trapped in the $\delta^{12}$ cage.²³,²⁴

Figure 2. Observed variations in the methane gas contents in the vapour phase as a function of time. The black and red symbols correspond to the behavior during hydrate formation and dissociation stages, respectively. The parts a to d are for the additives SDS, LL, BL and NL, respectively. The insets (1) and (2) in each part in this figure are the temporal changes in the temperature.

Figure 3. Characteristic Raman signatures of CH₄ encaged in the large and small cages of sI. The blue lines are fitted Lorentzian to the recorded data (red dots).
clathrates, rather their collective role is important for greenhouse gas storage applications. Further, the effect of additives is not the same on all greenhouse gas clathrates. 28–32 The methane storage capacity in the presence of investigated bioadditives is similar to SDS (see Table 1). The perfect unit

| Expt no | Additive | Temperature (K) | Pressure (kPa) | CH₄ uptake (mol) | Hydrate yield (%) | Time taken for 90% gas uptake (min) |
|---------|----------|-----------------|---------------|------------------|------------------|-------------------------------------|
| 1       | SDS      | 278.5           | 6800          | 0.208            | 82.0             | 30                                  |
| 2       | SDS      | 280.2           | 6850          | 0.206            | 81.0             | 35                                  |
| 3       | LL       | 270.6           | 6570          | 0.191            | 74.9             | 34                                  |
| 4       | LL       | 272.0           | 6500          | 0.171            | 68.5             | 42                                  |
| 5       | LL       | 272.4           | 6520          | 0.191            | 75.0             | 43.5                                |
| 6       | BL       | 269.2           | 6590          | 0.215            | 84.5             | 52                                  |
| 7       | BL       | 269.3           | 6630          | 0.201            | 79.1             | 36                                  |
| 8       | BL       | 269.6           | 6580          | 0.200            | 78.8             | 52                                  |
| 9       | BL       | 268.8           | 6430          | 0.182            | 71.5             | 58.5                                |
| 10      | NL       | 269.0           | 6550          | 0.188            | 73.8             | 49                                  |
| 11      | NL       | 269.0           | 6600          | 0.177            | 69.6             | 45                                  |
| 12      | NL       | 269.0           | 6600          | 0.177            | 69.6             | 45                                  |

*Formation kinetics is measured from after the hydrate nucleation. All the experiments were conducted with 1.6 mol solution and 0.5 wt % additive.

Table 1: Hydrate Onset Conditions, Total Gas Uptake during the Phase Change

Figure 4. Pressure–temperature (p–T) trajectories of the CO₂–H₂O system in the presence of 0.5 wt % additives. The black and red symbols are recorded behavior during freezing and thawing cycles, whereas the blue curve represents the computed phase boundary curve. (A) With SDS, (B) without any additives (dots) and with LL (stars), (C) with BL (dots) and (D) with NL (stars).

In summary, we conducted experiments to store the greenhouse gases namely CH₄ and CO₂ in the form of gas hydrates. The isochoric experimental configuration, without continuous stirring, is user-friendly for upscaling. Addition of 0.5 wt % dry powders of N. nucifera (Indian lotus), P. betle (betel), and A. indica (neem) have dramatic influence on the hydrate formation capacity in the CH₄–H₂O system, whereas no hydrate formation occurred in the CO₂–H₂O system. Greater subcooling is necessary for the hydrate systems in the presence of these bioadditives. However, methane storage capacity and kinetics of gas uptake are comparable with the 0.5 wt % SDS system. The natural occurrence, less preparation, and cost

**CONCLUSIONS**

We also conducted similar experiments with CO₂ gas and found that these bioadditives are not useful in CO₂ hydrates. Figure 4 shows the p–T trajectory in the CO₂–H₂O system, which possesses all the bioadditives and linearly or significantly less pressure reduction, often less than pure water, in the temperature range 264–293 K. However, the addition of 0.5 wt % SDS indicates the hydrate formation. The average hydrate conversion in the CO₂–H₂O system without any additives is 17.3% (see Figure 4B), whereas the addition of SDS increases it to 55.8% (see Figure 4A). However, as shown in Figure 4B no hydrate formation occurred with LL. On the other hand, the addition of betel (see Figure 4C) and neem (see Figure 4D) leaf powders is also less useful for CO₂ hydrates, and average conversion is only 14.5 and 8.3%, which is less than that in the pure water system. Earlier we also noticed that certain amino acids, for example, l-methionine is a good promotor for both CH₄ and CO₂ hydrates, whereas l-phenylalanine does not have equal promotion effect for these greenhouse gases. 28 Thus, we can conclude that these bioadditives do not promote CO₂ hydrates.

The chosen bioadditives are relatively inexpensive and widely occur in all seasons. Unlike the starch powders, these materials are capable of forming hydrates in nonstirred conditions which is an added advantage in the scale-up process. Further, the kinetics of gas uptake is also significantly faster and is more or less similar to SDS (see Table 1). As already stated, it would be difficult to assign the rapid and efficient hydrate formation to a single chemical constituent. However, we can separate water-soluble parts from these bioadditives. Thus, we conducted another set of experiments using water-soluble extracts from these bioadditives, and the methane gas uptake and the formation kinetics is identical to the earlier experiments using betel and NL powders. However, the gas uptake is ~40% lower in the hydrates from the LL extracts. Nevertheless, the advantages such as an efficient and rapid hydrate conversion related to these bioadditives are attractive, and these are excellent materials for methane gas storage applications.
factors are attractive for their usage in methane storage applications.

**EXPERIMENTAL SECTION**

**Materials.** High-purity (99.95%) methane gas is used to conduct experiments and is obtained from Bhuruka Gas Company. Millipore water type 1 (deionised) is used in the preparation of the sample solution. The fine powders of bioadditives were made from dried (at ambient temperature under shade for several days) leaves. The dry leaves were powdered in a domestic mixture (Philips-HL1643) and were sieved using a BSS-60 sieve. The powder (0.5 wt %) was added to the water and was mixed for about half-an-hour using a magnetic spinner.

**Apparatus.** A high-pressure reactor vessel (250 mL volume) made of SS-316 is used as the hydrate synthesizer, which can resist a pressure of up to 10 MPa. A mixture of glycol and water in an appropriate ratio is used as a coolant to decrease/increase the temperature to the desired value in the reactor vessel using the closed loop chiller (ANCRYO AL RSS-40). Temperature measurements were done using a platinum resistance thermometer (Pt 100) placed inside the thermowell with an accuracy of ±0.2 K. A pressure transducer (WIKA, type A10 for pressure range 0−25 MPa with ±0.5% accuracy) is used for pressure measurements.

**Procedure.** The aqueous solution (29 g) was poured into the reactor vessel, and the reactor vessel is clamped tightly. The methane gas is filled up to desired pressure into the reactor through an inlet valve using the Teledyne ISCO syringe pump. The pump connection is removed, and the chiller is set to lower temperature into the hydrate stability zone. After some time, the pressure in the reactor vessel falls abruptly with temperature increase, indicating the hydrate formation. The temperature and pressure data are recorded for every 30 s. The molar concentration of methane gas (ΔnH2) in the hydrate phase during the experiment at time t is defined by the following equation

\[
\Delta n_{H2} = n_{t0} - n_{t} = (P_{V}/Z_{0}RT_{0}) - (P_{V}/Z_{t}RT_{t})
\]

where Z represents the compressibility factor, calculated using the Peng−Robinson equation of state, available gas volume (V) during the process was assumed as constant, that is, the volume changes because of phase transitions were neglected. n_{t0} and n_{t} denote the number of moles of methane gas at zero time and at time t, respectively.

**Raman Measurements.** The Raman measurements were performed using the instrument (Horiba, T-64000) coupled with an air-cooled argon ion laser (514.5 nm). The gas hydrate sample is loaded into the Linkam FTIR 600 stage at atmospheric pressures and 153 K. The laser is focused on the sample only during the data acquisition using 50x lens. The GRAMS/3 software was used to fit the recorded data to the Lorentzian components. The peak position, full width at half-maximum intensity, and peak intensity of the individual peaks were allowed to vary as free parameters in the peak-fitting procedure.

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**Notes**

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**REFERENCES**

(1) Koh, C. A.; Sloan, E. D.; Sum, A. K.; Wu, D. T. Fundamentals and applications of gas hydrates. *Annu. Rev. Chem. Biomol. Eng.* 2011, 2, 237−257.

(2) Uchida, T.; Kvanme, B.; Coffin, R. B.; Temna, N.; Oyama, A.; Masutani, S. M. Review of fundamental properties of gas hydrates: breakout sessions of the international workshop on methane hydrate research and development. *Energies* 2017, 10, 747.

(3) Chong, Z. R.; Yang, S. H. B.; Babu, P.; Linga, P.; Li, X.; Review of natural gas hydrates as an energy resource: Prospects and challenges. *Appl. Energy* 2016, 162, 1633−1652.

(4) Dashiti, H.; Yew, L. Z.; Lou, X. Recent advances in gas hydrate-based CO2 capture. *J. Nat. Gas Sci. Eng.* 2015, 23, 195−207.

(5) Prasad, P. S. R.; Esvari, C. V. V. Clathrate hydrates: A powerful tool to mitigate greenhouse gas. In *Carbon Utilization*; Goel, M., Suddhakar, M., Eds.; Springer: Singapore, 2017; pp 157−168.

(6) Karamalidin, M.; Varaminian, F. Water desalination using R141b gas hydrate formation. *Desalin. Water Treat.* 2014, 52, 2450−2456.

(7) Babu, P.; Nambiar, A.; He, T.; Karimi, I. A.; Lee, J. D.; Englezos, P.; Linga, P. A review of clathrate hydrate based desalination to strengthen energy-water nexus. *ACS Sustainable Chem. Eng.* 2018, 6, 8093−8107.

(8) Cha, M.; Shin, K.; Kim, J.; Chang, D.; Seo, Y.; Lee, H.; Kang, S.-P. Thermodynamic and kinetic hydrate inhibition performance of aqueous ethylene glycol solutions for natural gas. *Chem. Eng. Sci.* 2013, 99, 184−190.

(9) Ferrin, A.; Musa, O. M.; Steed, J. W. The chemistry of low dosage clathrate hydrate inhibitors. *Chem. Soc. Rev.* 2013, 42, 1996−2015.

(10) Sun, M.; Firoozabadi, A.; Chen, G.-J.; Sun, C.-Y. Hydrate size measurements in anti-agglomeration at high watercut by new chemical formulation. *Energy Fuels* 2015, 29, 2901−2905.

(11) Rogers, R. E.; Kothapalli, C.; Lee, M. S.; Woolsey, J. R. Catalysis of gas hydrates by biosurfactants in seawater-saturated sand/ clay. *Can. J. Chem. Eng.* 2003, 81, 973−980.

(12) McLaurin, G.; Shin, K.; Alavi, S.; Ripmeester, J. A. Antifreeze act as catalysts for methane hydrate formation from ice. *Angew. Chem., Int. Ed.* 2014, 53, 10429−10433.

(13) Borchardt, L.; Casco, M. E.; Silvestre-Albero, J. Methane hydrate in confined spaces: an alternative storage system. *ChemPhysChem* 2018, 19, 1298.

(14) Linga, P.; Clarke, M. A. A review of reactor designs and materials employed for increasing the rate of gas hydrate formation. *Energy Fuels* 2017, 31, 1−13.

(15) Prasad, P. S. R. Methane hydrate formation and dissociation in the presence of hollow silica. *J. Chem. Eng. Data* 2015, 60, 304−310.

(16) Wang, W.; Ma, C.; Lin, P.; Sun, L.; Cooper, A. I. Gas storage in renewable bioclasteres. *Energy Environ. Sci.* 2013, 6, 105−107.

(17) Falkharian, H.; Ganji, H.; Naderi Far, A.; Kameli, M. Potato starch as methane hydrate promoter. *Fuel* 2012, 94, 356−360.

(18) Babakhani, S. M.; Alamdari, A. Effect of maize starch on methane hydrate formation/dissociation rates and stability. *J. Nat. Gas Sci. Eng.* 2015, 26, 1−5.
(19) Wang, W.; Zeng, P.; Long, X.; Huang, J.; Liu, Y.; Tan, B.; Sun, L. Methane storage in tea clathrates. *Chem. Commun.* 2014, 50, 1244–1246.

(20) Nagashima, H. D.; Takeya, S.; Uchida, T.; Ohmura, R. Preservation of carbon dioxide clathrate hydrates in the presence of trehalose under freezer conditions. *Sci. Rep.* 2016, 6, 19354.

(21) Takeya, S.; Nakano, K.; Thammawong, M.; Umeda, H.; Yoneyama, A.; Takeda, T.; Hyodo, K.; Matsuo, S. CO₂ processing and hydration of fruit and vegetable tissues by clathrate hydrate formation. *Food Chem.* 2016, 205, 122–128.

(22) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008.

(23) Chari, V. D.; Prasad, P. S. R.; Murthy, S. R. Structural stability of methane hydrates in porous medium: Raman spectroscopic study. *Spectrochim. Acta, Part A* 2014, 120, 636–641.

(24) Uchida, T.; Hirano, T.; Ebinuma, T.; Narita, H.; Gohara, K.; Mae, S.; Matsumoto, R. Raman spectroscopic determination of hydration number of methane hydrates. *AIChE J.* 1999, 45, 2641–2645.

(25) Ensikat, H. J.; Ditsche-Kuru, P.; Neinhuis, C.; Barthlott, W. Superhydrophobicity in perfection: the outstanding properties of the lotus leaf. *Beilstein J. Nanotechnol.* 2011, 2, 152–161.

(26) Dwivedi, V.; Tripathi, S. Review study on potential activity of *piper betle*. *J. Pharmacogn. Phytochem.* 2014, 3, 93–98.

(27) https://www.neemfoundation.org/about-neem/chemistry-of-neem/.

(28) Prasad, P. S. R.; Kiran, B. S. Clathrate hydrates of greenhouse gases in the presence of natural amino acids: storage, transportation and separation applications. *Sci. Rep.* 2018, 8, 8560.

(29) Prasad, P. S. R.; Kiran, B. S. Are the amino acids thermodynamic inhibitors or kinetic promoters for carbon dioxide hydrates? *J. Nat. Gas Sci. Eng.* 2018, 52, 461–466.

(30) Sa, J.-H.; Kwak, G.-H.; Han, K.; Ahn, D.; Cho, S. J.; Lee, J. D.; Lee, K.-H. Inhibition of methane and natural gas hydrate formation by altering the structure of water with amino acids. *Sci. Rep.* 2016, 6, 31582.

(31) Bavoh, C. B.; Nashed, O.; Khan, M. S.; Partoon, B.; Lal, B.; Shafi, A. M. The impact of amino acids on methane hydrate phase boundary and formation kinetics. *J. Chem. Thermodyn.* 2018, 117, 48–53.

(32) Liu, Y.; Chen, B.; Chen, Y.; Zhang, S.; Guo, W.; Cai, Y.; Tan, B.; Wang, W. Methane Storage in a Hydrated Form as Promoted by Leucines for Possible Application to Natural Gas Transportation and Storage. *Energy Technol.* 2015, 3, 815–819.