Performance Evaluation of Polydimethylsiloxane-Solvent Blends as Defoamer for Crude Oil Foam

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Abstract. The study is directed at the use of polydimethylsiloxane-based defoamer formulated with different solvent blends that are capable of breaking and preventing crude oil foam. The control or elimination of the foam that arises in oil and gas industrial processes is a crucial factor in the smooth and efficient operation of the plant. Foam can reduce available capacity of processing vessels, and interfere with the efficiency of the process. Foaming problem is common in the three-phase separators in crude oil flowstations; it can result in level control difficulties and carryover of valuable crude oil into the gas scrubbers and eventually to the gas flare, resulting in loss of production. The effectiveness of these solvent blended defoamers in controlling crude oil foam was determined using foam-rise or Bikerman test method. The collapse rates of the foam with the application of each defoamer sample at various treatment rates (10ppm, 15ppm and 20ppm), were observed as against a blank as control. It was observed that at 10ppm treatment, defoamer A had the highest foam collapse rate (0.0108mm/s). At 15ppm treatment, defoamer G had the highest foam collapse rate (0.0110mm/s), and at 20ppm treatment, defoamer E had the highest foam collapse rate (0.0108mm/s). This shows that defoamer A, which is the conventional formulation (i.e. 20 %vol. silicone + 80 %vol. kerosene), had the highest foam collapse rate at the lowest dosage of 10ppm. On the overall, the highest foam collapse rate (0.0110mm/s) was obtained with defoamer G at 15ppm treatment. Defoamer G is 20 %vol. silicone + 80 %vol. of a (1:1 v/v) blend of kerosene and crude palm kernel oil. This suggests that the presence of crude palm kernel oil in the solvent blend had a remarkable effect on the crude oil foam collapse rate. Conclusively, the performance of defoamers varies considerably with the kind of solvent or blend of solvents used for the dispersion of the silicone fluid. It is also worthy of note that the treatment dosage of a defoamer, together with the foam collapse rate are key factors that influence the selection of an effective defoamer.

Keywords: production chemical; flowstations; silicone products; crude oil emulsion

1. Introduction

Petroleum-based foams are amongst the most important and abundant types of non-aqueous foams. Furthermore, the complexity of the continuous phase in these foams is higher than in other non-aqueous foams. This is because the composition of crude oil varies greatly depending on the well location and age. Crude oil is a naturally occurring mineral oil consisting of a variety of organic compounds, mainly saturated and aromatic hydrocarbons, as well as complex compounds such as resins and asphaltenes [1].

Foams may occur in any stage of oil recovery and processing, and they can be desirable or a nuisance; since it is the bubbles that have sufficient buoyancy to rise to the surface that are described as foams [1]. For example, oil foams can be useful as drilling fluids or gas blocking agents during extraction from porous media, but undesirable during gas/oil separation, oil/water separation and during refining.

An additional complexity of petroleum foams, apart from oil composition, is that they usually contain water, particles (sand, clay, corrosion products, paraffin crystals, precipitated asphaltenes, etc.) or even additives introduced during the oil extraction phase (surfactants commonly used as bactericides, anti-corrosion, anti-oxidants, emulsion breakers, asphaltene dispersants, anti-scale, etc). These factors produce petroleum foams that may exhibit different types of behaviour, showing that foaming of liquids arises from the presence of impurities [2,3]. The amount of foam that a system can create, the stability of the foam and, even, the capacity to create gas/liquid films depend on the characteristics of the gas dissolved in it. Gases that do not have an
affinity for the crude oil tend to form unstable foams. However, for gases soluble in the oil, foam can be formed, and the extent of formation will depend on the pressure and temperature of the system.

The composition of the crude oil is equally important to the eventual foaming properties. Several constituents can promote the formation of foam and its stabilization. Mechanical problems that may generate foam are leaky seals on pumps, high-pressure flows, poor system design (tank, pump inlet, outlet and manifold design) and pressure release.

A defoamer is a chemical additive that reduces the foam in foaming liquids in industrial processes. The terms ‘anti-foam agent’ and ‘defoamer’ are often used interchangeably. In industrial processes, foams pose serious problem; they cause defects on surface coatings, they prevent the efficient filling of containers, reduction of pump efficiency (cavitation) and reduce capacity of storage tanks. Modern anti-foams are complex formulated specialty chemicals but generally consist of an insoluble oil phase containing hydrophobic solids dispersed within it. The anti-foam is typically provided in a dispersed form, with droplets of controlled particle sizes and distribution in the surfactant solution [4]. The significant property of a defoamer is that it is generally insoluble in the foaming medium and has surface-active properties. An essential feature of a defoamer product is its low viscosity and ability to spread rapidly on foamy surfaces. It has affinity for the air-liquid surface where it destabilizes the foam lamellas. This causes rupture of the air bubbles and breakdown of surface foam. Anti-foams are introduced in surfactant solutions to prevent the formation of excessive foam [5]. A typical anti-foam consists of an oil (polydimethylsiloxane or hydrocarbon), dispersed hydrophobic solid particles, or a mixture of both.

Among the five types of product-based defoamers, silicone-based defoamers are the widely used anti-foaming agent in non-aqueous foaming systems such as in the crude oil production and oil refining systems [1]. Silicone-based defoamers are polymers with silicon backbones. The silicone compound often contains hydrophobic silica dispersed in an organomodified silicone fluid. Polydimethylsiloxane is a particularly efficient defoamer ingredient because of its low surface tension, spreading capability, thermal stability, chemical inertery and water insolubility. Silicone based defoamers can be formulated as 20 %vol liquid products, as solutions and as aqueous emulsions. Organic modification of the polydimethylsiloxane with polyethers or other organic groups renders the products more compatible and allows the formulation of highly efficient defoamers with excellent compatibility characteristics for high performance applications. Emulsifiers or suitable solvents are added to aid handling and efficient dispersion within the foaming medium.

It is a well-known fact that the performance of foam-control agents varies considerably with the type of foaming surfactants [4].

Three steps can characterize the working mechanism of a defoamer: first, a defoamer droplet has to enter the foam lamella. Due to its highly surface-active properties, the defoamer droplet has a strong tendency to migrate to the air/water-surfactant interface. Secondly, the defoamer droplet spreads and pushes aside the stabilizing surfactants. Without the stabilizing surfactants, the foam lamella locally becomes much less elastic usually referred to as “reverse Marangoni effect‘. Thirdly, this kind of destabilization facilitates rupture of the foam lamella. To increase defoamer efficiency, it is a common approach to add finely divided hydrophobic particles, such as hydrophobic silica or waxes, to the formulation. The reason for this is that the hydrophobic solid particles are able to destabilize the foam lamella by a de-wetting process. In simple terms, the surfactant film, which stabilizes the foam lamella, is not able to wet the hydrophobic solids and collapses (i.e. shrinks back). An unstable area results where the lamella is thus destabilized [4].

The most noticeable form of foam is foam floating on the stock surface, thus, the case with crude oil formation. Surface foam may cause problems with liquid levels resulting in overflow and carryover. This might reduce the process efficiency and availability of process equipment. Hence, this paper seeks to formulate different blends of silicone-based defoamers using solvents and combination of solvents; afterwards, determine their effectiveness in controlling crude oil foam formation. This will proffer solution that will control foaming in the crude oil flow station using defoamers.

2. Materials and method

The materials used are; glass capillary tube, micropipette, air sparger, glass measuring cylinder (500ml), crude oil, siliccones such as kerosene., diesel, refined palm kernel oil (RPKO) and crude palm kernel oil (CPKO); stopwatch, hydrometer and pH meter. The properties of the solvents and their blends, such as
turbidity, colour and phase separation, were determined through visual examinations while measuring instruments like hydrometer and pH meter were used to determine the specific gravity and pH respectively.

The method used for the defoamer test is the foam-rise or Bikerman test method [6].

A 100ml of fresh crude oil was poured into 500ml glass cylinder. The glass capillary tube was inserted in the glass cylinder with the air sparger tube connected to it, with the other end of the tube connected to the air sparger compressor. The air sparger system, which has capacity to deliver air at a constant flow rate of 94 ml/min, was operated for a period of 2 min before been switched off for observation. The following were determined: height of foam generated immediately after 2 min, height of foam that collapsed after 30 sec and the time taken for the entire foam to collapse. The first run (without defoamer) is the blank. The procedure above was repeated with the addition of 10ppm, 15ppm and 20ppm respectively, of the various defoamers.

Table 1 Defoamers and their composition

| S/N | Defoamer products | Composition |
|-----|-------------------|-------------|
| 1   | Defoamer A        | 20 %vol. Silicone + 80 %vol. kerosene |
| 2   | Defoamer B        | 20 %vol. Silicone + 80 %vol. diesel |
| 3   | Defoamer C        | 20 %vol. Silicone + 80 %vol. refined palm kernel oil |
| 4   | Defoamer D        | 20 %vol. Silicone + 80 %vol. crude palm kernel oil |
| 5   | Defoamer E        | 20 %vol. Silicone + 80 %vol. of a (1:1 %v/v) blend of kerosene and diesel |
| 6   | Defoamer F        | 20 %vol. Silicone + 80 %vol. of a (1:1 %v/v) blend of kerosene and refined palm kernel oil |
| 7   | Defoamer G        | 20 %vol. Silicone + 80 %vol. of a (1:1 %v/v) blend of kerosene and crude palm kernel oil |
| 8   | Defoamer H        | 20 %vol. Silicone + 80 %vol. of a (1:1 %v/v) blend of diesel and refined palm kernel oil |
| 9   | Defoamer I        | 20 %vol. Silicone + 80 %vol. of a (1:1 %v/v) blend of diesel and crude palm kernel oil |
| 10  | Defoamer J        | 20 %vol. Silicone + 80 %vol. refined palm kernel oil |

3. Results and discussion

Table 2 Physical properties of the Defoamers and their components

| Components/defoamers      | Colour      | pH  | Turbidity (visual examination) | Specific Gravity (SG) | Phase Separation |
|---------------------------|-------------|-----|---------------------------------|------------------------|-----------------|
| Crude palm kernel oil     | Light yellow| 4.38| Slightly turbid                 | 0.915                  | No Separation   |
| Kerosine                  | Yellow      | 4.99| Slightly turbid                 | 0.820                  | No Separation   |
| Refined palm kernel oil   | Yellow      | 5.24| Clear liquid                    | 0.921                  | No Separation   |
| Silicone                  | Colourless  | 9.11| Clear liquid                    | 0.970                  | No Separation   |
| Diesel                    | Medium brown| 9.28| Slightly turbid                 | 0.810                  | No Separation   |
| Defoamer A                | Colourless  | 4.60| Very turbid                     | 0.9106                 | No Separation   |
| Defoamer B                | Brown       | 5.03| Slightly turbid                 | 0.901                  | No Separation   |
| Defoamer C                | Yellow      | 4.84| Clear liquid                    | 0.8486                 | No Separation   |
| Defoamer D                | Light brown | 6.32| Very turbid                     | 0.841                  | No Separation   |
| Defoamer E                | Orange      | 4.06| Clear liquid                    | 0.924                  | No Separation   |
| Defoamer F                | Yellow      | 5.00| Clear liquid                    | 0.840                  | No Separation   |
| Defoamer G                | Colourless  | 5.20| Clear liquid                    | 0.842                  | No Separation   |
| Defoamer H                | Light brown | 5.19| Clear liquid                    | 0.843                  | No Separation   |
| Defoamer I                | Amber       | 5.27| Clear liquid                    | 0.840                  | No Separation   |
| Defoamer J                | Yellow      | 5.85| Clear liquid                    | 0.845                  | No Separation   |
The foam heights and foam collapse rates for the blanks were the same in each set of experiments. There were variations in foam heights and foam collapse rates for the various defoamers at the different treatment rates of 10ppm, 15ppm and 20ppm. The collapse rates $R_c (\text{mm/s})$ were obtained using the equation below.

$$R_c (\text{mm/s}) = \frac{\text{Height of the entire foam column}}{\text{Time taken for complete collapse}}$$  

Eqn. 1.0

At various injection doses (0, 10, 15, 20ppm), the different defoamers applied were observed for the height of foam-collapse in 30sec. From Figure 1.0, defoamer A showed increasing order of foam collapse within 30 sec with respect to increasing defoamer dose. Defoamer B showed decreasing order of foam collapse within 30 sec with respect to increasing defoamer dose. Other trends can be, readily seen in the figure. However, defoamer B had the highest height of foam-collapsed in 30sec of 22.5mm at 15ppm dosage.
Figure 2 Collapse rate of the entire foam column versus defoamer treatment

At various injection doses (0, 10, 15, 20ppm), the different defoamers applied were observed for the collapse rate of the entire foam column. From Figure 2.0 It was observed that at 10ppm treatment, defoamer A had the highest foam collapse rate (0.0108mm/s). While at 15ppm treatment, defoamer G had the highest foam collapse rate (0.0110mm/s), and at 20ppm treatment, defoamer E had the highest foam collapse rate (0.0108mm/s). This shows that defoamer A, which is the conventional formulation (i.e. 20%vol. silicone + 80%vol. kerosene), had the highest foam collapse rate at the lowest dosage of 10ppm. On the overall, the highest foam collapse rate (0.0110mm/s) was obtained with defoamer G at15ppm treatment. Defoamer G is 20%vol. Silicone + 80%vol. of a (1:1 %/v/v) blend of kerosene and crude palm kernel oil.

4. Conclusion

This research has enabled the study of silicone dispersed in readily available solvents such as diesel, kerosene, and palm kernel oil (crude and refined) and their blends as defoamers for foamy crude oils. Some of the defoamers were effective in resolving crude oil foam with high foam collapse rates. The performance of defoamer G can be further evaluated in a crude oil flowstation pilot plant. This is to further validate the research findings and for possible commercial application.

References

[1] Tarek, K. (2015). I - Anti-foaming agents. 1st ed. Available at: http://tarek.kakhia.org/books_eng/Defoamer.Tarek_kakhia.pdf [Accessed 16 Feb.2017].
[2] Shaban, H. I (1995). A Study of Foaming and Carry-Over Problems in Oil and Gas Separators. Gas Separation and Purification. 9 (5) pp 81-86 https://doi.org/10.1016/0950-4214 (95)93944-F
[3] Lewis, V.E and Minyad, W.F. (1994) Antifoaming and Defoaming in Refineries. Foams: Fundamentals and Application in the Petroleum Industry (Advances in Chemistry, Vol. 242) Chapter 12, pp 461–483.doi: 10.1021/ba-1994-0242.ch012
[4] Jha, B., Christiano S. and Shah D. (2000). Silicone Anti-foam Performance: Correlation with Spreading and Surfactant Monolayer Packing. Langmuir, 16 (24), pp.9948
[5] Garrett, P. (1993). Defoaming: Theory and Industrial Applications, Garrett, PR, Ed, Marcel Dekker, New York.
[6] Denkov N. (2004). Mechanisms of Foam Destruction by Oil-Based Anti-foams, Langmuir 20 (22), pp.9467-9468.