Study on Surfactant-Solvent Mixture Formulation and Its Application on Pesticide Emulsion Product

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Abstract. Nettle caterpillars (Setothosea asigna) are one of the common insects found in palm tree plantation which significantly reduce palm oil production by eating palm tree leaves. Surfactant is commonly used as an emulsifier and stabilizer in the pesticide mixture to refrain the mixture from separating. Commercial surfactants that are being used by the farmers holds the emulsion for approximately 2 hours. The performance of Diethanolamide (DEA) as surfactant for the insecticide mixture was investigated in this research. The various concentration of DEA in pesticide mixture showed the increasing mixture stability up to 24 hours before separating. Commercial surfactant used by the farmers is at 7-10% of the mixture. Meanwhile, DEA lowers the percentage of usage to 5%. The reduction of percentage of surfactant usage leads to the reduction of surfactant cost. Sample A5B5 found to be the best among other surfactants. Sample A5B5 has the density of 0.878 g/cm³, viscosity of 19.72 cP, surface tension of 24.311 dyne/cm, and contact angle of 31.783°.

1. Introduction

Indonesia is considered as an agricultural country in the world with the biggest palm oil production 33,500,692 ton/year [1]. Oil palm is one of the plantation sub-sector in Indonesia that can sustain the country economically. Indonesia has the area of 116,728 km² oil palm plantation. This proves that agriculture can be a way for Indonesians to improve their prosperity. Although oil palm plantation has the advantage to prosper Indonesia but it also faces many problems and pests are one of that problems. Nettle caterpillars (Setothosea asigna) are one of the common pests found in palm tree plantations which significantly reduce palm oil production by eating palm tree leaves.

Pests control can be made by using pesticide. Pesticide usage also faces many problems. Natural factor, water properties as solvent, low stability emulsion, and wetting ability are the common problems faced by farmers. These problems affect to unequal pesticide dispersion, unstable pesticide emulsion, and low ability of emulsion mixture to wet leaves.

Adjuvant technology is the solution to overcome the problems when applying pesticide emulsion product. Adjuvant is a material added into pesticide formulation to modify pesticide activities or properties of pesticide formulation [5]. Surfactant is one of the adjuvant material commonly used in pesticide emulsion. Adding surfactant can decrease surface tension, increase emulsion stability, and decrease contact angle, which are considered as important physical properties.
Low emulsion stability is a common problem faced by farmers. It means emulsion can only hold its stability for a short period of time. Farmers needed pesticide emulsion that can hold up its stability for 24 hours. Surfactant that is used by farmers was found to be ineffective in increasing emulsion stability to 24 hours. Alternative surfactant that can increase pesticide emulsion stability needs to be clarified.

This research is conducted to get the best DEA surfactant-Ethanol 96% solvent that can hold pesticide emulsion product stability up to 24 hours and to get performance information about the best surfactant mixture. This research can help farmer to get pesticide emulsion product that have emulsion stability of 24 hours.

2. Methodology

This research is divided into 4 stages: sample preparation, surfactant mixture preparation, pesticide emulsion product selection, and surfactant formula performance test. Sample preparation is the stage where DEA surfactant is being made from amidation reaction. Surfactant Mixture Preparation is the stage where surfactant mixture is being formulated. pesticide emulsion product selection is the stage where pesticide emulsion product is being selected from its stability. Surfactant formula performance test is the stage to get information about pesticide emulsion product that can hold up to 24 hours.

2.1. Sample Preparation

DEA surfactant can be made through amidation reaction of methyl ester and diethanolamine. Ratio of the reaction is 1 methyl ester: 2 diethanolamine. First, methyl ester is heated up to 100°C and stirred by using magnetic stirrer. Second, Diethanolamine is mixed up with catalyst NaOH 50% with concentration of 1%. Third, methyl ester is mixed up with diethanolamine-NaOH 50% mixture. Methyl ester-diethanolamine mixture is heated up to 140°C for 4 hours.

2.2. Surfactant Mixture Preparation

This stage uses diethanolamide as surfactant and ethanol 96% as solvent. Solvent usage is to dissolve methyl ester residue from amidation reaction and to decrease DEA viscosity. DEA surfactant-Ethanol 96% solvent mixture formulation is divided into 9 formulas with the ratio of 1 DEA: 9 ethanol 96%, 2 DEA: 8 ethanol 96%, 3 DEA: 7 ethanol 96%, 4 DEA: 6 ethanol 96%, 5 DEA: 5 ethanol 96%, 6 DEA: 4 ethanol 96%, 7 DEA: 3 ethanol 96%, 8 DEA: 2 ethanol 96%, and 9 DEA: 1 ethanol 96%. Surfactant-solvent ratio can be seen on Table 1.

| Name | DEA-ethanol 96% ratio |
|------|-----------------------|
|      | DEA | Ethanol |
| A1   | 1   | 9       |
| A2   | 2   | 8       |
| A3   | 3   | 7       |
| A4   | 4   | 6       |
| A5   | 5   | 5       |
| A6   | 6   | 4       |
| A7   | 7   | 3       |
| A8   | 8   | 2       |
| A9   | 9   | 1       |

Table 1. Surfactant-Solvent Ratio

Surfactant made from Table 1. will be used as emulsifier in pesticide emulsion product. Surfactant is used in range of 1-5%. As the increasing amount of surfactant, the amount of water is decreasing. Formulas of surfactant that is used can be seen on Table 2.
Table 2. Surfactant and water percentage of use

| Name | Surfactant (%) | Water (%) |
|------|----------------|-----------|
| B1   | 1              | 38.8      |
| B2   | 2              | 37.8      |
| B3   | 3              | 36.8      |
| B4   | 4              | 35.8      |
| B5   | 5              | 34.8      |

2.3. Pesticide emulsion product selection

Materials used to make pesticide emulsion product are surfactant, diesel fuel, water, and cypermethrin. Percentage of diesel fuel and cypermethrin are the same for all pesticide emulsion product samples. Percentage of surfactant increases as percentage of water decreases. Percentage of each materials is the same exact amount as it is on the field. Emulsion then will be observed for 24 hours. Sample(s) that can hold up for 24 hours will be tested in further stage.

2.4. Surfactant Formula Performance Test

Pesticide emulsion product that can hold up to 24 hours will be analysed. There are 4 analyses done in this stage which are viscosity analysis, density analysis, surface tension analysis, and contact angle analysis.

3. Results and Discussion

3.1 Results

Table 3. DEA analysis result

| Analyses        | Results       |
|-----------------|---------------|
| Density         | 0.9762 g/cm³  |
| Viscosity       | 257.35 cP     |
| Surface Tension | 32.21 dyne/cm |
| pH              | 11.10         |

Samples A4B4, A4B5, and A5B5 are those that could hold up for 24 hours. These three samples will be analysed further to know their performance. Analyses that are conducted to know the performance of pesticide emulsion product, are density analysis, viscosity analysis, surface tension analysis and contact angle analysis.
Figure 1. Density of pesticide emulsion products

Figure 2. Surface tension of pesticide emulsion products

Figure 3. Viscosity of pesticide emulsion products

Figure 4. Contact angle of pesticide emulsion products

Figure 1 shows that sample A4B5 had the highest density than other samples and designated as rank 1. Sample A5B5 had the lowest density which makes it rank 3. Sample A4B4 left with rank 2. Figure 2 shows that sample A5B5 had the lowest surface tension, followed by sample A4B5 and sample A4B4. Designation was made that sample A5B5 is the rank 1, sample A4B5 is the rank 2, and sample A4B4 is the rank 3. Figure 3 shows that sample A4B5 had the lowest viscosity than other samples, as rank 1. Sample A4B4 as rank 2. Sample A5B5 as rank 3. Figure 4 shows that sample A5B5 had the lowest contact angle, Sample A5B5 as rank 1, sample A4B4 as rank 2, and sample A4B5 as rank 3.

3.2. Discussion

3.2.1. Diethanolamide Analysis Result

Density of DEA was 0.972 g/cm³ (data can be seen on Table 3). This result is smaller than the result of 0.995 g/cm³ by Hakim (2005) [2]. The difference caused by the material that was used during amidation reaction. Hakim 2005 used methyl ester from palm kernel oil while this research used methyl ester from palm olein.
As the viscosity of a fluid decreasing then the fluid will flow easier \[3\]. Viscosity of DEA is 257.35 cP (based on Table 3) while viscosity of water is 0.899 cP. From comparison between water and DEA, DEA found to be very viscous which makes it harder to flow.

Surface tension of DEA is 32.21 dyne/cm. This means that it takes force of 32.21 dyne or 0.03221 Newton to break surface layer with length of 1 cm.

pH with a value of 7 is considered to be normal or neutral \[pH\]. pH of DEA used in this research is 11 while pH of DEA from literature (Hakim 2005) was 8.5-10. This difference was caused by the usage of NaOH 50% as catalyst in amidation reaction while Hakim (2005) used sodium methylate as catalyst. NaOH is alkali compound that can increase pH value of DEA surfactant.

3.2.2. Pesticide emulsion mixture observation result

Sample A4B4, A4B5, and A5B5 are pesticide emulsion product samples that can hold its emulsion stability for 24 hours or even more. Emulsion stability is affected by the balance of attraction and repulsion force between molecule \[4\]. Emulsion stability reached its maximum when repulsion force was at maximum state and attraction force was at minimum state. Based on stability emulsion theory by Petrowski (1976) \[4\], sample A4B4, A4B5, and A5B5 had higher repulsion force and lower attraction force than other samples.

3.2.3. Surfactant Performance Analysis Result

Surface tension test was conducted to know emulsion stabilities and wetting abilities of pesticide emulsion product. Stability of pesticide emulsion product can be predicted if surface tension data is known. The lower the surface tension the longer stability of emulsion. Surface tension also affects wetting abilities of pesticide emulsion product. The higher the surface tension the weaker the wetting abilities. Weaker wetting abilities means that pesticide droplets need a bigger force to break its surface layer. From Figure 2, sample A5B5 had the lowest surface tension. This means sample A5B5 had the weakest surface layer and easier to break than other samples.

Viscosity test was conducted to know consistency level of pesticide emulsion product. The higher the viscosity, the closer the phase of one object to solidity. Viscosity of pesticide emulsion product affects pesticide fogging process. The stronger the bond between molecule, the higher in the viscosity. Fluids with high viscosity level will make it difficult for the fogging instrument. From Figure 3, sample A4B5 had the lowest viscosity. Viscosity as decision-making parameter, the value of 2 was assigned. This means sample A4B5 is the easiest pesticide emulsion product for the fogging instrument to fog it out.

Contact angle test has effect to pesticide emulsion wetting abilities. Contact angle with angle over 90\(^\circ\) has bad wetting abilities. Implication of bad wetting abilities is that liquid will find it difficult to wet a surface \[6\]. The lower the wetting abilities the faster liquid wet a surface. From Figure 4, sample A5B5 had the lowest contact angle. This means sample A5B5 had the fastest wetting abilities than other samples.

3.2.4. Decision Making Process

Decision making process is the part to decide which sample is the best surfactant mixture based on its data.

| Sample | A4B4 | A4B5 | A5B5 | Total |
|--------|------|------|------|-------|
| Density (Value = 1) | Rank 2 | Rank 3 | Rank 1 | 6 |
| | (2\*1 = 2) | (1\*1 = 1) | (3\*1 = 3) | |
| Surface Tension (Value = 3) | Rank 3 | Rank 2 | Rank 1 | 18 |
| | (1\*3 = 3) | (2\*3 = 6) | (3\*3 = 9) | |
| Viscosity | Rank 2 | Rank 1 | Rank 3 | 12 |
Table 4 shows the decision-making process to determine the best pesticide emulsion product. Density as parameter had value of 1. Sample A5B5 had the best density value. Surface tension as parameter had value of 3. Sample A5B5 had the best surface tension value. Viscosity as parameter value of 2. Sample A4B5 had the best viscosity value. Contact angle as parameter value of 3. Sample A5B5 had the best contact angle value. Emulsion stability as parameter value of 1. Sample A5B5 had the best emulsion stability because it can hold up for 48 hours.

Surface tension and contact angle have the highest value as parameter because surface tension and contact angle have the most effect on wetting abilities than other parameter. Viscosity has the second highest value as parameter because it affects fogging process difficulties. Density has the lowest value as parameter because it doesn’t affect much on wetting abilities and fogging process yet only to know molecule weight of each samples. Emulsion stability also has the lowest value as parameter. This is because sample A5B5 is the only sample that can hold up for 48 hours so it affects the best sample decision.

4. Conclusion

The best DEA surfactant-ethanol 96% mixture ratio that can hold up pesticide emulsion product stability for 24 hours was 5 DEA:5 ethanol 96% with 5% of use. Pesticide emulsion sample made by using 5 DEA:5 ethanol 96% surfactant mixture or sample A5B5 had density value of 0.878g/cm$^3$, viscosity value of 19.72 cP, surface tension value of 24.311 dyne/cm, and contact angle value of 31.783°. This knowledge might have a significant role, for farmers, to make the suitable pesticide emulsion product.

5. Reference

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