



Evaluation of antifoaming behaviour of polysiloxane mixed with fluoroalkyl as antifoam in degraded amine solution

E.L.S. Ng^a, K.K. Lau^{a,*}, S.F. Lim^b, S.Y. Chin^c, B. Partoon^d

^a Centre of Carbon Capture, Utilization and Storage (CCUS), Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia

^b Faculty of Engineering, Universiti Malaysia Sarawak, Kota Samarahan, 94300, Sarawak, Malaysia

^c Department of Chemical Engineering, College of Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang Darul Makmur, Malaysia

^d Department of Biological and Chemical Engineering, Aarhus University, Universitetsbyen 36, 8000, Aarhus C, Denmark

A B S T R A C T

The removal of CO₂ from natural gas by absorption in amine-based solvent is a vital process for oil and gas industries. However, this process frequently struggles to meet its market specifications due to the degradation of amine solution by contaminants in the absorption system which often leads to foam formation and cause issues such as reduction in process performance. The aim of this study is to evaluate the antifoaming performance of Polymethylhydrogensiloxane (PMHS) with Hexafluorobutyl Acrylate (HFBA) antifoam in the methyldiethanolamine (MDEA) and piperazine (PZ) solution degraded by glycine, heptanoic acid and bicine. The antifoaming performance of PMHS + HFBA antifoam in this study has been found to be superior compared to the PDMS antifoam. The highest antifoaming performance for PMHS + HFBA and PDMS antifoam is in the presence of heptanoic acid with the highest average foaming tendency reduction of 61.91 % and 42.39 % respectively. This is attributed to the higher spreading coefficient of PMHS + HFBA antifoam that enables it to rupture foam at a faster rate. This study will demonstrate the importance of the continuous improvement of the use antifoams in reducing foam formation for absorption systems.

1. Introduction

Carbon capture, utilization, and storage (CCUS) provides the necessary approaches and technologies to reduce CO₂ emission to the environment as its releases leads to several environmental impact such as rise in global temperature and change in weather patterns [1]. Moreover, the removal of CO₂ is also a requirement for industrial processing as to reduce corrosion in processing equipment, maintain the economic value of natural gas, and reduce operational cost [2,3]. The absorption process is an established method used in the acid gas removal system to remove CO₂ for natural gas stream [4]. Some of the common types of amines used in acid gas removal system are Monoethanolamine (MEA), Diethanolamine (DEA), Methyldiethanolamine (MDEA), and Piperazine (PZ) [2,5]. Absorption columns (and regenerators) are susceptible to foaming due to high dispersion of natural gas in degraded amine solution by contaminant such as organic acids, condensed liquid hydrocarbon, and heat stable salts [3,6–9]. These foams are a cluster of gas bubbles encased by foam films (liquid/gas interface barrier). Form

formation occurs when the foam films surrounding the gas bubbles are able to resist breakage. The presence of contaminant reduces the surface tension of the liquid medium which increases the stability of the foam film and hence, foam formation takes place [10].

The presence of foam formation cause several operational issues such as reduction in absorption process efficiency and loss of amine solvent during regeneration [11–13]. Hence, antifoam is added to reduce foam formation and to ensure the stability of the acid gas removal process [13]. Antifoams are compounds consisting of either oils, solid particles or a mixture of both [14]. They are typically added into a liquid medium to eliminate or reduce foam formation. The important aspect for an antifoam is that they are insoluble in a liquid medium (hydrophobic), and have a low surface tension (~20–30 mN/m) [15,16].

1.1. Studies on foam formation and behaviour for acid gas removal process

Based on Fig. 1, the formation of foam begins as a cluster of gas

Abbreviations: MEA, Monoethanolamine; DEA, Diethanolamine; MDEA, Methyldiethanolamine; PZ, Piperazine; HCB, Hydrocarbon-based; PAG, Polyalkylene glycol; PDMS, Polydimethylsiloxane; PPG, Polypropylene Glycol; PMHS, Polymethylhydrogensiloxane; HFBA, Hexafluorobutyl Acrylate; Carbon Dioxide, CO₂; N₂, Nitrogen; IPAE, loaded aqueous 2-(isopropylamino)ethanol; SCFH, Standard Cubic Feet Per Hour.

* Corresponding author.

E-mail address: laukokkeong@utp.edu.my (K.K. Lau).

<https://doi.org/10.1016/j.rineng.2024.102784>

Received 6 June 2024; Received in revised form 9 August 2024; Accepted 24 August 2024

Available online 26 August 2024

2590-1230/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

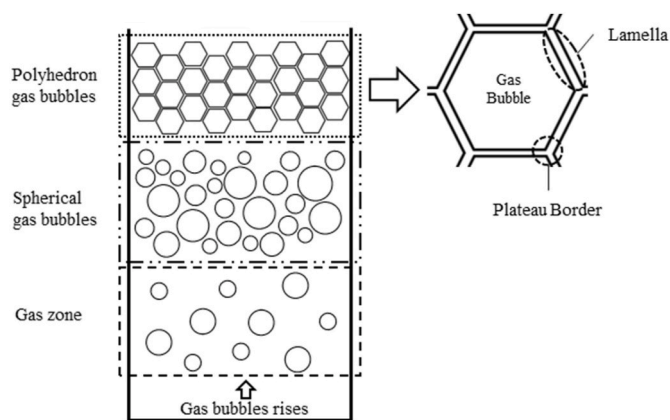


Fig. 1. Foam Formation and structure [20,21].

bubbles starts to rise upwards from the bottom of the foaming column due to buoyancy force. The gas zone is the area where the bubbles are first formed. While the bubbles continue to rise upwards, the liquid flows downwards due to gravity. A thick liquid foam film is formed between the spherical gas bubbles as they move closer to each other. This is because most of the liquid has flowed downwards to the gas zone where there is no foam film between gas bubbles. This foam film will shrink in size as the gas bubbles continues to rise upwards and the liquid flows downwards [17,18]. While the foam film shrinks in thickness as it approaches the top of the liquid surface, the gas volume in the gas bubbles increase. This results in the formation of polyhedral-shaped bubbles at the top section of foam structure (polyhedron gas bubble zone in Fig. 1) [19].

The thin layer of foam film that surrounds the polyhedric gas bubbles are called lamella [18,22]. A Plateau border is formed when three or four lamellas are connected at its verticals. The polyhedral foam have a higher tendency to rupture due to the presence of thinner foam film as compared to the bottom spherical foam [3,23].

Foam ruptures when the foam formation loses its stability and breaks due to a process called the thinning process. The three steps in this thinning process are liquid drainage, foam coarsening and foam coalescence (foam rupture). Liquid drainage is where the liquid in the foam film flows downwards to the Plateau border due to difference in gravity and capillary pressure [20,17]. This will lower the liquid volume in the foam films which leads to foam coarsening and foam coalescence [24]. Foam coarsening occurs when the gas diffuses between varies sizes of gas bubbles due to difference of gas pressure. Smaller gas bubbles with higher pressure diffuse into a bigger gas bubble with lower pressure. The transferring of gas changes the size of the smaller gas bubbles to a bigger gas bubbles, leading to the reduction in the number of smaller gas bubbles [24,25]. Foam coalescence is when gas bubbles fuse with each other. This process occurs when the foam film is very thin and unstable, causing the foam film to break and form a larger bubble. This reduces the number of gas bubbles and eventually leads to collapse of foam formation [22]. These three mechanisms are dependent on each other. Liquid drainage leads to thinner and drier foam films and thereby encouraging film rupture. Foam coarsening leads to the formation of larger gas bubbles which reduces the stability of the gas bubbles. Unstable foam films leads to the rupture of foam film through foam coalescence [23].

In recent years, several studies on the foaming behaviour in activated amine solution in the presence of various contaminants have been reported. For instance, some experimental works conducted in degraded amine solution has proven that the presence of contaminant such as organic acid (C4 to C8 and C10), corrosion inhibitors (HCB), solid particulate (iron sulfide), heavy hydrocarbon (C7,C8,C16) increases foaming tendency [3,7,26–28] and foam stability [7,26]. In addition to that, the previous works has also evaluated the effect of temperature and gas

flow rate using MDEA + PZ solution in the presence of organic acid and heavy hydrocarbon where the increase in both parameters increase both foam tendency and foam stability [29]. From these studies, it is shown that foaming is an issue that needs to be addressed and further emphasize the importance of the foam prevention method, especially with the use of chemical antifoaming agents.

1.2. Antifoam theory and mechanism

The addition of antifoam reduces foam formation by increasing the rate of the thinning process which causes the foam film to destabilize and rupture. As expressed in Equations (1) and (2), the entering coefficient (E), spreading coefficient (S) are used to indicate the ability or inability of an antifoam to reduce foam formation [30].

$$E = \sigma_F + \sigma_{AF} - \sigma_A \quad (1)$$

$$S = \sigma_F - (\sigma_{AF} + \sigma_A) \quad (2)$$

where σ_F is the surface tension of foaming liquid, σ_{AF} is the interfacial tension of foaming liquid/antifoam and σ_A is the surface tension of antifoam.

Firstly, the entering coefficient must first be positive. A positive entering coefficient ensures that the oil droplet enters the foam film surface. A positive spreading coefficient ensures that the antifoam particle (oil droplet) spreads radially across the foam film surface and forms an oil lens which stretches overtime and promotes thinning of the foam film by bridging-stretching or spreading-fluid mechanism. In the bridging-stretching mechanism, the foam film ruptures once the middle oil lens is torn apart due to stretching [31]. The spreading-fluid entrainment is where liquid in the foam film is dragged away from the oil lens, leading to thinning of the foam film and eventual rupture [32].

1.3. Types of antifoams used in acid gas removal system

Particularly in acid gas removal, three types of antifoams that are commonly known to be used are silicone oil, polyglycol, and alcohols, or a combination of them. The selection antifoam depends on the types of solvent, operating parameter such as temperature and gas flow rate, and severity of foam formation [14]. A previous review paper has analyzed the types of antifoam used in acid gas removal along with their advantages, disadvantages and key findings [33]. In brief, silicone-based antifoam such as PDMS (used in previous experimental work [29]) has low surface tension, good dispersibility, good thermal stability [34], versatile [35], and is able to reduce considerable amount of foam height. However, it creates deposition when in excess [36], and increases foam stability (foam break time). In a recent study, the addition of silicone-based antifoam can increase foam stability of a liquid solution [37]. This is because the presence of impurities and silicon-based antifoam increases the elasticity of the foam film and may retard liquid drainage.

Subsequently, polyglycol-based antifoam such as polyalkylene glycol (PAG) [38] forms less deposition [39], has low/medium surface tension and also able to reduce the foam height to a lower level, but suffers from low thermal stability where it thickens up and causes blockage in pumps [36]. Next, the alcohol-based antifoam like oleyl alcohol with isopropyl alcohol [40] is less expensive, has low/high surface tension [41] and able to suppress foam formation within a short amount of time. However, it is less effective compared to silicone and polyglycol antifoam as it degrades to organic acid and cause more foam [14]. Lastly, the mixed based antifoam such as a mixture of PDMS, PAG, PPG and silica [42,43] has better dispersibility, low fouling, and higher thermal stability.

Among the antifoaming agents that are available, the silicone-based antifoams such as PDMS are recommended to be used in amine solution because of its low surface tension of approximately 21 mN/m which makes it suitable for many amines solvent that have higher surface