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Review

Review of Biosurfactants Gas Hydrate Promoters

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Abstract: Biosurfactants are promising additives for gas hydrate technology applications. They are believed to have better eco properties than conventional kinetic hydrate promoters such as sodium dodecyl sulfate (SDS). In this article, the research advances on the use of biosurfactants for gas hydrate formation enhancement have been reviewed and discussed in detail to provide current knowledge on their progress in green chemistry technologies. Specifically, the use of bio promoters in carbon capture, gas storage and transportation are discussed. By far, biosurfactants seem to perform better than conventional hydrate promoters and have the potential to lead to the commercialization of gas hydrate-based technologies in terms of improving hydrate kinetics.

Keywords: CO_2 capture and storage; anti-agglomerants; gas hydrates promotion; gas hydrate technologies; biosurfactants

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1. Introduction

Gas hydrates are inclusion compounds that consist of gas and water molecules [1–3]. In the hydrate structure, the hydrogen-bonded water molecules engage the gas molecules at low temperatures and high-pressure conditions [4–7]. The stories and issues of hydrate have majorly been associated with flow assurance challenges in the oil and gas industry, where they mostly form and plug oil and gas transmission pipelines [8–11]. However, in recent times, gas hydrate has found several useful applications in areas of gas storage and separations, desalination, potential energy sources, and CO_2 capture and sequestration. This recent advancement is driven by the desire to develop and search for novel gas hydrate additives to enhance the gas hydrate application techniques.

Contrary to the use of hydrate inhibitors to prevent gas hydrate formation in pipelines, gas hydrate promoters are used to enhance hydrate formation in hydrate application-based techniques. The purpose of hydrate promoters is to speed up the hydrate formation kinetics of these processes. Generally, to achieve this, surfactants are mostly used. The commonly used surfactant in the literature is sodium dodecyl sulfate (SDS) [1,11–13]. The gas hydrate promotional mechanisms of SDS have been extensively reported in the literature [14–18]. Aside from the high hydrate promotional impact of synthetic surfactants, they are generally toxic and difficult to dispose of. Hence, the search for environmental and biodegradable additives for gas hydrate promotion in hydrate-based applications is imminent.

In the search for alternative hydrate promoters, biosurfactants are potential candidates that could provide the required green regulatory requirements without compromising hydrate promotional efficiency [19]. Aside from their green nature, biosurfactants are very stable at high pH, temperature, and saline conditions [20–23]. Literature has shown that their class of surfactants are by far prospective candidates that could replace the use of conventional gas hydrate kinetics promoters [22,24]. Despite the presence of comprehensive reviews on the use of conventional surfactants in hydrate-based applications, there is no concise collective and focused review on the use of biosurfactants in hydrate-based technologies [24–26]. The absence of such reviews places the process of biosurfactants technology in gas hydrate application on a poor knowledge-based level with no critical understanding of the state-of-the-art research advance made by far. This knowledge gap, if well filled, would provide the gas hydrate community with relevant in-depth ideas on the kind of biosurfactants to use or develop towards technological commercialization. Such a piece of work would also guide and provide relevant knowledge for future biosurfactant development for hydrates application purposes.

Therefore, in this review, we discussed the effect of various biosurfactants on the thermodynamics and kinetics of hydrate formation. A detailed discussion on the effect of each biosurfactant on gas hydrate formation behaviour is also presented. Also, the mechanism of action of different biosurfactants on hydrate formation is presented with possible prospects and recommendations towards the development of more efficient bio-additives for hydrate-based technologies.

2. Biosurfactants and Their Application in Gas Hydrate Technologies

Biosurfactants are microorganism-based extracted surface-active molecules. They are mostly considered green alternative additives to surfactants. Due to their environmental and biodegradability potential, they are mostly used in areas such as pharmaceuticals and therapeutics, cosmetics, food additives, emulsifiers, detergents and cleaners, and dispersants for bioremediation. Gas hydrate-based technologies such as gas storage and transportation, carbon capture, gas separations, and gas hydrate inhibition have found the use of biosurfactants very useful as shown in Figure 1. In Gas hydrate technological applications, the use of biosurfactants has hydrate-forming capabilities. One of the areas in which biosurfactants can improve is by using hydrate methods for gas separations and transportation. The storage and transportation of liquefied natural gas (LNG) is mostly accompanied by high energy costs and explosive hazards. Thus, the use of hydrate methods is believed to reduce the energy and hazard factors for better transportation. However, finding the best way to form natural gas storage faster and keep it solid for longer periods is a challenge. It is in this regard that biosurfactants are relevant in this area of gas hydrate formation.

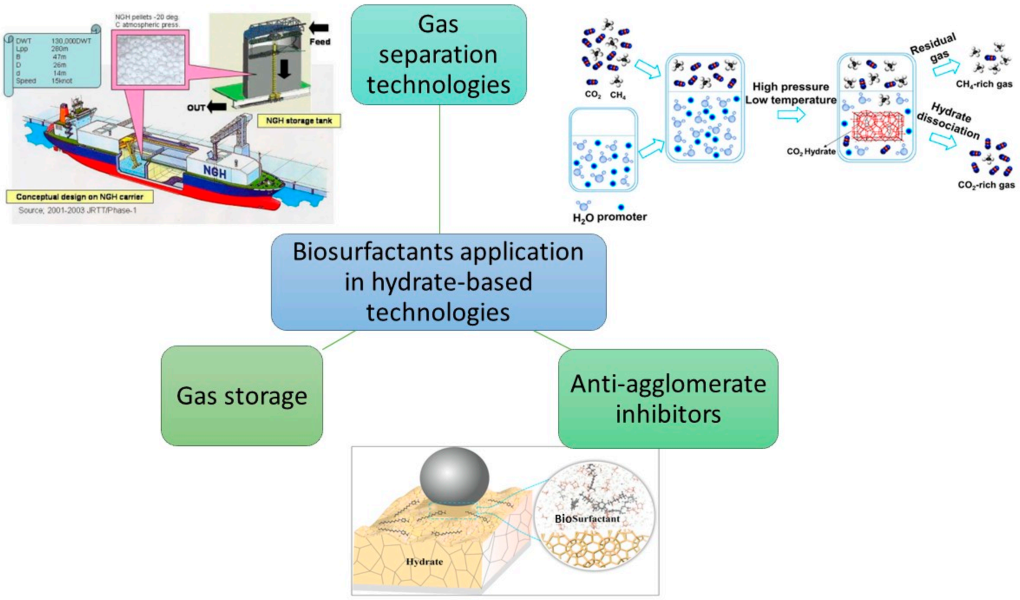

Figure 1. Common gas hydrate–based technologies that could potentially use biosurfactants.

In the area of carbon dioxide capture and disposal, attention has been drawn to the use of a gas hydrate-based approach. The hydrate-based gas separation process (HBGS) specifically is a potential method for separating and capturing CO_2 from fuel and flue gas mixtures. This process uses the gas hydrate phase behaviour conditions to select CO_2 from the mixtures. With the thermodynamic feasibility zone for CO_2 capture from hydrates, biosurfactants are green solvents that have been suggested to potentially overcome the slow hydrate formation behaviour for effective and fast separations. Also, in the storage of CO_2 hydrate in gas hydrate formations and geological sediments, the use of biosurfactants becomes necessary to resolve the existing low CO_2 hydrate formation in the sediments. Biosurfactants are also potential gas hydrate anti-agglomerate inhibitors that can prevent hydrate plugs in oil and gas pipelines with less environmental issues.

Biosurfactants in all gas hydrate-based technologies aim to enhance gas hydrate formation process by either increasing the nucleation time, hydrate formation rate, and storage capacity. Specifically, biosurfactants are able to promote or enhance gas hydrate formation by increasing gas solubility, supporting micelle formation, and providing the nucleation sites for hydrate formation (see Figure 2). This promising gas hydrate formation enhancement could potentially influence the commercialization prospect of most gas hydrate-based technologies. In the field of gas hydrates, biosurfactants have recently been spotted and explored due to their natural existence in hydrate deposit environments in the marine and permafrost areas via culture-independent studies. Since then, several types of biosurfactants for most plant and bacterial sources have been used for hydrate studies. Table 1 shows the biosurfactants used for hydrate promotion studies in the literature. From Table 1, biosurfactants from bacterial sources are the most widely studied biosurfactants for hydrate studies.

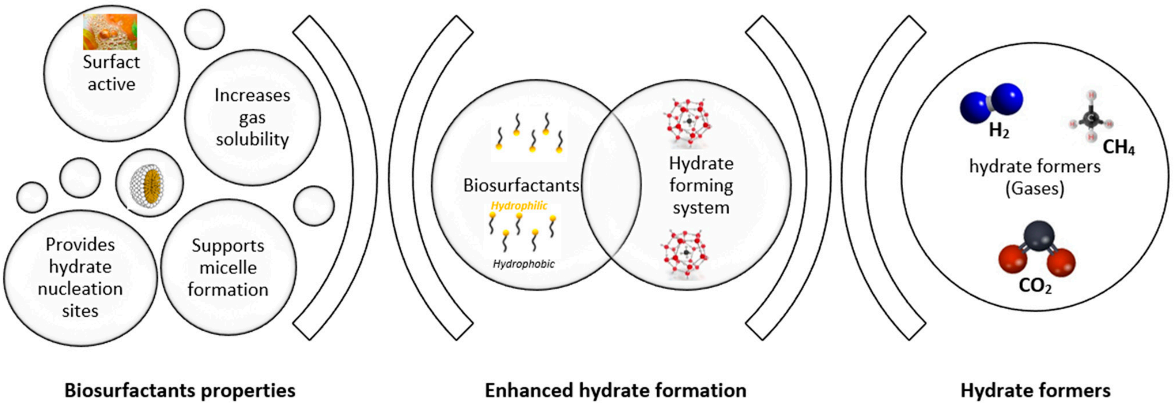

Figure 2. Properties of biosurfactants suitable for gas hydrate promotion.

Table 1. Biosurfactants synthesized by various microbes for gas hydrate applications.

Biosurfactant	**Microorganisms**	**Ref.**
Rhamnolipid	Pseudomonas aeruginosa	[27–33]
Cocos nucifera	Cocos nucifera oil	[34]
Surfactin	Bacillus subtilis bacterium	[29,30,35,36]
Sulfonated lignin/lignosulfonate	Wood pulp/biomass	[37–40]
Sunflower oil-based promoters (SFOPs)	Sunflower oil	[41]
Emulsan	Acinetobacter calcoaceticus	[28,29]
Hydroxylated fatty acid	Corynebacterium Lepus	[28]
Snomax	Pseudomonas syringae	[28]
Phospholipids	Thiobacillus species, Corynebacterium species	[28]

The main reason biosurfactants are used for gas hydrate application purposes resides in their biodegradability and low toxicity levels [42–44]. Aside from that, they can be synthesized to have varying chain lengths and active hydrophilic and hydrophobic groups for higher surface activity in aqueous systems. An additional advantage of biosurfactants is their stability at extreme temperatures, salinity, and pH conditions. However, they require some add-on facilities and time for their purification and separation from the microbial solution.

3. The Impact of Biosurfactants on Hydrate Formation

In hydrate-based technological applications, chemicals are mostly used to promote the hydrate formation process. This is mostly achieved kinetically or thermodynamically in the presence of chemicals. The kinetics hydrate promoters are used to achieve fast hydrate onset formation times, a high rate of hydrate formation, and a high gas storage or consumption capacity. SDS is the most common kinetic hydrate promoter [1,12,13,45–48]. On the other hand, thermodynamic hydrate promoters such as tetrabutylammonium bromide (TBAB), tetrahydrofuran (THF), and acetone are used to increase the temperature and pressure conditions required for hydrate formation [49,50]. Since the use of biosurfactants as hydrate promoters is still actively ongoing, their thermodynamic promotional effect on hydrate formation is discussed alongside their kinetic behaviour. Table 2 presents the list of biosurfactants used for hydrate storage and CO_2 capture. The gas hydrate guest molecules studied in the presence of biosurfactants are CO_2, CH_4, and natural gas (consisting of CH_4, C_2H_6, and C_3H_8), with much emphasis on CH_4 hydrates.

Table 2. List of biosurfactants used for hydrate-based application.

Biosurfactant	Gas System	Conc. (ppm)	Remarks	Ref.
Rhamnolipid	CO_2	0.001156 g/mL	• Rhamnolipid reduces the hydrate formation time of SDS by 20 times. • Rhamnolipid forms hydrate seven times quicker and 20% more than SDS. • Rhamnolipid increases CH_4–CO_2 replacement ability by 72, with more CO_2 storage capacity.	[48]
Cocos nucifera	CH_4	0.01–0.05 mol	• CDS excellently promotes gas hydrate formation like SDS and exhibits less forming effect. • 90% CH_4 could be stored as hydrate pellets for 12 days under controlled conditions in CDS.	[34]
Bacillus subtilis bacterium	0.90 CH_4 + 0.06 C_2H_6 + 0.04 C_3H_8	100	• The biosurfactant produced large nodule-like hydrates, which demonstrate their ability to stabilize formation in porous media.	[29]
Sulfonated lignin	CH_4 and CO_2	300–1000	• The sulfonated lignin promotes hydrate formation more than SDS. It also has the ability to stabilize dissociation.	[38,40]
Sunflower oil-based promoters (SFOPs)	CH_4	286–1500	• SFOP slightly reduces hydrate nucleation time, growth rate, and storage capacity compared to SDS.	[41]
Rhamnolipid and surfactin	CH_4	200–1000	• Rhamnolipid and surfactin perform better as hydrate promoters than SDS.	[30]
Surfactin	CH_4	0.5–1 wt.%	• Surfactin perform better as a hydrate promoter than SDS.	[36]

Table 2. *Cont.*

Biosurfactant	Gas System	Conc. (ppm)	Remarks	Ref.
Calcium, sodium, and potassium lignosulfonate	CH_4	0.1–5 wt.%	• Lignosulfonates have the ability to promote CH_4 hydrate growth and rate with a high capacity of up to 170 v/v.	[39]
Rhamnolipid	CH_4	0.1–1 wt.%	• At 0.5 wt.%, rhamnolipid can minimise hydrate agglomeration.	[33]
Hydroxylated fatty acid, rhamnolipid, emulsan, snomax, surfactin, and phospholipid	$0.90\ CH_4$ + $0.06\ C_2H_6$ + $0.04\ C_3H_8$	1000	• Biosurfactants promote natural gas hydrate formation in sand/clay porous media systems with and with seawater.	[29]
Rhamnolipids	CH_4	100–1000	• Rhamnolipids are green gas hydrate kinetic promoters in silica gel systems.	[31]
Rhamnolipids	CH_4	100–1000	• Rhamnolipids are green gas hydrate kinetic promoters in silica gel systems.	[32]

3.1. Thermodynamic Impact

The thermodynamic hydrate promotion of additives is key to overcoming the high pressure and low temperature of hydrate formation suitable for commercial hydrate technologies. Generally, surfactants are known as kinetic hydrate promoters and not thermodynamic promoters. This implies that surfactants have a negligible effect on hydrate thermodynamic properties. However, this is mainly known for conventional gas hydrate kinetic promoters and some studied surfactants in the literature. In the presence of biosurfactants, the thermodynamic behaviour of the gas hydrate formation conditions has not been extensively reported on CO_2 and natural gas hydrates. Contrary to the status quo, Arora et al. [32] claimed that the presence of rhamnolipids biosurfactant promotes methane hydrate phase boundary conditions by increasing the hydrate formation region in the pressure range of 9–11 MPa in a silica-gel porous-media system. These findings are staggering if well confirmed in different systems since such findings suggest a dual hydrate promotional impact of biosurfactant. However, in their study, they further estimated the CH_4 hydrate dissociation enthalpies in the presence of biosurfactants. The CH_4 dissociation enthalpies were 17–22 KJ/mol K with and without rhamnolipids biosurfactant. However, the widely reported methane hydrate dissociation enthalpies with and without most additives in the range from 50 to 60 KJ/mol K, depending on the pressure. This inconsistency could be due to the presence of the rhamnolipids biosurfactant, the porous media systems, or experimental errors. If the latter is not the case, then the rhamnolipids biosurfactant and/or the porous media might have some potential impact on the hydrate crystal structure, which is likely not the case. Thus, we recommend hydrate crystal structure analyses and simulations such as RAMAN or NMR to further verify this phenomenon. However, Hou et al. [33] confirmed the hydrate structural characteristics and morphology using powder X-ray diffraction, Raman spectroscopy and cryo-scanning electron microscopy. They showed that rhamnolipid did not affect hydrate structure, but it could increase the large and small cavity ratio value and hydration number. In general, surfactants are considered kinetic promoters and not thermodynamic promoters. The next sections discuss the studies of gas hydrates in the presence of biosurfactants.

3.2. Kinetic Impact

The use of kinetic gas hydrate biosurfactants promoters has been reported more in the literature compared with thermodynamic biosurfactants. Although biosurfactant has been used for different gas hydrate technologies, their kinetic behaviour on gas hydrate formation can be useful to other hydrate-based technologies. Thus, the priority of this discussion is not to limit the performance of each studied biosurfactant to a specific hydrate technology, but rather show how each biosurfactant performs kinetically in various hydrate former systems.

3.2.1. Rhamnolipids

Rhamnolipids are common biosurfactants consisting of crystalline acids that are mainly made up of rhamnose-based β-hydroxy fatty acids as shown in Figure 3. Pseudomonas aeruginosa is the main productional source of rhamnolipids [51–53]. Rhamnolipids are the most studied biosurfactant for gas hydrate applications, especially for CO_2 capture. Like SDS, most biosurfactants including rhamnolipids have strong hydrophilic and hydrophobic heads. During hydrate formation in biosurfactants, the hydrate formation promotional effect is governed by the strong interaction between the water molecules and the biosurfactants' hydrophilic head. The hydrophobic head of the biosurfactants on the other hand interacts with the gas molecules. In addition, the micelles' formation of biosurfactants at high concentrations leads to the formation of more hydrates because the micelles act as hydrate nucleating sites, which promote the solubility of the guest molecules in the aqueous bulk liquid phase.

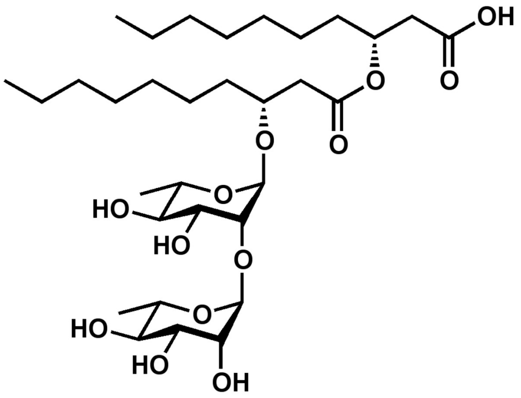

Figure 3. General chemical structure of rhamnolipids.

A rhamnolipid solution produced from Pseudomonas aeruginosa is reported as an effective biosurfactant for enhancing CO_2 hydrate formation with a high formation rate [48]. The presence of rhamnolipids reduces the induction time and the total time of the process by 99% and 84% compared to SDS. Furthermore, the use of rhamnolipids increases CO_2 replacement with CH_4 and also improves CH_4 recovery. Jadav et al. [30] also confirmed that 200 ppm of rhamnolipid solution yields a hydrate conversion of about 14% more than SDS and increases the amount of gas consumed by 20%, with the hydrate kinetic growth rate enhanced to seven times higher than that of SDS. Despite the hydrate promotion impact of rhamnolipids, they are known for their anti-agglomerate behaviour, which arises from their surfactant nature [33].

3.2.2. Lignosulfonates

Lignosulfonates are bio-based additives produced from wood pulp using sulfite pulping. They are amorphous and water-soluble anionic polyelectrolytes [54,55]. The chemical structure of lignosulfonates is shown in Figure 4. The biomass origin, sulfite pulping conditions, post-extraction fractionation, and chemical modifications determine the lignosulfonate composition, structure, molecular weight distribution, and abundance of functional groups. The three tested derivatives are calcium-lignosulfonates (Ca-LS), sodium-lignosulfonates (Na-LS), and potassium-lignosulfonates (K-LS). Ca-LS promotes hydrate formation in a similar range as Na-LS and K-LS. The optimum Ca-LS concentration of 0.50 wt.% yields a high gas uptake and volumetric capacity of 167 v/v in 1000 min. Also, the induction time of hydrate formation was improved (shortened) in the lignosulfonates systems. At high concentrations, the lignosulfonates gas hydrate promotion strength is reduced [39].

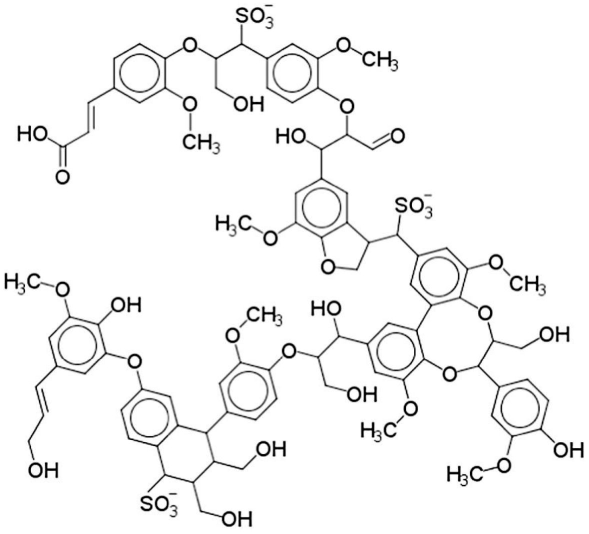

Figure 4. General chemical structure of lignosulfonates.

3.2.3. Surfactin

Surfactin is a biosurfactant, which is originally made from the culture broth of bacillussubtilis [56–58]. Surfactin is a cyclic lipopeptide (Figure 5) of seven amino acids and different 3-hydroxy fatty acids, with the main component being 3-hydroxy-13-methylmyristic acid. In hydrate studies, the surfactin used is produced from marine-derived bacterial species using the Polymerase Chain Reaction (PCR) technique [36]. According to Bhattacharjee et al. [36], surfactin significantly promotes methane hydrate formation compared to pure water and SDS (at 1 wt.%). Bacillussubtilis bacterium from the ATCC 21332 species has also been used for hydrate studies [35]. The Bacillussubtilis bacterium was cultured anaerobically with glucose as a carbon source. The hydrate testing in porous media confirmed that the surfactin shorten the hydrate nucleation time and increased the hydrate formation markedly. The hydrate morphology in the presence of surfactin appears to be large and nodule-like under the anaerobically generated surfactin. The morphology is similar to marine hydrate formation in anaerobic bacteria.

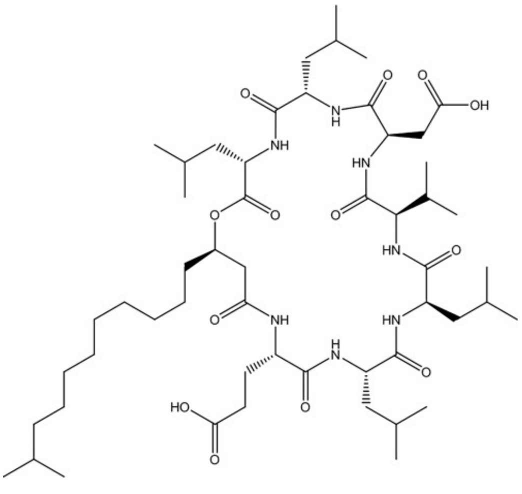

Figure 5. General chemical structure of surfactin.

The production of the surfactin biosurfactant via anaerobic activities in hydrate formation zones controls the hydrate stability and growth formation in hydrate sediments [35].

Jadav et al. [30] also tested surfactin on methane hydrate formation and claimed that lower concentrations of surfactin (<200 ppm) have a negligible impact on methane nucleation. At 400 ppm, surfactin exhibits higher hydrate formation than water due to its hydrate promotional impact at such a concentration. In comparison to rhamnolipid and SDS, rhamnolipid performs better than surfactin at lower concentrations (200 ppm), while surfactin is better that rhamnolipid at slightly higher concentrations (400 ppm) [30]. However, it is advisable not to study their hydrate promotional impact above 400 ppm. This is because at such concentrations, their performance reduces and might lead to hydrate inhibition. It is recommended that for hydrate inhibition purposes, both rhamnolipid and surfactin can be tested at concentrations below their CMC but not at less than 400 ppm [30].

3.2.4. Sunflower Oil-Based Promoters (SFOPs)

SFOPs are surfactants specifically synthesized to exhibit suitable hydrophilic and hydrophobic properties for gas hydrate-based applications. They could appear in different forms but for gas hydrate-related studies, only two types of SFOPs are used (see Figure 6). The two types are similar in the presence of branched structures with several carboxylic acid and sulfonate groups but differ in the number of hydrophilic groups [41].

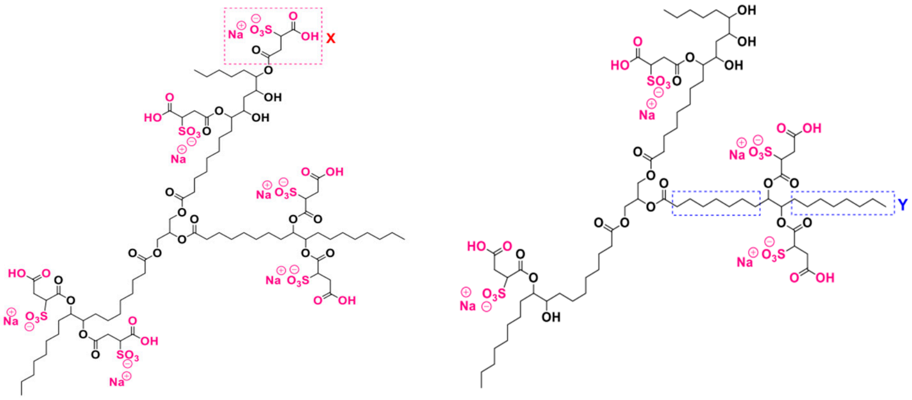

Figure 6. General chemical structure of sunflower oil−based promoters.

Through an experimental and molecular dynamics simulation study, Farhadian et al. [41] proved that sunflower oil-based promoters (SFOPs) have the potential to promote methane hydrate formation behaviour more than SDS. Specifically, SFOP with six hydrophilic groups increased the methane hydrate formation rate constant of SDS by 2.5 times. However, their ability to reduce hydrate nucleation time was poor compared with SDS. Thus, aside from being used as promoters, SFOPs might have some potential as anti-agglomerate gas hydrate inhibitors.

3.2.5. Cocos Nucifera

Cocos nucifera biosurfactant produced from the fatty acids of coconut has been studied for its gas hydrate formation enhancement and storage for gas storage and transportation applications. Experimental evidence exhibits that CDS acts as a good gas hydrate promotor like SDS. It also exhibited mild foaming behaviour than SDS [34]. In the methane hydrate system, Cocos nucifera has similar promotional strength as SDS. In the area of gas storage, CDS has proven to lower the hydrate decomposition rate by maintaining about 90% of gas stored in it for 12 days under certain thermodynamic conditions [34].

3.2.6. Sulfonated Lignin (SL)

Sulfonates lignin is a soluble polymer with anionic properties. It is mostly synthesized from by-products of wood pulp using sulfite pulping [59–61]. SL is a novel surfactant used for hydrate applications as a gas hydrate promoter. Ge et al. [37] recently claimed that SL could promote natural gas hydrate formation and store the hydrate under controlled thermodynamic conditions. In natural gas systems, SL increases the hydrate storage capacity from 300 ppm to 500 ppm, however above 500 ppm, the hydrate storage capacity is similar with no significate changes. Compared to other surfactants (sodium dodecyl sulfate, silicone surfactant, and ethylene diamine tetraacetamide), SL performs better in hydrate storage capacity [37]. Like most surfactants, SL does not exhibit a significant effect on gas hydrate phase behaviour. Mofrad et al. [40] further confirmed that SL stores more natural gas as a hydrate than SDS by 14% at 500 ppm. SL could store hydrates in solid form for longer periods with a slower decomposition rate than SDS. SL also has similar behaviour to sunflower biosurfactants in terms of hydrate formation nucleation effect. They both prolong hydrate nucleation time. However, SL further promotes CO_2/CH_4 gas mixture hydrate systems with a higher gas consumption capacity than SDS, THF, and tetra-n-butyl phosphonium bromide (TBPB). The SL hydrate promotional performance is enhanced when mixed with THF [38].

3.2.7. Comparative Analysis on the Impact of Biosurfactants on Hydrate Formation

To evaluate the performance of reported biosurfactants in the literature, a relative hydrate promotional potential method was reported by Bavoh et al. [62]. This method was used in an attempt to overcome the barriers or limitations that affect gas hydrate kinetic behaviour [63,64], especially the effects of reactor type, roughness, stirring speed, cooling gradient, etc. In Figure 7, it is observed that almost all reported biosurfactants have the ability to enhance the hydrate nucleation processes, which is a key property or ability for their use in most gas hydrate applications. Amongst the reported biosurfactants, SFOPs have demonstrated a strong superiority in promoting gas hydrate formation nucleation time within 71–89% promotional strength. The performance of SFOPs on hydrate formation kinetics is supported by the work of Farhadian et al. [41]. They confirmed that SFOPs increased the transfer of gas molecules to the growing hydrate surface, which led to enhancing the kinetics of methane hydrate formation by their ability to improve the hydrogen bonds between water–water molecules.

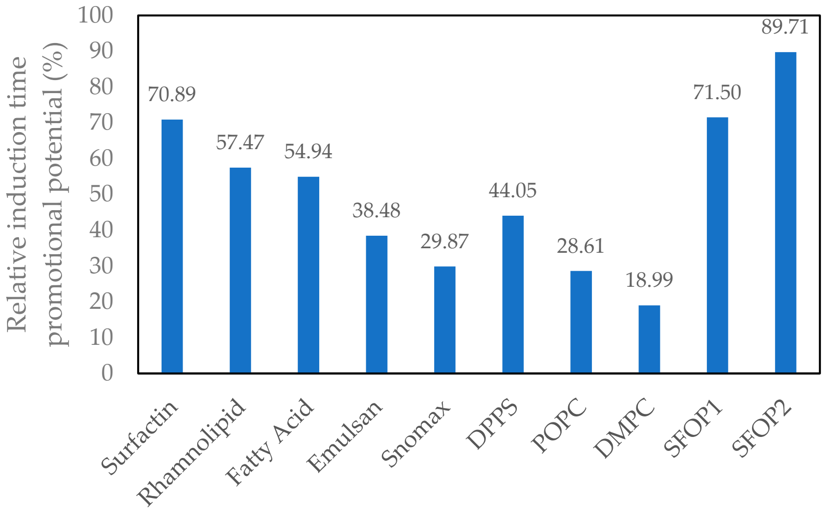

Figure 7. Relative induction time promotional potential of some reported biosurfactants [28,41].

Aside SFOPs, surfactin could promote the gas hydrate formation rate and time more than rhamnolipid, fatty acid, emulsan, snomax, DPPS, POPC, and DMPC as shown in Figures 7 and 8. All the biosurfactants promote both the hydrate nucleation time and rate of formation except fatty acids. Fatty acid turns out to have a slow impact on hydrate growth rate, which could disadvantage its application in gas hydrate technologies such as gas separation and storage. However, this behaviour of fatty acid could be useful in the flow assurance industry to manage gas hydrate plug formation. The performance of surfactin over these biosurfactants is due to their higher ionic nature and capability of interacting with the hydrate-forming media than the other biosurfactants. Also, surfactin supports a more favourable environment with a high surface adsorption, micellar formation, and hydrophilic and hydrophobic moieties that allows it to bring together hydrocarbon gases in the hydrate forming system than other biosurfactants.

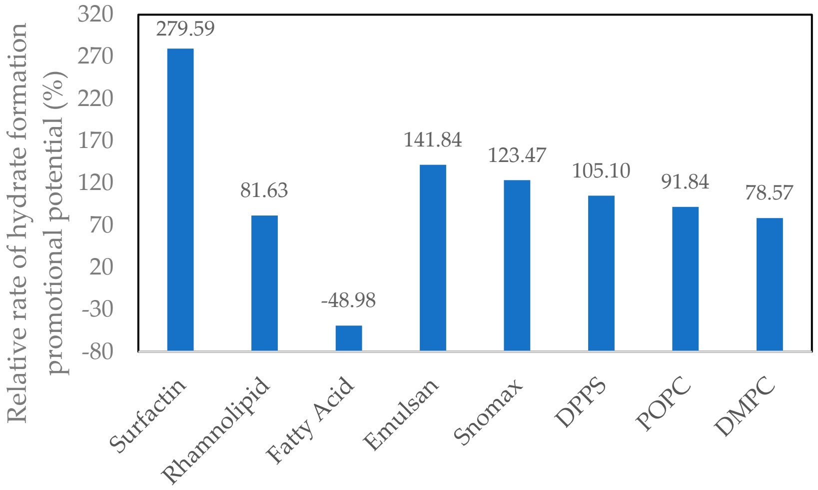

Figure 8. Relative rate of hydrate formation promotional potential of some reported biosurfactants [28].

4. Modelling/Simulation Studies

In the quest to find potential green chemicals of gas hydrate technological applications, the use of experimental results provides poor information on the atomistic and macroscopic behaviour of additives on hydrate formation. However, understanding the macroscopic mechanism and the interaction between different additives and the hydrate systems is very important to develop new additives and tailor additive synthesis for specific hydrate applications. Aside studying the microscopic behaviour of biosurfactants in gas hydrate systems, the use of empirical models to predict the hydrate formation behaviour in the presence of biosurfactants is useful for design and operational purposes. In view of this molecular dynamics (MD) simulation method is an effective tool that is used to provide atomistic studies of hydrates in the presence of additives. Also, the use of modified gas hydrate thermodynamic or kinetic models is also employed to predict the hydrate formation behaviour in additives.

Modelling and simulation studies on the use of biosurfactants for hydrate applications are rarely reported in the literature. The modelling study by Palodkar and Jana [27] was designed to give more insight to hydrate formation behaviour in silica-gel porous media with a biosurfactants (rhamnolipids) system. Their model is basically a mathematic approach, which incorporates the chemical potential of important factors that affects hydrate promotions in porous media and surfactant systems. The models also incorporate other critical factors such as porous material nonuniform size and shape of internal pores, hydrates surface rekindling effect, hydrate formation in the interstitial and interior pore spaces of the unconsolidated porous particles, surface tension effect, and effect of salt ions on hydrate nucleation and growth. The model performance in relation to experimental data shows an average absolute relative deviation (AARD) of 3.45–7.78. However, the model is quite flexible and can predict a wide range of porous media systems, such as varying biosurfactants concentrations, different temperatures and pressures, diverse porous material and their particle sizes, and fixed bed saturation [27].

A molecular dynamic (MD) simulation by Farhadian et al. [41] using Gromacs 5.1.4 package was used to study the hydrate promotion behaviour of sunflower oil biosurfactants. The molecular structures of the biosurfactants and water molecules were built using the Gaussian 03 program package and TIP4P/ice, respectively. The LINCS algorithm was used to constrain all bonds including hydrogen atoms. They proposed that the presence of enhanced hydrogen bonds between water–water molecules mainly controls the hydrate promotion impact of biosurfactants. This behaviour leads to an increasing transfer of gas molecules to the growing hydrate surface [41]. The current modelling and simulation studies lack a detailed representation of the behaviour of most studied biosurfactants on hydrate formation behaviour. Especially in areas for providing molecular-level hydrate promotion mechanisms using biosurfactants for different gas hydrate formers.

5. Biosurfactants Hydrate Promotional Mechanism

The impact of biosurfactants is similar to conventional surfactants. Palodkar and Jana [27] postulated an interfacial tension reduction-enhanced hydrate formation growth mechanism for biosurfactants. This mechanism is based on the ability of biosurfactants to disrupt and reduce the interfacial tension between the parental phases of the hydrate structure. Thus, increasing the ability of the hydrate crystals to form favourable structures for further hydrate growth or gas uptake. This behaviour is controlled by several properties of the biosurfactants. The main factors that affect the biosurfactants' hydrate promotional impact are the critical micelle concentration and kraft point temperatures. Aside from the critical micelle concentration and the kraft point, other parameters such as the interfacial tension, adhesion energy, and contact forces mostly affect the hydrate promotional behaviour of biosurfactants (Figure 9). The interfacial tension and contact forces reduction, which leads to hydrate promotion, are achieved by minimizing the surface energy and forces connected to the gas hydrate systems. This is mostly controlled by the hydrophilic and hydrophobic properties of the biosurfactants [35]. Hou et al. [33] showed that the presence of biosurfactants in hydrate systems smoothens the hydrate morphology of the hydrate structure. This was confirmed via powder diffraction (PXRD) analysis. They claimed that increasing the biosurfactant (rhamnolipid) concentration further smoothens the hydrate surface. This morphological smoothening effect was speculated as an ordered surface-motivated hydrate anti-agglomeration effect. Based on a research perspective, the promotional mechanism of biosurfactants is not well established in the literature and thus requires critical attention from the gas hydrate community, especially natural gas hydrate formation systems [37,40].

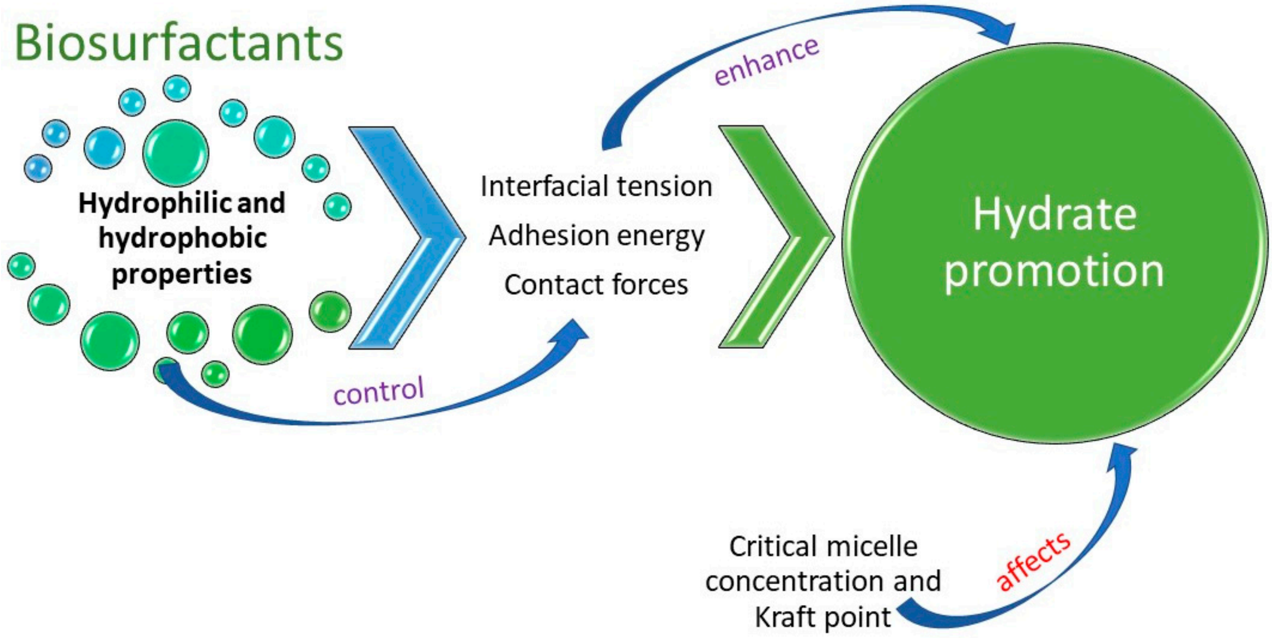

Figure 9. Factors that control and affect hydrate promotion in biosurfactants.

6. Recommendations and Prospects

The use of biosurfactants for gas hydrate-based applications has shown promising performances in lab-scale experimental evidence as discussed in this paper. Therefore, in relation to the maturity of commercializing hydrate-based technologies, the rate of hydrate formation using biosurfactants should be improved with more experimental studies on new biosurfactants on different gas hydrate formers. Also, synergistic studies of biosurfactants and conventional surfactants and other biomolecules (such as amino acids) could possibly yield an improved additive for high hydrate formation yields. The regeneration of biosurfactants takes time and poses as a demerit for their applications. It is therefore recommended to develop biosurfactants that could easily be regenerated in chemical processes. In systems like gas separations and capture, the selectivity of biosurfactants is very critical and requires more experimental investigations in varying mixed-gas systems. The hydrate promotion mechanism of biosurfactants is poorly discussed in the literature. This knowledge gap needs to be filled to provide insight into screening, selecting, and modelling biosurfactant behaviour for hydrate-based technologies. Hence, the use of MD simulations to study the molecular behaviour of biosurfactants is needed in the literature. Techno-economic analysis alongside pilot scale testing of gas hydrate technologies in the presence of biosurfactants is needed to pave the way for the successful application of surfactants in gas hydrate-based technologies.

7. Conclusions

In this manuscript, we reviewed almost all the relevant literature on the use of biosurfactants in gas hydrate applications. The findings of this work conclude that biosurfactants are potential molecules that could replace conventional surfactants in gas hydrate-based technologies. The widely used biosurfactants for gas hydrate studies are from bacterial sources with a few others from plant sources. The use of biosurfactants enhances the hydrate formation kinetics by increasing their gas-to-hydrate storage capacity while providing substantial self-preservation potentials. The gas hydrate nucleation time and growth rate can be increased by 18–89% and 78–279%, respectively, in the presence of biosurfactants. Specifically, surfactin, rhamnolipid, and sunflower-based biosurfactants are the best bio-additives that could be used in the gas hydrate technological-piloting stage. Biosurfactants promote hydrate formation by the ability of their hydrophobic and hydrophilic to alter and reduce the interfacial tension, adhesion energy, and contact forces between hydrate, water, and gas molecules. The behaviour of biosurfactants as hydrate promoters can be potentially adopted for anti-agglomerate hydrate inhibition application. By far, biosurfactants exhibit a negligible effect on hydrate structural and phase behaviour properties. Nonetheless, further experimental, modelling, and MD simulations are needed to fully comprehend the role of biosurfactants on gas hydrate promotional mechanisms. Such studies will unfold the potential of biosurfactants for commercial future hydrate-based technologies.

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