Formulation Technology of Brown Planthopper Insecticide Product of EC (Emulsifiable Concentrate) form Using Diethanolamide Surfactants

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Abstract: Emulsifiable Concentrate (EC) is one form of brown planthopper insecticide which circulated widely in the market. EC formulation is an emulsion due to the use of oil-based solvent and water as a carrier medium. The aim of this study was to generate the appropriate formulation technique in brown planthopper insecticide formulation. Insecticide formulations used buprofezin as active ingredient, Solvesso 150 as solvent, surfactant diethanolamide (DEA) and water. The result this research shows that the formulation technique which is based on lyophilic and hydrophilic phase is the most suitable formulation technique. The observation of the physicochemical properties was pH: 10.42 ± 0.148; density of 0.9973 ± 0.00 g/cm³; droplet size of 2.453 ± 0.084 μm; surface tension of 23.544 ± 0.222 dyne/cm; contact angle of 17.572 ± 0.248 o and the viscosity of 9.448 ± 0.180 cP.

Keywords: Insecticide, Brown Planthopper, Formulation technique, Diethanolamide, Buprofezin

1. Introduction

The main objective of formulation technology is optimizing the biological activities of pesticides, and produce a safe and appropriate product. However, due to the diversity of active ingredients of the available pesticides, there has been a variety of formulations types that have developed, which most of them depend on the physicochemical properties of the active ingredients and the type of additive influences the form of the insecticide formulation produced. Some of the circulating formulations include Emulsifiable Concentrate (EC), Wettable Powder (WP), Solution Concentrate (SL), Soluble Granule (SG), Suspension Concentrate (SC), Granule (GR) and many more [1].

Homogeneity is the main key to the development of the brown planthopper insecticide formulation in the form of EC (Emulsifiable Concentrate). It is expected that the active ingredients and surfactants used in the formulations are spread evenly in the emulsion system. The main problem in the formulations of brown planthopper insecticide is the active ingredient that is not water soluble, so that it requires oil solvents to dissolve it, while the application requires water as the carrier of the active ingredient, thus the emulsion system will be formed [2].

Emulsion is a heterogeneous system consisting of two phases of liquid that are not mixed but one liquid is well dispersed in another liquid in the form of droplets (globules) with the diameter of more than 0.1 μm or 0.1-50 μm. The granular phase is called as the dispersed phase or the internal phase or also called as the discontinuous phase, while the liquid phase in which the granules are dispersed is called as the dispersing phase or the external phase or continuous phase [3].

In this study, we discuss the formulation technique which is part of the technology in the process of brown planthopper insecticide formulation. The characteristics of each material used in the formulation techniques are crucial to be known, thereby the formulation process runs maximally which is required in industrial formulation requirements. The scope of this study is to investigate the physicochemical properties of the brown planthopper insecticide formulations produced.

2. Research Methodology

A. Location of the Study
This study was carried out at the Surfactant and Bioenergy Research Center (SBRC) laboratory - LPPM IPB, Baranangsiang IPB Campus, Bogor.

B. Materials and tools
The materials used in this study were Diethanolamide (DEA) surfactant obtained from SBRC LPPM IPB, the active ingredient of buprofezin from PT. Nufarm and the solvents of solvesso 150 from PT. Samiraschem Indonesia. The formulation tool used was a rotor stator homogenizer, Daihan Homogenizer, HG-15D model. Other tools include pH Meter (pH Meter Schott, Microscope (Leica ICC 50 HD) density meter (Anton Paar DMA 4500M density meter), potentiometer (Spinning Drop Tensiometer), viscometer (Brookfield DV-III Ultra Rheometer), contact angle meter (Phoenix 300 Contact Angle Analyzer) used for sample analysis.

C. Technique Determination of the Brown Planthopper Insecticide Formulation
The brown planthopper insecticide formulation techniques were done based on the order of ingredients in mixing method. Variations in formulations consisted of three types, they are: (1) Dissolving buprofezin with solvesso 150 in the mixing 1 for 10 minutes and dissolving DEA surfactant with water in the mixing 2 for 5 minutes. After that, both of the mixtures were mixed in the mixing 3 for 10 minutes. The flow chart of formulation 1 is presented in Figure 1. (2)
Mixing the ingredients of buprofezin, solevesso 150 and water in mixing 1 for 15 minutes. Then, add the DEA surfactant in mixing 2 for 10 minutes. Flow chart of formulation 2 is presented in Figure 2. (3) Mixing buprofezin, solevesso 150 and DEA in mixing 1 for 15 minutes, then add some water to the mixing 2 for 10 minutes. Flow chart of formulation 3 is presented in Figure 3.

\[ Y_{ij} = \mu + A_i + \varepsilon_{ij} \]

Where

- \( Y_{ij} \) = Observation of physicochemical properties of insecticides on the formulation technique in the i-level and the j-replication
- \( \mu \) = Average
- \( A_i \) = Effect of formulation techniques in the i-level (i = 1, 2, 3, 4)
- \( \varepsilon_{ij} \) = Normal distribution of random effect (0, \( \sigma^2 \)) on the i-level formulation technique for j-replication

The data obtained were analyzed for diversity tested by analysis of variance (ANOVA) followed by Duncan test if the results of the variance analysis showed a significant effect of treatment on the response of variables [4].

3. Result and Discussion

A. Technique Determination of the Brown Planthopper Insecticidal Formulation

Most of farmers preferred to choose the emulsion insecticide formulation because it was easy and effective to use, compared to the suspension form. This was because the stock which was in the form of suspension could clog the spray holes on the sprayer. Moreover, the stock which was in the form of emulsion affected the dispersion of active ingredients so that it worked well and optimal during the application.

EC formulation is a stock in the form of liquid concentrate with a fairly high active ingredient. Because of the use of oil-based solvents from the insecticide, the addition of water will form the emulsion [2].

The ingredients of the brown planthopper insecticidal formulations consist of buprofezin which acted as an active ingredient, solevesso 150 as a solvent, diethanolamide (DEA) surfactant as an emulsifier and water as a carrier. The availability of these ingredients as the formulation materials raise questions about how to produce the emulsion product.

B. The Analysis of Physicochemical Properties of the Brown Planthopper Insecticide Products

The following is the analysis result of brown planthopper insecticide based on the formulation techniques carried out as follows: pH ranges from 10.03 to 10.27; the density ranges from 0.99726 - 0.99746 g / cm³; droplet sizes range from 2,453 - 3,284 µm; surface tension ranges from 22,663 - 25,210 dyne / cm; the contact angle ranges from 17,572 - 17,862°; viscosity ranges from 4,673 - 26,890 cP. The average recapitulation of the analysis result of the physicochemical properties of insecticides is presented in Table 1.
further test result shows that the average substance of the brown planthopper insecticide. Duncan's the dispersed phases in the form of oil and the dispersing formulation tech.

The measurement of DEA solution generate a value of 0.148. The correlation curve of the formulation techniques on pH parameter observation of the brown planthopper insecticidal formulation ranged from 10.03–10. The pH scale produced showed that brown planthopper insecticides were alkaline. The average value with the lowest pH was in the application of F3 formulation technique of 10.03 ± 0.014, then the F2 formulation technique was 10.15 ± 0.028, and the highest average density of the F1 formulation technique was 10.42 ± 0.148. The correlation curve of the formulation techniques on pH parameters is presented in Figure 4.

Note: Different letters show that the treatment has a significant effect on the response at the 5% level of significance (ANOVA test).

1) pH
The pH scale or acidity level is used to express the acidity or alkalinity of a substance. The pH scale is also related to the hydrogen ion concentration as a component of acidity and hydroxyl ion concentration as a component of alkalinity [5]. In neutral pH condition, the concentration of the two ions is balanced but if the hydrogen ion concentration is greater than the hydroxyl ion, the pH tends to be acidic (low). In general, the pH scale of a substance is in the range of 0-14. The range of pH scale 0-6 indicates acidic substance, while the range of pH scale 8-14 shows that the substance is alkaline.

The results of pH analysis of the brown planthopper insecticide obtained were influenced by the formulation technique through a variety of analyzes at a 95% confidence interval. From the data obtained, it is concluded that the formulation technique showed a significant effect on the pH scale of brown planthopper insecticide. The result of the pH parameter observation of the brown planthopper insecticidal formulation ranged from 10.03–10. The pH scale produced showed that brown planthopper insecticides were alkaline. The average value with the lowest pH was in the application of F3 formulation technique of 10.03 ± 0.014, then the F2 formulation technique was 10.15 ± 0.028, and the highest average density of the F1 formulation technique was 10.42 ± 0.148. The correlation curve of the formulation techniques on pH parameters is presented in Figure 4.

brown plant hopper insecticides using formulation techniques variations was significantly different from F1 formulation techniques, yet it was not significantly different between the formulation techniques of F2 and F3.

The mixing process in the F1 formulation technique generated a higher pH scale compared to other formulation techniques (F2 and F3). This condition was allegedly due to the F1 formulation technique, the oil phase contained in the buprofezin solution was dispersed evenly in DEA solutions that had a high pH. This was due to the ability of DEA surfactants which were more likely binding the water than oil. Thus, the mixing process of DEA surfactant and water was processed optimally before it binded the oil. This was indicated by the droplet dispersion with the average of small diameter in F1 formulation technique which was 2.453 ± 0.084 µm. The higher homogeneity of insecticide product was, the better DEA surfactants covered the globules, so that there was no amalgamation. Thus, the high pH condition of DEA surfactant was more dominant.

2) Density
The analysis result of the density parameter of brown planthopper insecticides were influenced by the formulation techniques through a variety of analyzes at 95% confidence interval. From the data obtained, it can be concluded that the formulation technique showed a significant effect on the density value of brown-plantopper insecticide product. The observation result of of the density parameters for the brown planthopper insecticide product. The correlation curve of the formulation techniques on density parameters is shown in Figure 5.

The alkalinity of the brown planthopper insecticide formulation were obtained from the use of DEA solution. The measurement of DEA solution generate a value of 10.59. The pH scale was significantly different since the formulation technique had an effect on the mixing between the dispersed phases in the form of oil and the dispersing phase in the form of water that were not maximum in the substance of the brown planthopper insecticide. Duncan's further test result shows that the average pH scale of the
The significantly different density values were presumably because the formulation technique factors affected the solubility of the ingredients used in the brown planthopper insecticide formulation. Duncan's further test results showed that the average value of density using a variety of formulation techniques was significantly different. F1 formulation technique generated the lowest density value. This was presumably because the DEA surfactant is a type of nonionic or non-charged surfactant in the hydrophobic group. The hydrophobic group that was located in the head was an ester or hydroxyl group, thus it will be easy to bind to water molecules. The well-binding ability to the water was used in F1 formulation technique in order to produce insecticide with good homogeneity. Besides, in the F1 formulation technique the oil phase mixing was carried out separately so that the process of dissolving buprofezin with solvesso 150 could be processed optimally. Then, the two solutions were mixed to obtain the insecticide of the brown planthopper. The density of each mixing result in F1 formulation technique was the oil phase in the form of buprofezin solution of 0.92844 g / cm³ and the water phase in the form of DEA solution of 0.99593 g / cm³. The measurement of density values that indicated the level of homogeneity of the solution was also evidenced in the measurement of low surface tension in the F1 formulation technique of 23.554 ± 0.222 dyne / cm².

High density values were generated sequentially in F3 formulation techniques and F2 formulation techniques. The aim was for practicality and cost efficiency if it is applied to the formulation industry. The process of F2 and F3 formulation techniques required one reactor tank, while F1 formulation techniques required a pair of reactor tanks. However, the use of the F2 formulation technique had a weakness in the form of material solubility. When the mixing process of buprofezin, water and solvesso 150, the problem was the inability of water to dissolve buprofezin optimally. The technical condition of the F2 formulation caused two phase solutions which were not mixed well between the water and solvesso 150 solvents. The addition of DEA surfactant at the end of the process caused DEA surfactants to be not optimally covering the surface of the globula wall. The same thing happened in the F3 formulation technique. The process of mixing buprofezin, DEA and solvesso 150 surfactants was carried out at the beginning of the formulation. Water mixing at the end of the process caused water particles bound by DEA surfactants being smaller because most were bound to solvesso 150 solvents.

3) Droplet Size

Emulsion products have good homogeneity when they have small and uniform droplet sizes. The smaller droplet size indicates that the emulsion has high homogeneity. Thus, the observation of the droplet size parameter was needed to see how much the value of homogeneity. The measurement of droplet value was carried out to ensure the emulsion system of the brown planthopper insecticide product which have micro particle. In the emulsion system, droplets size was more than 0.1 µm or 0.1-50 µm in the form of granules which were dispersed well on the liquid. The smaller droplets size identifies a good emulsion [3].

The droplet analysis results of the brown planthopper insecticide product were influenced by the formulation technique through a variety of analyzes at a 95% confidence interval. From the data obtained, it was concluded that the formulation technique showed a significant effect on the value of the insecticide of brown planthopper product. The observation result of the of droplet size parameter on the brown-plantthopperinsecticide formulation ranged from 2.453-3.284 µm. The average value with the smallest droplet size was in the use of F1 formulation technique which was 2.453 ± 0.084 µm, then the F3 formulation technique was 3.282 ± 0.022 µm, and the largest droplet size average of the F2 formulation technique which was 3.282 ± 0.022 µm. The correlation curve of the formulation techniques on droplet size parameters is shown in Figure 6.

![Figure 6: Correlation curve of insecticidal formulation techniques on droplet size parameters](image-url)

Duncan's further test result showed that the average droplet size of the brown planthopper insecticide formulation using a variety of formulation techniques was significantly different from the F2 formulation technique, and not significantly different from F1 and F3 formulation techniques. The observation of the smallest droplet size was found in F1 formulation technique. This shows that the F1 formulation technique determined the formation of an emulsion system that had a good homogeneity value. The formulation process utilized DEA surfactant to be well dissolved in water because of its nature which prefers water rather than oil. DEA surfactant is easier to bind the water molecules since DEA is a type of nonionic surfactant or does not have a charge on the head (hydrophobic) which is an ether or hydroxyl group. The mixing process of F1 formulation technique was closely related to mixing process which was based on each group of ingredients. The formulation process used DEA surfactants to make it well soluble in the water, since it is as the non-ionic surfactant which is more soluble in the water rather than in oil. In the polar head (hydrophilic) of DEA surfactant is the oxygen ether group or hydroxyl. While on the non-polar tails (hydrophobic) is the hydrocarbon chain[6]. The group of ingredients consisted of buprofezin which dissolved at solvesso 150 (non polar) and DEA which dissolved in water (polar). Thus, the mixing process could maximize the functions of each group of substances first, and then the formulation process generated high homogeneity which was indicated from the small droplet sizes.

Cost efficiency and the selection of more practical formulation techniques in industrial applications were shown in the formulation techniques of F2 and F3. However, mixing the three ingredients directly generated the result of the formulation with lower homogeneity because it had relatively large droplet sizes. Meanwhile, in the F2
formulation technique which was mixing buprofezin, water and solvesso 150 first, the ability of water to dissolve buprofezin was very small. The condition of this formulation technique caused two phase solutions of water and solvesso 150 solvent unmixed. Thus, the formulation process to produce a small droplet size did not run optimally when mixing the DEA at the end of the process.

The observation results of the droplet size were further supported by the observation of the surface tension and contact angle parameters. F1 formulation technique that had the smallest droplet size showed a good level of homogeneity since the DEA surfactant was better in covering the globsules formed. Thus, it maximized the ability of DEA surfactant to reduce surface tension and form small contact angles.

4) Surface Tension
The molecules on the liquid surface have special properties that most molecules do not have in liquids, namely surface tension. The surface tension of a liquid is internal pressure caused by the attraction of molecules to the bottom surface of the liquid surface. A fluid molecule creates an inward attraction, or internal pressure which limits the tendency of fluid to flow and form a large interface with other substances [7]. The main characteristic of surfactant is as a surface active ingredient [8]. The force of attraction of the fluid surface against the air is lower because of the influence of surfactant compounds. The analysis results of the surface tension parameter of the brown planthopper insecticide were not influenced by the formulation technique through a variety of analyzes at a 95% confidence interval. From the data obtained, it can be concluded that the formulation technique did not show any significant effect on the surface tension value of the brown-plant hopper insecticide product. The observation results of the surface tension parameter on the brown planthopper insecticide formulations ranged from 23,554-26,433 dyne / cm. The average value with the smallest surface stress was on the use of F1 formulation technique which was 23,554 ± 0.222 dyne / cm, then the F3 formulation technique which was 24,995 ± 1.065 dyne / cm, and the highest surface tension average in F2 formulation technique which was 26,433 ± 1.802 dyne / cm. The correlation curve of the formulation techniques on the surface tension parameters is shown in Figure 7.

![Figure 7: Correlation curve of insecticidal formulation techniques on surface tension parameters](image)

A small surface tension value indicates the attraction force between small particles on the surface of a solution. This becomes the advantage in the formulations especially for insecticide product. Low surface tension from insecticide solution can reduce the contact angle of insecticide on leaf surfaces, thereby it increases the spread of insecticide spray areas [9]. F1 formulation technique is the appropriate technique to formulate the brown planthopper insecticide and produce low surface tension. The mixing process in the F1 formulation was carried out by the mixing principle based on the group of ingredients in the form of buprofezin which was dissolved in solvesso 150 (non-polar) and DEA which was dissolved in water (polar). Therefore, the mixing process could maximize the function of DEA surfactants that prefer to dissolve in water and buprofezin which dissolve in solvesso 150. Thus, the formulation process generated a low surface tension value because of DEA surfactant which is able to reduce surface tension, so that it can dissolve well.

The result of surface tension parameter was further supported by the observation results of the contact angle parameters sequentially from the smallest was F1 formulation technique which was 17,572 ± 0.248° and F3 which was 25,907 ± 0.719° and F2 which was 27,052 ± 1.156°. Formulation techniques of F2 and F3 had relatively higher surface tension values. The F2 formulation technique was by mixing the buprofezin, water and solvesso 150 first. Then, the addition of water and solvesso 150 aimed to dissolve buprofezin. However, the ability of water to dissolve buprofezin is smaller than solvesso 150. Solvesso 150 is an oil phase that cannot be dissolved by water. The addition of DEA surfactant can mix the two phases. However, this formulation technique had the disadvantage on the ability of binding DEA surfactant to water which was not maximum. Likewise the F3 formulation technique, the addition of water at the end of the process caused the binding of water molecules by DEA surfactants to be limited.

5) Contact Angle
Contact angle parameter is related to the ability of insecticide formulation to spread widely on the surface area. The surface that becomes the object depends on the work system of the insecticide. Insecticide with contact poison work systems, will be able to stick the substance to the target insect skin and insecticide with the stomach poison work system, will be able to attach on leaves or even itenables in both work systems; contact and stomach. Penambahansurfaktanapada formula insectisidamemilikigunapenguapatingkatefektitasinspektisid atersebut. Droplets of solution containing surfactants can penetrate and spread between the layers of insect skin and fine hairs on the leaf surface, through capillary. However, droplets of solution without surfactant cannot spread and only stick on the surface of the skin and leaves [10].

The analysis results of the contact angle parameter of the brown planthopper insecticide were influenced by the formulation techniques through a variety of analyzes at a 95% confidence interval. From the data obtained, it was concluded that the formulation technique showed a significant effect on the contact angle value of the brown planthopper insecticide product. The observation result of the contact angle parameter of the brown planthopper insecticidal formulation ranged between 17,572°-27,052°. The first formulation of F1 was 17,572 ± 0.248°, the second
formulation F2 was $27.052 \pm 1.156^\circ$, and the third formulation of F3 was $25.907 \pm 0.719^\circ$. The correlation curve of the formulation techniques on the contact angle parameters is shown in Figure 8.

Duncan's further test results showed that the average contact angle of the result of brown planthopper insecticide formulation using a variety of formulation techniques was significantly different in the F1 formulation technique, yet it was not significantly different from the formulation techniques of F2 and F3. Based on the results of the study, it is known that the ability of insecticidal formulation produced by F1 formulation technique was more effective in spreading on the leaf surface since it had the lowest contact angle value of $17.572^\circ$. The value of contact angle was significantly different because the process of mixing the ingredients was based on the ability to form a good solution. DEA surfactant has good ability to bind water molecules compared to oil molecules. However, buprofezin can dissolve well by solvesso 150 compared to water. The two different solutions were grouped into the oil phase and the water phase. Then the two phases were mixed well after formulation. This application was applied in F1 formulation technique.

The observation results of the contact angle values with the formulation techniques of F2 and F3 were not significantly different. The F2 formulation technique generated the highest contact angle value. The process of mixing buprofezin, water and solvesso 150 first aimed to dissolve buprofezin. However, the ability of water to dissolve buprofezin was very low compared to solvesso 150. The oil phase found in solvesso 150 was insoluble of water and caused two layers formed. The addition of DEA surfactant caused the two phases mixed. However, this formulation technique has the disadvantage of binding DEA surfactants to water that was less extent. Meanwhile, in the F3 formulation technique, water mixing was carried out at the end of the process. The ability of DEA surfactant that tend to bind water molecules caused DEA surfactant bound to many oil molecules since they were first mixed. Thus, the water as a dispersing medium for oil was less bound by DEA surfactant.

6) Viscosity
Observation of insecticidal viscosity parameters was crucial to be conducted since it is closely related to the use of it when using spray equipment. The high viscosity causes the difficulty on the mixing process and dissolving perfectly with the water. The analysis results of the viscosity parameters of the brown planthopper insecticide that were not influenced by the formulation techniques through a variety of analyzes was at 95% confidence interval. From the data obtained it can be concluded that the formulation technique did not show any significant effect on the value of the viscosity of the insecticide of the brown planthopper. The average value of the first formulation parameters of F1 was $9.448 \pm 0.180$ cP, the second formulation of F2 was $8.813 \pm 1.488$ cP, and the third formulation of F3 was $8.750 \pm 0.283$ cP. The correlation curve of the formulation techniques to the viscosity parameters is shown in Figure 9.

High viscosity is due to the high concentration of particles, as well as the flow properties of the substance depending on the viscosity and density of the fluid. Fluid which is easy to flow have low viscosity and vice versa, thus the substances which are difficult to flow have high viscosity[11]. The F3 formulation technique generated a lower viscosity value. This was because of the mixing process by adding water at the end of the process could cause the mixed water particles having a low density. Therefore, it causes the flow of particle easier to move. Otherwise, the F1 formulation technique that had high viscosity because the mixing process was carried out based on the ability of DEA surfactant to bind water and the ability of solvesso 150 to dissolve buprofezin well. The mixing process of those two solutions were optimally formulated and they formed smaller particles then got denser. The density of these particles caused the liquid more difficult to flow, thereby it had a higher viscosity value.

Visual observations on the formulations result of the brown planthopper insecticide based on variations in formulation techniques did not show a significant difference. The appearance of the insecticidal formulations had the same white color and density. The following are insecticide samples through variations in formulation techniques which are shown in Figure 10.
4. Conclusion

The best formulation technique for brown planthopper insecticide was F1 formulation technique through the mixing process of each group of substances namely hydrophilic groups in the form of DEA and water and hydrophobic surfactants in the form of buprofezin and solvesso 150 based on the parameters of droplet size, surface tension and contact angle. The observation results of the physicochemical properties were pH 10.42 ± 0.148; density of 0.9973 ± 0.00 g / cm³; droplet size of 2.453 ± 0.084 µm; surface tension of 23.544 ± 0.222 dyne / cm; the contact angle of 17.57 ± 0.248° and the viscosity of 9.448 ± 0.180 cP.

References


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