Study on Palm Oil-Based Glycerol Ester as An Antifoaming Agent

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Abstract. Foamation is the major obstacle in many industrial processes. Glycerol ester as one of the products made to increase the added value of glycerol as by product of biodiesel production is expected to act as antifoaming agent to solve the problem. The objective of this study is to measure the performance of glycerol ester to suppress the formation of foam at concentration 0,5%, 1,0%, 1,5%, and 2,0%. The performance tests of glycerol ester were conducted measuring density, viscosity, foamability and foam-stability in solution of Sodium Dodecyl Sulphate (SDS) and heterogenous foaming agent NF24. A commercial antifoam silicone oil is used in this study to compare the performance data. All experimental data analyzed using one-way analysis of variant and duncan test at 95% confidence level. Glycerol ester has a effect to decrease the density of foaming solution. The viscosity of the foaming solution increased with increasing the concentration of glyserol ester. Glycerol ester and silicone oil had no significant effects on suppressing foam height in SDS solution. However, the significant effect of glycerol ester to suppress foam height was indicated in NF24 solution. Foam-stability test showed that the addition of glycerol ester has not significant effect in both foaming solution. While silicone oil has a significant effct to decrease the stability of foam ini both foaming solution.

1. Introduction

Antifoaming agents or defoamers were studied their performances on suppressing the formation of foam or break down a stable foam. Stable foams are the main cause of the problems in many industries as they decrease efficiency, product quality, and even environmental issues. Hence, antifoaming agents have been widely used in many industrial processes such as phosphoric acid production, waste water treatment, and fermentation processes that generate the undesirable foams. Several studies have been discussed about an antifoaming agent entities (Joshi 2006) [1]. The dispersed antifoam in the form of droplets on a micron scale on a foaming medium is referred to as "heterogeneous" antifoam and might have been derived from a class of oil and/or hydrophobic particles. While the soluble or partially soluble antifoam of the foaming medium is referred to as "homogenous" antifoam and can be derived from nonionic surfactant groups, fatty alcohols, fatty acids, polymers, and certain organic materials (Joshi 2006, Marinova 2012; Denkov 2014) [1,2,3]. However, the solubility of antifoam in the foaming medium is determined by the characteristics of the foaming medium itself.

Saat ini penelitian dan pengembangan silicone oil sebagai antifoaming agent telah banyak dilakukan untuk penggunaannya di berbagai proses industri. Penggunaannya saat ini adalah dalam bentuk bahan aktif yang diemulsikan di dalam medium tertentu. Namun, diketahui bahwa penggunaan silicone oil sebagai antioaming agent memberikan dampak negatif pada produk akhir yang diperoleh, seperti scattering pada produk cat dan kelemahannya yang bersifat non-edible. Sehingga saat ini banyak dikembangkan antifoaming agent berbasis nabati yang dapat larut atau sebagian larut pada medium dan aman dikonsumsi. Antifoaming agent turunan pati, minyak nabati, asam lemak dan kompositnya telah banyak dikembangkan.

Recently, the research and development of silicone oil as an antifoaming agent has been widely used for its use in various industrial processes. Its current use is in the form of an emulsified active ingredient in a particular medium. However, it is known that the use of silicone oil as an antioaming agent has a negative impact on end product, such as scattering on paint products and also because it is non-edible. Hence, nowadays natural-based antifoaming agent which can be soluble or partially soluble in medium and safe to consume has been widely developed. Antifoaming agents derived from starches, vegetable oils, fatty acids and composites have been widely developed.

Glycerol ester is a derivative product of palm oil made by esterification process of glycerol and free fatty acids. Glycerol ester is one of the efforts to increase the added value of glycerol as by product of biodiesel production. The products of esterification process of glycerol and free fatty acid include trisilglycerol (TAG), diacylglycerol (DAG), monoacylglycerol (MAG), and unreacted free fatty acid (FFA) (Mardaweni 2017) [4]. These four fractions have the alleged ability to suppress the formation of foam or break up the foams that have been formed based on the literature discussed earlier. However, a study on glycerol ester which is a mixture of the four fractions as an antifoaming agent is still very limited. Therefore, this study will test the performance of glycerol ester to suppress the formation of foam or break up the foam from some foaming medium.

2. Methods

The research method of this study consists of several parts and all tests are carried out at room temperature (30°C). In this research, the performances of glycerol ester as an antifoaming agent compared with commercial antifoaming agent silicone oil. Each ingredient tested in concentration working 0.5%, 1%, 1.5%, 2% and 0% as control.

2.1. Analysis of Phisycochemical Properties of Glycerol Ester and Slilicone Oil

The glycerol ester used in this study was made by esterification process of glycerol as by product of biodiesel production and oleic acid of palm oil. The analysis of glycerol ester was performed to determine the physicochemical components and properties of glycerol ester including color (visual) test, density, viscosity, free fatty acid content. Meanwhile, analysis of silicone oil used as a comparison in this study includes color (visual), density, and viscosity.

2.2. Analysis of Phisycochemical Properties of Foaming Medium

For analysis of foaming medium, two types of foaming mediums prepared from the anionic surfactant Sodium Dodecyl Sulfate and the NF24 (formulated foaming agent) were tested. Each of the material was dissolved using water until a solution concentration of 1 wt% was obtained. Solution preparation is carried out by homogenizing the material and water at sufficient stirring speeds to prevent foam forming. The analyzes include density, viscosity, surface tension and visual observation (color).

2.3. Analysis of Influence of Glycerol Ester and Silicone Oil on Phisycochemical Properties of Foaming Medium

This analysis was carried out by homogenizing glycerol ester and silicone oil according to the concentration used into a 1 wt% foaming medium using a homogenizer at 2000 rpm for 20 seconds. The mixture was further analyzed for visual appearance, density, viscosity, and surface tension.

2.4. Performance Test of Glycerol Ester and Silicone Oil as An Antifoaming Agent

The performances test of glycerol ester as antifoaming agent performed include foamability test (foamability) and foamstability (foam stability) against the foaming medium. Performance tests were performed using the Bartsch Method hand-shakes method using a 100 ml diameter measuring cup. The glycerol ester (0%, 0.5%, 1%, 1.5%, and 2%) is then added to the glass cylinder contained about 20 ml foaming solutions. The cylinder is tightly plugged and the foam generated by 10 up-and-down hand shakes. The kinetic of foam destruction is afterward monitored for 15 min. Foamability is characterized by the height of the foam formed right after the shaking stop (t = 0). While Foamstability is characterized based on the height of the foam formed per unit of time (t> 15). Due to the effects of water drainage after shaking, the height of the formed foam is calculated based on the difference from the height of the foam and the solution (h total) by the height of the mixture in the measuring cup before shaking. Foamability and foamstability are measured by the formula:

$$\text{Foamability; Foamstability} = \frac{\text{height of foam formed } (h_f)}{\text{initial solution height}} \times 100\%$$

3. Results and Discussion

3.1. Physicochemical Properties of Glycerol Ester, Silicone Oil, and Foaming Medium

The glycerol ester used in this study is glycerol ester of esterification reaction of glycerol obtained from the production process of biodiesel as a by-product and oleic acid of palm oil. Because the fatty acids used are oleic fatty acids, the glycerol ester obtained is glycerol ester oleate or glycerol oleate.

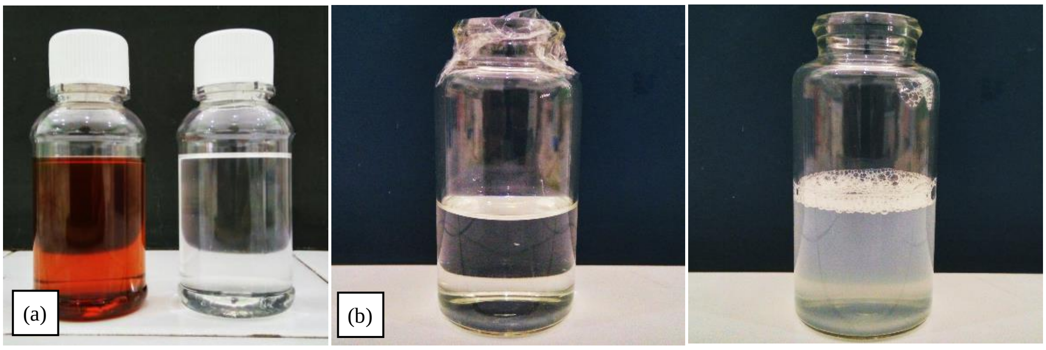


Figure 1. visual appearance (a) glycerol ester (left) and silicone oil (right), (b) SDS solution 1 wt% and (c) NF24 solution 1 wt%.

Based on visual observations, seen in Figure 1 (a), the glycerol ester oleate used has a dark brown appearance while silicone oil has a clear, colorless appearance. The appearance of a brown glycerol ester is influenced by the raw material of oleic fatty acid that having a natural brownish-brown color. Based on physical physicochemical test, glycerol ester oleate used in this research has FFA content 0.9568%, density 0.9526 g.cm^{-3} and viscosity 170.6 cP at temperature 30ºC. While silicone oil has a density value 0.9631 g.cm^{-3}. Two types of foaming agents based on their constituent components are used to measure the ability of glycerol ester oleate as an antifoaming agent. The foaming medium with a single constituent component is obtained by dissolving an petroleum-based anionic surfactant Sodium Dodecyl Sulfate (SDS) in water to obtain a concentration of 1 wt%. Then, as a comparison, NF24 foaming agent was obtained from the formulation of several palm oil-based surfactant types and some additives.

Foaming agent is then dissolved in water until obtained the same concentration. The visual appearance of these two mediums can be observed in Figures 1 (a) and (b). The foaming medium SDS 1 wt% has a clear appearance at room temperature, while the foaming medium NF24 1 wt% has a cloudy or opaque appearance. The visual difference between the two mediums is influenced by the solubility of the foaming agent constituent in water, where low solubility will result in a opaque medium. Particularly for the foaming agent of NF24, the nonionic surfactant component used may be one of the factors of turbidity, beside the influence of other additives that used in formulating. Nonionic surfactants are known to have a cloud point which makes them divide into two phases, soluble and insoluble phases, when dissolved into water at certain temperatures.

The physicochemical properties of the foaming medium are important in this study, to study the effect of the addition of glycerol ester to the medium. Most cases in the realm of antifoam use, the medium used is not a by-product or even waste for a process in the industry. Most precisely the main product in which the effect of adding additives is highly considered to be the effect on the final product of the process. In this research, the medium of foam used observed the value of density, viscosity, and surface tension conducted at room temperature (30°C). Based on the result of the research, it is known that the SDS medium 1 wt% has density, viscosity, and surface tension of 0.9980 g.cm^{-3}, 1.51 cP, and 33.01 mN.cm^{-2}, respectively. The value of these three parameters is not much different from the value of the foaming medium used as the comparison in this study, NF24 1 wt%. The density, viscosity, and surface tension of NF24 1 wt% soluble medium were 0.9962 g.cm^{-3}, 1.49 cP, and 29.34 mN.cm^{-2}, respectively.

3.2. Influence of Glycerol Ester and Silicone Oil on Physicochemical Properties of Foaming Medium

3.2.1. Visual Appearance of Foaming Medium

The visual appearance of the effect of the addition of glycerol ester and silicone oil in detail can be seen in Figure 2. It appears that there is a fundamental difference between the behavior of glycerol ester in both medium and silicone oil in both mediums, where glycerol ester forms an emulsion with a medium exhibited by a turbidity change of the medium. In plain view, the medium turbidity increases with

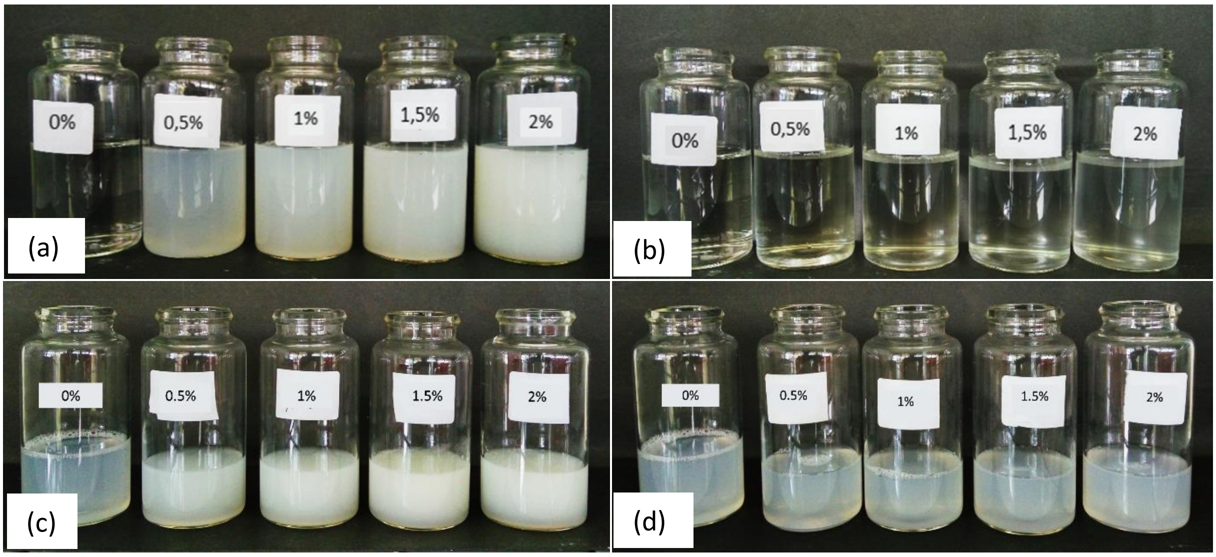


Figure 2. Penampakan visual: (a) gliserol ester + SDS; (b) silicone oil + SDS; (c) gliserol ester + NF24; (d) silicone oil + NF24.

increasing concentrations of glycerol ester in the medium. In contrast to glycerol ester, silicone oil can not form an emulsion with SDS medium but slightly affects the NF24 medium visually. Silicone oil is separated with SDS medium and rises to the surface in seconds after homogenization. The results showed that the surfactant of SDS and NF24 can increase the solubility of glycerol ester in water. Meanwhile, silicone oil can only partially dissolve on NF24 medium.

3.2.2. A Density of Foaming Medium

Density is one of the parameters used to study the phenomenon of emulsion formation between two different phases of polarity. It has been described in chapter one that one of the factors affecting the ability of an antifoaming agent to suppress or destroy the foam is the solubility of the antifoaming in the medium, in this case, the solubility is the formation of microemulsion (d <0.1 μm) or macroemulsion. The change in density of the froth medium can be seen in Figure 3. It is seen in the figure, that silicone oil tends not to affect the density of the medium at all levels of concentration. This trend is supported by visual visibility of silicone oil + medium mixture which has been discussed in sub section of 3.2.1 .. While based on figure 3, glycerol ester tends to decrease the density of the mixture. This supports the previous hypothesis, where it is suspected to form an emulsion between glycerol ester and the two mediums. The density value with the decreasing trend is due to the smaller density of glycerol ester compared to the density of the two mediums. When a medium is mixed with a constituent of lower density, feeding the medium (mixture) will increase in mass and volume. But because the constituent mass is smaller than the vomule, eat the added volume of the mixture greater than the addition of the mass. So the final density of the mixture is smaller than the initial density.

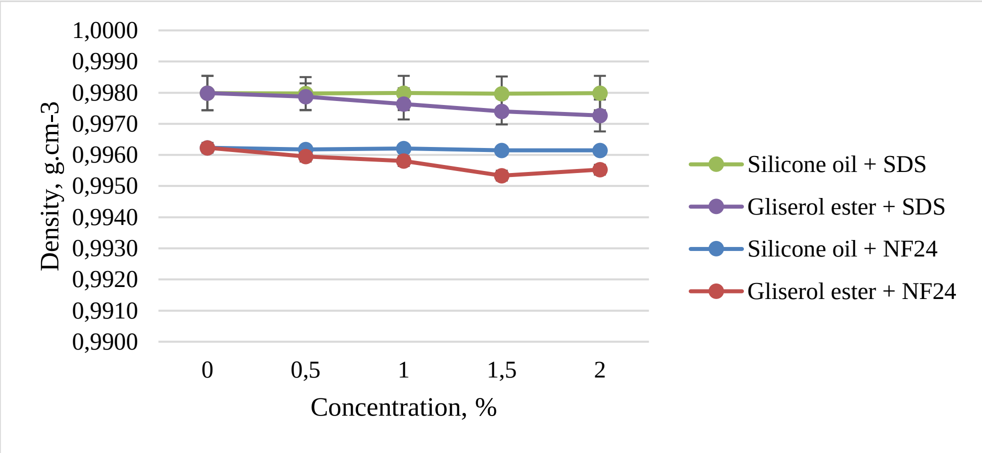


Figure 3. Density of medium as the function of glycerol ester and silicone oil concentration.

3.2.3. Viscosity of Foaming Medium

The medium viscosity regulation (dispersion phase) is one way to stabilize the gas / water emulsion system through the mechanism of inhibition of "macrosyneresis" or "drainage". Drainage is the outflow (down) liquid / medium of the foam from the foam due to gravity (Fainerman 2001) [5]. In Stokes law, the effect of viscosity is inversely related to the rate of separation of an emulsion system. The inhibition of macrosineresis results in the medium layer in the foam lamela wide enough that the antifoam droplet is not capable of damaging the foam layer conformation and resulted in the loss of active antifoam power and improved foam stability.

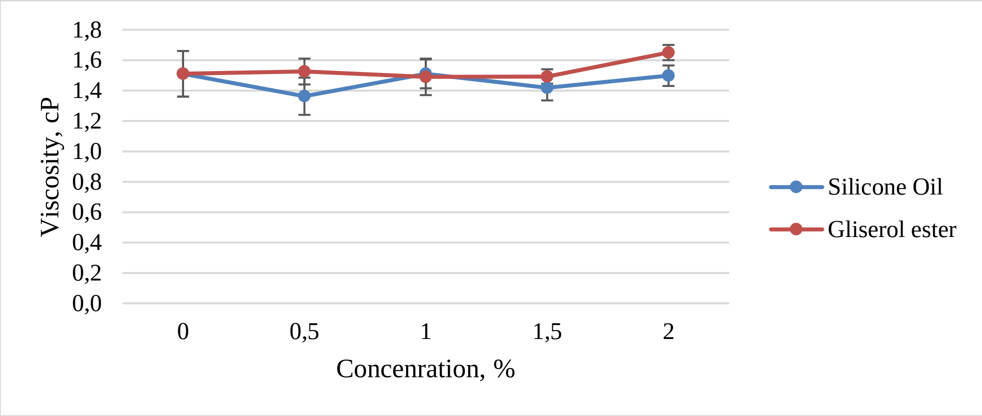


Figure 4. Effect of concentration glycerol ester and silicone oil on viscosity of foaming medium SDS.

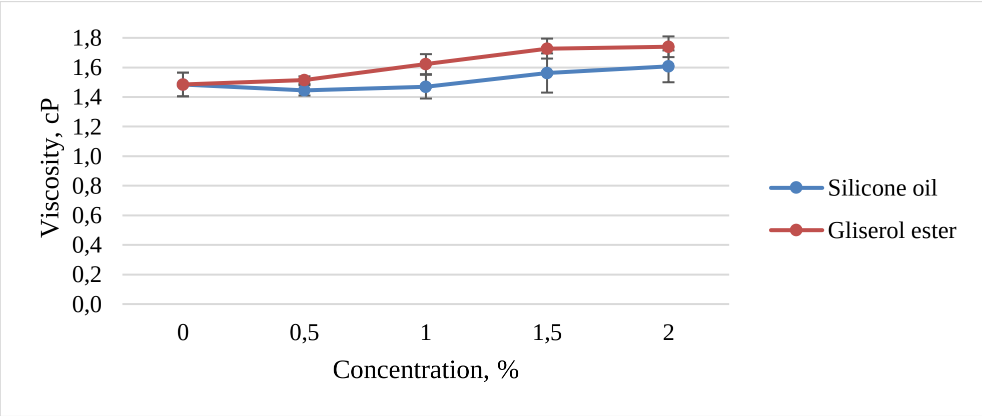


Figure 5. Effect of concentration glycerol ester and silicone oil on viscosity of foaming medium NF24.

Based on Figure 4., glycerol esters have a tendency to increase the medium of SDS and NF24. While silicone oil only affects the viscosity of NF24 medium, it is marked by the upward trend in Figure 5. As the theories presented in sub section of 3.2.1. and 3.2.2, the emulsion formation is characterized by an increase in the final viscosity value of the mixture. This data is in accordance with the law of stokes previously mentioned, particularly in mixed systems between silicone oil and SDS medium, where separation occurs within seconds and results in a mixed viscosity value that is unlikely to change.

3.2.4. Surface Tension of Foaming Medium

Based on the data in this study, Figure 6 and 7, silicone oil tend not to affect the surface tension of the foam medium. This data is in accordance with previously described density and viscosity data, where silicone oil is separated from the foaming medium. Meanwhile, there is difference of data pattern between data of influence of glycerol ester to SDS medium and data of influence of glycerol ester to medium NF24. Against the medium of SDS, glycerol esters tend to decrease the surface tension of the medium. In contrast, to the NF24 medium, glycerol ester tends to increase the surface tension of the medium.

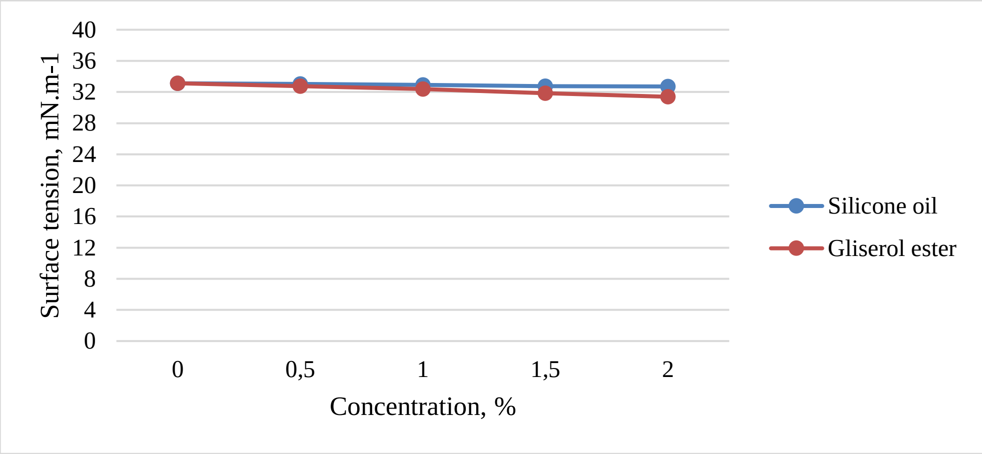


Figure 6. Effect of glycerol ester and silicone oil on surface tension medium SDS.

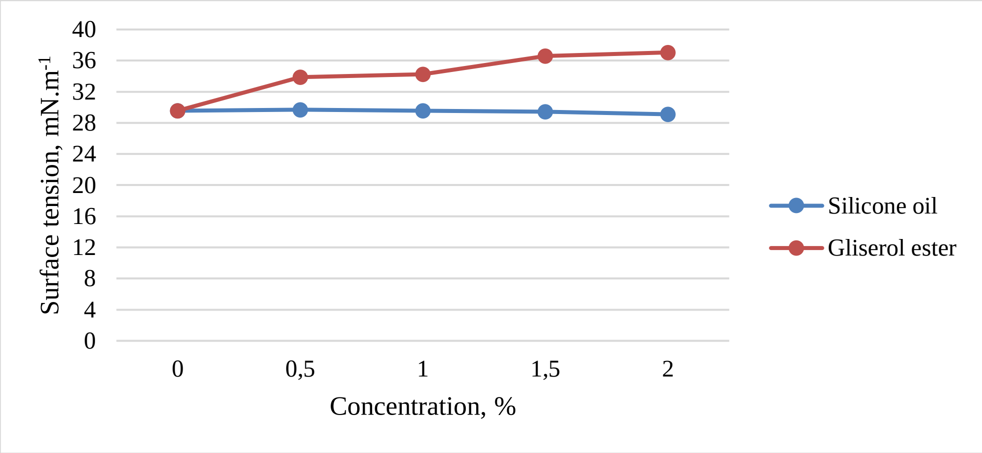


Figure 7. Effect of glycerol ester and silicone oil on surface tension medium NF24.

3.3. Performance Test of Glycerol Ester and Silicone Oil

3.3.1. Influence of Glycerol Ester and Silicone Oil on Foamability of Foaming Medium

The performance test of glycerol ester oleate as an antifoaming agent can be seen in Figure 2. Based on the observation result, both types of medium have difference ability to produce foam or foamability when there is no addition of glycerol ester oleate or silicone oil, control 0%. Base on the experimental data, glycerol ester has better ability to prevent the formation of foam than silicone oil. But there is a very clear difference, that it turns out silicone oil can also prevent the formation of medium foam NF24 1 wt%. The same characteristic is not found in the silicone oil performance data on SDS medium 1 wt%, where the formation of foam tends to be unaffected when compared with glycerol ester oleate.

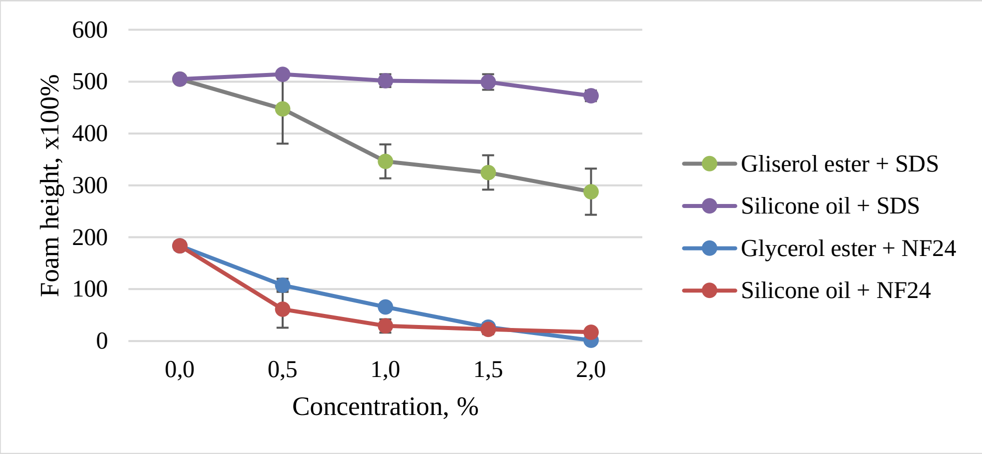
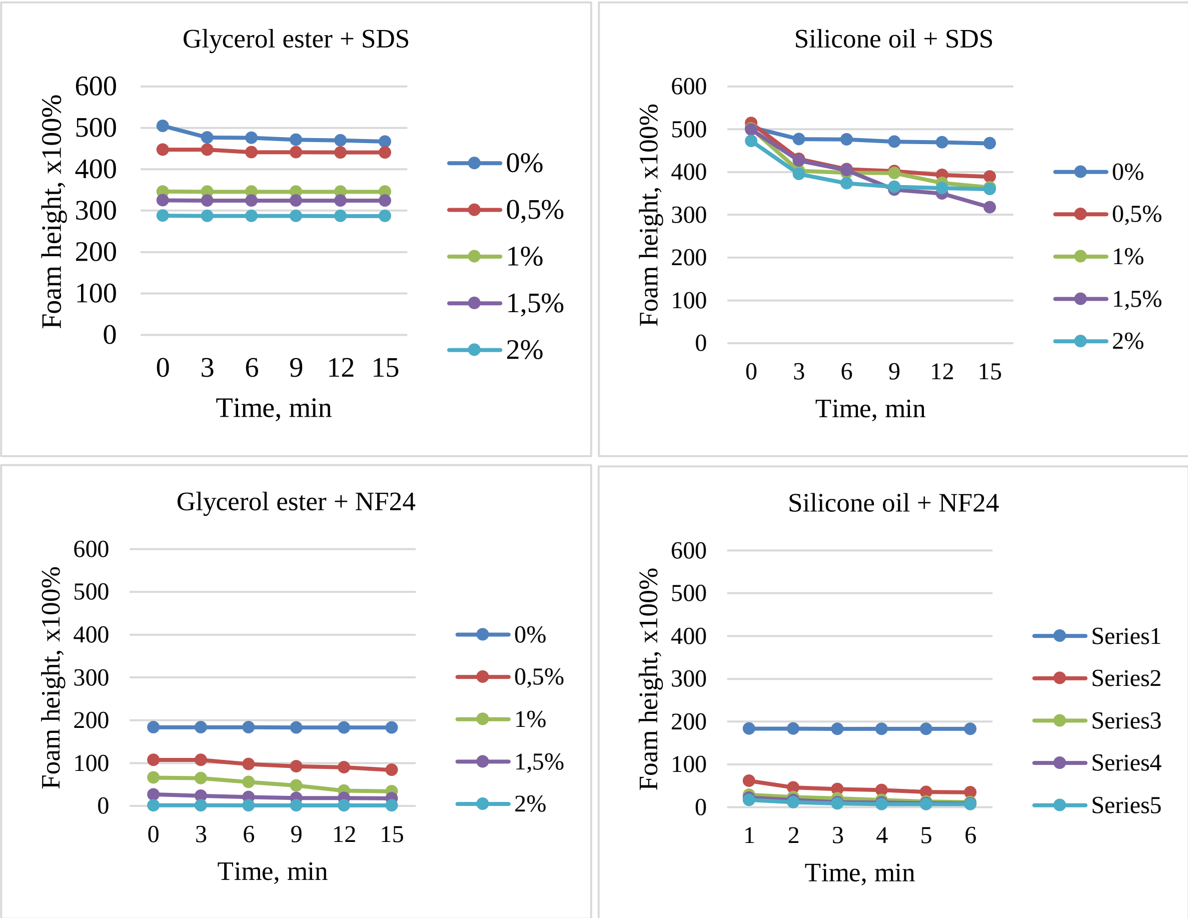


Figure 8. Foamability test of glycerol ester and silicone oil in medium SDS 1 and NF24.

It should be noted that glycerol ester oleate is not a single component such as silicone oil. Glycerol ester oleate is a mixture of the esterification reaction of glycerol and palm oil fatty acid, wherein the final product obtained is affected by the process conditions such as temperature, duration of operation, stirring, and the presence of water vapor during reaction. The product thus obtained is a mixture of unreacted oleic fatty acids, glycerol monooleate (GMO), glycerol dioleate (GDO), and glycerol trioleate. Free fatty acids and glycerol trioleates are constituents that can easily form emulsions with water or even soluble in water when surfactants are present with the right characteristics. In this study, the surfactant SDS used is a surfactant with high HLB value, so it has a good detergency properties to dissolve both components of glycerol ester oleate. While GMO and GDO are soluble or partially soluble nonionic surfactants in water. The solubility of the glycerol ester oleate compositing components is particularly important as it relates to the ability of the surfactant in the foaming medium to adsorbed on the glycerol ester oleic molecules. As the glycerol ester oleic concentration increases in the foaming medium, more surfactant molecules are adsorbed and implies an increase on the surface tension value of the froth medium. The more adsorbed surfactant molecules, increase the ability of the medium to form an air-air emulsion system (foam) will decrease more noticeably from the data shown in Figure 8.

There is a clear difference between the performance of silicone oil in preventing foam formation in SDS 1 wt% and NF24 1 wt%. In SDS medium, silicone oil tends not to affect the foaming ability of the medium, but the performance of silicone oil in preventing the formation of NF24 medium foam has shown a positive result. This is due to the insoluble nature of silicone oil or forming emulsions in the medium of SDS. However, the data were not found on observations of silicone oil performance in NF24 medium. Data, Figure 8, shows that silicone oil can prevent the formation of foam on NF24 medium. NF24 is a foaming agent obtained from the formulation of several surfactant components with different ionic properties and HLB values. The presence of short-chain surfactants in a surfactant formulation may act as a foam booster and improve the detergency of the formula. Therefore, silicone oil in the NF24 medium can be dissolved better than in SDS medium and implies a decrease in medium-foaming capacity as described in the first section of Section 3.2.1..

3.3.2. Influence of Glycerol Ester and Silicone Oil on Foamstability of Foaming Medium



Figue 9. Effect of glycerol ester and silicone oil on foamstability of foaming mediums.

One theory of foam stability has been alluded to in Section 3.2.3., Ie an increase in viscosity which can inhibit the rate of water drops of the medium from the foam. In addition to viscosity, several factors that affect the ability of antifoam to prevent or destroy foam are concentration of surukan, antifoam concentration and the presence of co-surfactant as a foam booster. However, in this study the concentration of surfactant is not one of the topics of discussion. Based on the data shown in Figure 9., the decrease in foam stability only occurs in the addition of silicone oil into the SDS foaming medium. The presence of co-surfactants such as nonionic surfactants on NF24 medium and directly present in glycerol ester increases the resistance of foam to droplet glycerol ester or silicone oil..

4. Conclusion

The effect of addition of glycerol ester to medium SDS and NF24 has been done and compared the result with performance of silicone oil as commercial antifoam. Glycerol ester tends to decrease the foamability of both mediums, whereas silicone oil can only decrease the foambaility of NF24 medium. However, glycerol ester can not decrease the foam stability of both mediums through the "destruction" mechanism of foam as is the case with the SDS foam due to the presence of silicone oil. So the terminology of antifoaming agent can be used to show the effect of glycerol ester on foaming medium.

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