IOP Conference Series: Materials Science and Engineering

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To cite this article: Tomi Erfando *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **509** 012145

IOP Conf. Series: Materials Science and Engineering **509** (2019) 012145 doi:10.1088/1757-899X/509/1/012145

The utilization of *citrus hystrix* and *citrus limon* as an organic demulsifier formulation

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Abstract. During the production process, emulsion problems often occur. The emulsion is water dispersed in the oil phase. Emulsions are a problem that needs to be surmounted by a demulsification mechanism to separate the water phase from the oil. It is transformed into a chemical compound that is expected can be emulsion blocking or usually known as demulsifier. Environmental issues need to be assessed as result of commercial demulsifier usage generally formulated from chemical active compounds that difficult to decipher the environment. Organic demulsifier is one of the best solutions to prevent environmental pollution without diminishing its main functions of emulsion breaker. Bottle test method is an empirical test in which a number of potential demulsifier formulas with various variations are added to a series of tubes or bottles. Organic demulsifier can be divided into 4 formulas that consisting of organic such as *Citrus Hystrix*, *Citrus Limon*, and Liquid Soap as supporting materials. Furthermore, there is a comparative formulas derived from the commercial demulsifier and base case condition of the oil emulsion without any addition. Based on temperature test, concentration test, and the effectiveness of each formula that obtained optimal condition appropriate higher demulsification efficiency. Based on the research, optimal condition of organic demulsifier is formula 2 (5 mL, 70°C) derived from the mixture of Citrus Limon and liquid soap, with demulsification efficiency amount 23 mL (92%). The result obtained from the organic and local material can increase emulsion breakdown process effectiveness compared by commercial demulsifier and base case condition.

1. Introduction

Crude oil is seldom produced alone. It is generally commingled with water that creates a number of problems during oil production. Produced water occurs in two ways: some of the water may be produced as free water, i.e. water that will settle out fairly rapidly, and some of the water may be produced in the form of emulsions. An emulsion is a dispersion of water droplets in oil [1]. Emulsions are stabilized by surface active agent or surfactants–termed emulsifiers. These species concentrate themselves at the oil-water interface and form interfacial films which reduce the interfacial tension and promote emulsification and dispersion of droplets. Many naturally occurring emulsifiers are present in crude oil and include: asphaltenes, resins, organic acids and bases–all these emulsifiers tend to be concentrated in the higher boiling-point fractions and therefore tend to be higher in concentration in heavier crude oils [2].

Emulsion stability is an indicator that needs to be controlled to prevent the degradation of petroleum quality [3]. Some emulsions are difficult to treat and cause a number of operational problems such as expensive pumping due to increase of crude oil viscosity, corrosion of pipes and pumps, poisoning catalysts, et al. Therefore, demulsification/desalting process of petroleum emulsion is necessary to remove as much water and salt as economically possible [4]. In order to minimize the production problems related to crude oil emulsions and environmental concerns, petroleum operators need to prevent the formation of or break down these emulsions. The emulsification of water in oil is normally difficult due to the immiscibility between these two liquid phases. However, shear mixing imposed on the fluids during production and the existence of natural surfactants in the petroleum's composition contribute to formation of such emulsions [5]. The most important objective of any oil production facility is the separation of water and other foreign materials from produced crude. Emulsion is a heterogeneous mixture that consists of at least one immiscible liquid intimately dispersed in another in the form of droplets, making it difficult to separate pure clean crude from the emulsion. Crude oil emulsions are undesired because breaking the emulsion, thereby separating the crude from the emulsions is a challenge in today's oil producing industry [6].

When oil mixed with water, the level of quality and economical of crude oil will be decrease. Thus, it is necessary to formulate a demulsifier to separate water from the oil emulsion, so the quality of the oil will be better. In the manufacture of demulsifier formulation, it must consider the impact of the composition used, especially on the environment. Zhou *et al.* [7] state that the term "green", however, has not been well defined, although the US Environmental Protection Agency (EPA) provided a guideline for green chemistry. The lack of standard definition makes it hard to evaluate the environmental impact of chemicals.

Therefore, this study was conducted to minimize the negative impact of the use of chemicals on the environment and physical. An organic demulsifier is one of the right ideas in preventing environmental pollution without diminishing its main function as an emulsion breaker [3]. So, that evaluation on local demulsifier formulation to commercial demulsifier is done to test the effectiveness of the formulation to be made. This is done in order to produce an effective and environmentally friendly demulsifier.

2. Materials and Methods

2.1. Equipment

The equipment which used in making formulations are a squeezer, stirring rod, knife, filter. The instrument which using in Bottle Test Method, is a 100 mL sized bottle, 50 mL beaker, 250 mL beaker, 300 mL beaker, 10 mL measuring cup, 25 mL measuring cup, heater, volumetric flask, digital balance, and water bath. Water bath is an important instrument method to maintain the temperature conditions of the emulsion.

2.2. Materials

The compositions that used in the manufacture of this organic formulation are the essence of *Citrus Hystrix* (Kaffir Lime), *Citrus Limon* (Lemon), and the supporting material is dishwashing liquid soap that contain an anionic surfactant. The commercial demulsifier using SP-169. commercial demulsifiers are used as a comparison of the formulated organic formulas. And then, there is the oil sample from A Field will be used as an emulsion which will be tested for the effectiveness of its separation when added with a demulsifier to determine the effect of adding a local demulsifier to the breakdown of an oil emulsion.

2.3. Methods

The demulsification methods that used in this experiment is Bottle Test Methods. The bottle test is an empirical test in which varying amounts of potential demulsifiers are added into a series of tubes or bottles containing subsample of an emulsion to be broken. After some specific time, the extent of phase separation and appearance of the interface separating the phases are noted [8]. This method is done by inserting emulsion that was prepared, which is 50 mL fluid (25 mL of water and 25 mL of oil) inside the bottle then it is placed into water bath under certain temperature for some hours. Temperature testing will be done at 60°C, 70°C, and 80°C, at the same time for concentration testing will be done by rising demulsifier volume as much as 1 mL, 3 mL, and 5 mL.

IOP Conf. Series: Materials Science and Engineering **509** (2019) 012145 doi:10.1088/1757-899X/509/1/012145

The application of research methods in laboratory studies of organic demulsifier formulations is Bottle Test Methods. The use of research methods is determined based on the conditions, both from the tools and materials from the research. Bottle Test Methods are carried out using a water bath to maintain temperature conditions during the demulsification process. In this study when using other methods such as BS & W Machine the results obtained were not significant. This is because when using the centrifugal principle in the BS & W Machine, the initial process of the emulsion will be given a solvent to dissolve the commercial demulsifier so that the demulsifier can react with the emulsion and produce a breakdown of the emulsion and good quality water separation. While the use of solvents is not in line with the principle of organic demulsifier formulation which aims to reduce the use of chemicals. If the organic formulation is used together with the solvent, it will affect the quality of the water separated from the emulsion, this is because the solvent cannot react well between the organic material used in this research. For this reason, researchers assume that Bottle Test Methods are the right research method in laboratory studies of organic demulsifier formulations. So the comparison does not lie in the type of method, but on the parameters that affect the effectiveness of the demulsification process.

2.4. Demulsifier Formulation
Formulation of *demulsifier* will be divided into several samples with different organic materials and local materials. The sample will be made into several formulations as follows:

2.4.1. Formulation of Formula 1. In the preparation of formula 1 formulations, the local ingredients used are *Citrus Hystrix* (Kaffir Lime) and liquid soap. *Citrus Hystrix* will be mixed with liquid soap with a ratio of 2:1.

2.4.2. Formulation of Formula 2. In the manufacture of formula 2 formulations, local materials used are *Citrus Limon* (Lemon) and liquid soap. *Citrus Limon* will be mixed with liquid soap with a ratio of 2:1.

2.5. Bottle Test Methods
Here are the steps of demulsification testing using the Bottle Test method. Add formation water to the bottle as much as 25 mL and warm it up in the water bath according to the test temperature for 15 minutes. The heated oil sample uses a heater with a heating temperature below the water heating temperature. Mix 25 mL of oil into the bottle. Homogenisation of the emulsion until stable by performing shaking for 2 minutes or as much as 100-120 times. After 5-10 minutes, inject the demulsifier formula that has been made into each bottle with a volume of 1 mL, 3 mL, and 5 mL. Then put it back in the water bath for up to 3 hours. Perform an examination every 30 minutes to see the separation that occurs.

2.6. Temperature Variation Test
The effect of temperature on the demulsification process is done by varying the heating temperature. Oil emulsion in field A that have been homogeneous with demulsifier formulations will be heated with temperature variations of 60°C, 70°C, and 80°C for 3 hours. The best temperature selection based on the highest % water separation.

2.7. Variation Test of Demulsifier Concentration
The effect of concentration as the addition of the volume of each formula to the optimization of the demulsification process is done by varying the number of injected demulsifiers. The variations of volume addition of the injected demulsifier were 1 mL, 3 mL, 5 mL.

3. Result and Discussion
The use of organic materials as well as local materials in the formulation of organic demulsifier in this study consists of Kaffir Lime (*Citrus Hystrix*), Lemon (*Citrus Limon*), and liquid soap. Determination of the use of local materials is based on the nature of the content of the material that is able to solve the emulsion. Here's a brief explanation of that;

- Citric Acid

Citric acid has a high demulsification efficiency because it has more carboxyl groups higher than other acids, so the demulsification efficiency using citric acid has a high value. In addition, citric acid is a type of acid that is non-toxic, non-irritating, and environmentally friendly [9]. Citric acid is also easy to find in citrus-like organic substances including citrus (*Citrus Hystrix*) and lemon (*Citrus Limon*). The citric acid content contained in kaffir lime is 45.8 g/L, while the citric acid content contained in lemon is 48.0 g/L [10].

- Surfactant

The liquid soap (detergent) is a cleaning liquid composed primarily of surfactants, which in general the surfactant used in liquid soap is an anionic surfactant. These environmentally friendly anionic surfactants were evaluated as demulsifiers to break water in crude oil emulsions using short intervals of microwave dielectric heating to follow the kinetics of the demulsification and the results of the evaluations were validated and confirmed by the classical “bottle test” procedure [11]. Sulaiman *et al.* [12] state that a liquid soap came from saponification of fatty acids and alkaline, this shall serve as the binder for demulsifier formulation from locally sourced material to bind the lipophilic and hydrophilic end.

Tests are carried out in several temperature conditions, formulas, and the addition of different quantity of demulsifiers to determine the effectiveness of using local ingredients as the main composition in the demulsifier formulation. In addition, in this study the optimum temperature, optimum quantity of demulsifier quantity, and the most effective formula to increase the efficiency of the demulsification process will be obtained.

3.1. Effect of Temperature

Basically temperature is one of the parameters that can affect the condition of an emulsion significantly. In this research the process of separation of water from oil emulsion will be determined based on temperature difference using water bath, which is at temperature 60°C, 70°C, and 80°C. The efficiency of the separation against the temperature difference shall be based on the percentage or the maximum amount of water that can be separated from the oil emulsion. Efficiency of separation at each temperature to be tested and can be seen by doing research for 3 hours using water bath. The emulsion will be in a stable temperature condition which can be seen how much water is separated. In this research there are 1 condition base case and 3 scenarios. The base case conditions are oil and water emulsions that have been homogeneous without any additional addition. As for the other 3 scenarios consisting of 2 organic demulsifier formulas and one of commercial demulsifier with each concentration/volume demulsifier difference injected into the emulsion. Each temperature will produce different levels of demulsification efficiency on each formula. The following describes the effect of demulsification efficiency of base case and other scenarios on the temperature conditions 60°C, 70°C, 80°C.

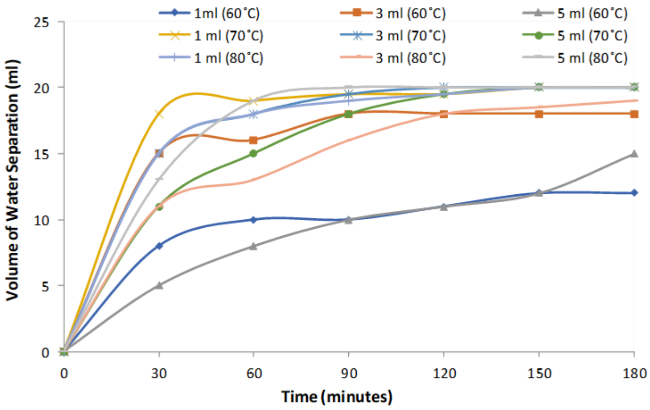

Figure 1. The results of the water separation volume acquisition against the test time on the formula 1.

Based on the test the data obtained as can be seen in figure 1 for the data obtained in formula 1 and figure 2 data acquisition resulted from figure 2 (formula 2). In the formula of formula 1 the highest separation volume was obtained at 60°C when adding 5 mL concentration of 22 mL, while for the whole at 70°C with various concentration additions resulted in a high separation of 20 mL as can be seen in figure 1. Different conditions occur in the formula 2 formula in which the highest separation occurs at 70°C with 5 mL concentration added, which is 23 mL, whereas a high separation gain of 20 mL is also obtained under predominant conditions at 70°C. So based on the data condition 70°C is a condition that is ideal for both organic formulas as can be seen in figure 2. When compared with the commercial demulsifier the highest separation gain occurred at a temperature of 80°C, which is 20.5 mL as can be seen in figure 3.

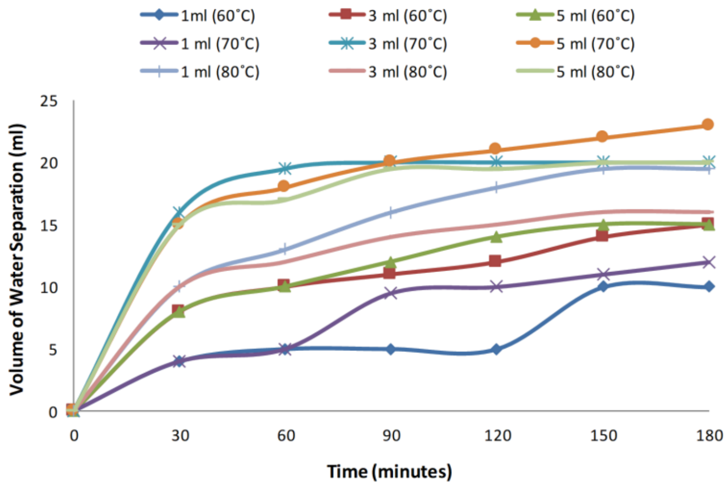

Figure 2. the results of the water separation volume acquisition against the test time on the formula 2.

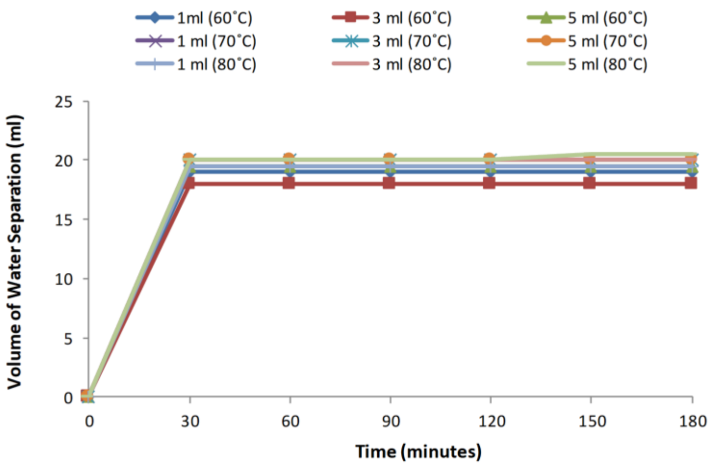

Figure 3. The water separation volume acquisition against the test time on the commercial demulsifier.

Based on this study, for some conditions and formulas, when the temperature rise occurs there is also an increase of the demulsification efficiency, especially in the type of formula derived from commercial demulsifiers. Abdulbari *et al.* [13] said that the viscosity of oil is very sensitive to temperature; as temperature increases, oil viscosity decreases much faster than does the density difference between water and oil. As a result, when viscosity is decreased, the water-droplet size increases. Whereas, only a few formulas of organic demulsifier experience an increase in demulsification performance when an increase in temperature. Based on the researcher's hypothesis, this happens because the chemical will work optimally at high temperature. Abdulkadir [14] said that application of heat to an emulsion after a demulsifier has been mixed with it increases the effectiveness of the chemicals, by reducing the viscosity of emulsion and also promoting intimate mixing of chemicals with emulsion. The reaction at the oil-water interface takes place at a more rapid rate at higher temperatures. While not all organic materials are resistant to high temperatures which can lead to a decrease in the performance of the organic composition. Njoku *et al.* [15] said that increase in temperature generally reduces the concentration of vitamin C. Also environment conditions that increase the acidity of citrus fruits also increase vitamin C levels. Thus, based on the results obtained the optimal temperature obtained from commercial demulsifier and organic demulsifier is different. Based on the highest demulsification efficiency value, the optimal temperature for organic demulsifier is 60°C and 70°C, while for commercial demulsifier is 80°C.

3.2. Effect of Concentration

Concentration is important that can affect the performance of the demulsifier. The optimum concentration can be seen based on the increase in the highest demulsification process of each formula. The performance of each formula will be different if given the addition in terms of concentration. In this study the concentrations to be applied are 1 mL, 3 mL, and 5 mL. The magnitude or the magnitude of the influence of concentration can be seen based on the explanation of each concentration. From each concentration will be obtained maximum demulsification data from some candidate formula. Here's an explanation of each of his concentrations.

Based on the test the data obtained as can be seen in the figures 1 and 2. In figure 1 it can be seen that in the formula 1 the highest separation gain is obtained when adding 5 mL demulsifier volume where the water is separated, that is equal to 22 mL. While for formula 2 the highest separation was obtained when the condition of volume injection demulsifier injected as much as 5 mL where the water separated, that is equal to 23 mL. For the condition of commercial demulsifier be evidenced that the highest demulsification volume was obtained at a concentration of 5 mL with a temperature of 80°C, that is equal to 20.5 mL. Meanwhile, the smallest demulsification volume obtained from this commercial demulsifier is 18 mL at the time (3 mL, 60°C) as can be seen in the figures 3. From the analysis of the three concentrations/volumes are 1 mL, 3 mL, and 5 mL, the increase in demulsification efficiency occurs when the concentration increases. The 5 mL concentration is the optimum concentration in increasing the demulsification efficiency between the concentrations of 1 mL and 3 mL. That is, when concentrations are added more and more, then the components that work in accelerating the demulsification process more and more. Hajivand and Vaziri [5] said that the concentration plays a significant role in the demulsification process because higher concentrations increase the rate of coalescence of droplets because of interfacial film thinning.

3.3. Effect of Various Formulation

Composition is the main thing that acts as supporting the effectiveness of demulsifier performance. Formulations continue to be performed with various compositions to obtain optimal formulas for improving demulsification efficiency. The demulsifier formulation using organic and local materials is one of the main ideas of this research. The use of organic materials as well as local materials can minimize the negative impact both physically and arising from the use of chemicals. In the manufacture of organic demulsifier formula, the compositions used are distilled water, lime, lemon and supporting materials such as; liquid soap. Then, here is the use of commercial demulsifier and base case conditions (without additional demulsifier) as a comparison formula (figure 4). The composition of local materials and organic materials used are determined based on the content contained in the material. The material is expected to meet the main function of the demulsifier as an emulsion breaker. So from a variety of organic materials and local materials are formulated to get the most effective formula. The following explanation of the effect of the composition of the ingredients of the formula in increasing the effectiveness of demulsification. As can be seen in figures 4 the highest demulsification volume acquisition on Base Case formula occurs under conditions 60°C. This is caused by the presence of a natural surfactant which can cause the oil emulsion to be stable, which will cause various problems of significant change to the characteristics and physical properties of oil [16]. These changes may affect the effectiveness of demulsification efficiency against temperature to be different.

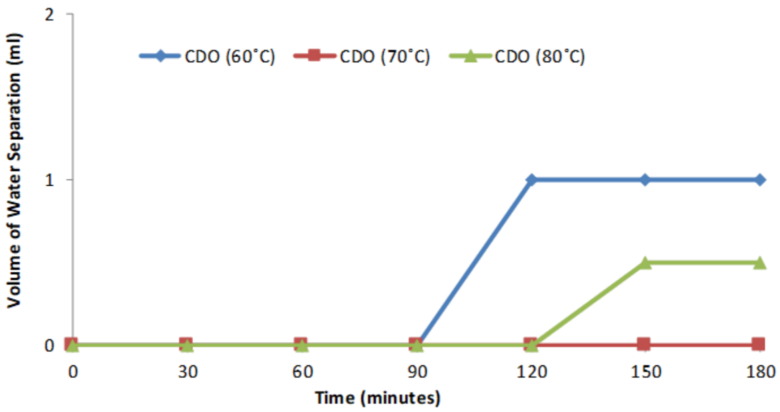

Figure 4. The water separation volume acquisition against the test time on the Base Case formula.

Based on the data obtained the two formulas yielded high efficiency, especially at the time of the addition of concentration as much as 5 mL, only the highest separation happened at different temperature between formula 1 and formula 2, that is equal to 22 mL (60°C; 5 mL) and 23 mL (70°C; 5 mL). This is probably due to differences in composition as can be seen in figure 1 and figure 2. For the condition of commercial demulsifier be evidenced that the highest demulsification volume was obtained at a concentration of 5 mL with a temperature of 80°C i.e., 20.5 mL. Meanwhile, the smallest demulsification volume obtained from this commercial demulsifier is 18 mL at the time (3 mL, 60°C) as can be seen in the figures 3. However, in terms of water quality, commercial demulsifiers produce poor water separation quality without solvent. This is due to the commercial demulsifier formula which tends not to be completely soluble to oil, thus contaminating the quality of the integral water.

From the analysis of some of the above formulas, the use of chemicals as main compositions in commercial demulsifier has a high demulsification efficiency level with a relatively short time. When compared to an organic formulation, when using a commercial demulsifier within approximately 5 minutes the oil emulsion has been emulsified. Whereas, the other formula takes approximately 30 minutes to 180 minutes to break the emulsion. However, the demulsifier efficiency value of organic demulsifier formula has a higher maximum efficiency point compared to commercial demulsifiers.

Water quality considerations are also one of the ideas of this local and organic material formulation that has been done, the use of commercial demulsifier tends to produce water quality is quite bad (turbid) if without using solvent. Thus, additional solvents are required to facilitate the commercial demulsifier soluble in oil and do not interfere with water quality. Meanwhile, using these local and organic formulas, without the addition of solvent separation of water from oil emulsion can be said to be effective and water quality produced is also better. Of the various formulas tested, in this study the optimal formula used is the formula 1 and formula 2.

The results of research using only pure organic ingredients without any mixture will be different from the mixed formula between organic and chemical additives including environmentally friendly such as liquid soap. The results obtained from organic ingredients in the form of fresh pure lime juice without any additions have not been able to increase the effectiveness of the emulsion breakdown process as produced by the formula derived from a mixture of kaffir lime with liquid soap. Where the highest separation obtained from the demulsifier formula of pure lime juice was 7 mL [3], whereas when compared with the formula derived from the kaffir lime mixture with the liquid soap produced the highest separation of 22 mL.

4. Conclusion

Based on the temperature test of the field oil emulsion of Field A under temperature conditions 60°C, 70°C, 80°C either formula 1, formula 2, commercial demulsifier, or Base Case formulas at various concentrations, the optimal temperature obtained from commercial demulsifier and organic demulsifier different. Based on the highest demulsification value, the optimum temperature for organic demulsifier is 60°C and 70°C, while for commercial demulsifier is 80°C. While, based on the concentration test with 3 difference of volume addition of demulsifier formula that is equal to 1 mL, 3 mL, and 5 mL at each formula and every temperature condition, the optimum concentration obtained is 5 mL. The value is obtained from the highest demulsification volume of formula 2 (5 mL, 70°C) of 23 mL. The effectiveness of demulsification depends on the composition of the formula being formulated. The highest demulsification efficiency of the local demulsifier formula is obtained from the formula 1 and formula 2 derived from a mixture of the essences of citrus with liquid soap. The value of the water separation volume is 22 mL and 23 mL from the initial volume of the emulsion consisting of 50 mL of fluid (25 mL of water and 25 mL of oil).

Acknowledgments
The authors gratefully acknowledge financial support from Universitas Islam Riau and Petroleum Engineering's laboratory for experiment facilities.

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