Malaysian Journal of Chemistry, 2024, Vol. 26(3), 19-28
(Special Issue: *The 4th International Conference on Recent Advancements in Science and Technology*)

Alkyldiethanolamide Surfactant Based on Ketapang Seed Oil in Herbicide Formulation

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Alkyldiethanolamide (ADEA) is a group of non-ionic surfactants that can be obtained from the amidation process, potentially reducing the surface tension of commercial herbicides and thereby increasing their effectiveness. The purpose of this research is to characterize ADEA surfactants produced from the synthesis of triglycerides based on ketapang (*Terminalia catappa)* seed oil with Lipozyme TL IM catalyst and the effect of adding surfactant with concentration 1-9% in herbicide formulations with the active ingredient isopropylamine glyphosate. The characteristics of the ADEA produced are an acid value of 72.62 mg KOH/g, a saponification value of 106.59 mg KOH/g, an HLB value of 5.68, a pH of 6.2, a density of 0.94 g/mL, and viscosity of 6.33 Cp. The effect of adding a surfactant concentration of 5% was the best formulation, which was able to reduce the surface tension of commercial herbicides from 22.03 dyne/cm to 14.66 dyne/cm.

Keywords: Surfactant; ketapang seed oil; herbicide; alkyldiethanolamide; surface tension

Received: November 2023; Accepted: December 2023

Herbicide is material chemistry that becomes a mainstay of farmers in controlling plant nuisance (weed), such as grass, reeds, and wild bushes on agricultural land. Herbicides containing the active ingredient glyphosate are herbicides that are widely used because they have a broad-spectrum control. Formulation herbicides generally have a highly active material, around 25-65%, and the residual material is added to other materials, such as surfactants and water [1]. The commercial herbicide formula currently widely used by the public consists of 48% isopropylamine (IPA) glyphosate, 15% polyoxyethyleneamine (POEA) surfactant, and water as a solvent. POEA surfactant is non-biodegradable, highly corrosive, and toxic to organisms and animals [2]. In general, glyphosate herbicides are applied to the surface of the leaves, so they have a high chance of being washed off by rainwater. For this reason, the addition of surfactant is needed to increase the herbicide's ability to penetrate the weed tissue [3]. As mentioned in [4], a strategy to enhance the effectiveness of active elements and mitigate the effects of environmental contamination involves incorporating surfactants. These substances diminish adverse effects on biodiversity preservation while potentially lessening other detrimental consequences on human health.

One of the surfactants that can be used to reduce the toxic impact is alkyldiethanolamide (ADEA), a group of non-ionic surfactants that can be obtained from an amidation process using methyl esters or fatty acids. This surfactant is biodegradable and non-toxic to the environment [5]. Surfactants containing lipophilic parts can interact with the cuticle, helping the active ingredients enter plant cells and thereby increasing the activity of the herbicide [6]. The addition of surfactants to herbicide formulations can reduce surface tension between the surface of weed leaves and the herbicide so that it can expand distribution on the surface. The expansion of herbicide distribution on the leaf surface causes a decrease in herbicide evaporation so that the herbicide application process is efficient. According to findings from [7], the efficacy of ADEA surfactant in pesticide application was highlighted. Specifically, when formulated from pure coconut oil methyl ester at an 8% concentration, it significantly impacted the efficacy of insecticides containing azadiractin as the active compound. Moreover, it successfully decreased surface tension levels from 41 dyne/cm to 28.1 dynes/cm. Previously, the addition of ADEA surfactant from palm oil to herbicide formulations was carried out by [8]. The results of this research are quite efficient in reducing surface tension compared to commercial herbicides, from a tension value of 36.27 dyne/cm to 30.73 dyne/cm.

In previous research, the source of raw material for ADEA surfactants applied in herbicides was commercial edible oil, so there would be competition with food ingredients. ADEA surfactant demand is expected to continue to increase due to its widespread application, for instance, within sectors like agrochemicals, cleaning, and cosmetics, as indicated. Ketapang seeds can be an alternative to commercial oils such as coconut or palm oil. Ketapang

†Paper presented at the 4th International Conference on Recent Advancements in Science and Technology (ICoRAST2023)

seeds have a high oil content, around 57-60% [10] and 40-57% [11]. The fatty acid content of ketapang seed oil is almost the same as the fatty acids of palm oil and coconut oil, so it has high prospects of being used as an alternative basic material to ADEA surfactant synthesis.

The ketapang plant (*Terminalia catappa* L.) is also a local plant that is found a lot in Lombok, West Nusa Tenggara, and generally in other regions in Indonesia, even in Southeast Asia [12]. Its existence is abundant and has not been utilized properly. For this reason, we have conducted research on alkyldiethanolamide surfactants made from ketapang seed oil and their effect on herbicide formulations with the active ingredient isopropylamine glyphosate. This formulation is expected to potentially increase the effectiveness of commercial herbicides. The herbicide mixture is formulated with the addition of a surfactant concentration of 1-9%.

EXPERIMENTAL

Chemicals and Materials

Aquadest, ketapang seed, diethanolamine, diethylether, lipozyme TL IM (Novozymes), ethanol 96%, n-hexane, anhydrous $MgSO_4$, KOH alcoholic, isopropyl alcohol, NaOH, phenolphthalein indicator, HCl, Na_2SO_4-$CuSO_4$, H_2SO_4, H_3BO_3 2%, herbicide with the active ingredient isopropylamine glyphosate 48%. The equipment used a set of soxhletation tools, glassware, analytical balance (DC-600A), desiccator, Water bath stirrer (WB-4MS Biosan), vacuum filtration, rotary evaporator (B-ONE RE-1000VN), pH meter (ATC-001), chromatography vacuum liquid (KVC), thin layer chromatography (TLC), Spectrophotometer Infra-Red (a Perkin-Elmer Model Frontier FTIR spectro-photometer (Perkin-Elmer, USA), homogenizer (RCC - JB60 100-3000 rpm), oven (Memmert), picnometer, viscometer Ostwald, hotplate stirrer (C-Mag HS7).

Methods

Extraction and Purification Ketapang Seed Oil

Extraction of Ketapang seeds was carried out using the soxhletation and evaporation methods [13]. A quantity of 35 g of powdered ketapang seeds was measured and subjected to a 6-hour soxhlet extraction using 250 mL of n-hexane as the extracting solvent. The oil extracted through Soxhlet was refined by passing it through a chromatography column filled with silica gel and eluted with n-hexane. Subsequently, the purified oil underwent solvent removal via a rotary evaporator operating at 60°C, 125 rpm, followed by the addition of anhydrous magnesium sulfate to eliminate any remaining water content.

Synthesis and Purification of Alkyldiethanolamide Fatty Acids

The reaction consists of ketapang seed oil and diethanolamine using an immobilized lipase enzyme as a catalyst (Lipozyme TL IM) at a certain temperature and time. Diethanolamine:oil ratio (10:0) g/g and Lipozyme:oil enzyme ratio (1.2:10) g/g, reaction time 1.13 hours and temperature 32°C. ADEA synthesis was carried out in a water bath stirrer. ADEA purification was carried out based on the method used by [14]. Purification can be carried out in several stages. First, separate the enzymes in the product mixture by filtering with filter paper. Second, separate the n-hexane fraction from the mixed glycerol and water layers using a separating funnel. Next, for the solidification of diethanolamine, the n-hexane fraction is chilled in a freezer for a duration of 5 hours and then filtered to separate solid ADEA from the gel-like substance.

Analysis and Characterization

Product characterization was carried out using several tests, including saponification number (AOCS Cd 3-25)[15], iodine number (AOCS-Cd 1d-92) [16], acid number (AOCS-Ca 5a-40 and AOCS-Cd 3d-63) [17,18], total nitrogen Content (AOCs Ac 4-91) [19] density (AOCS Ea 7-95) [20], viscosity measurement (Allam 2023) [21], pH (AOAC 2005) [22], surface tension [23].

FTIR Analysis

Ketapang seed oil and ADEA surfactant were analyzed using an infrared spectrophotometer (FTIR) to identify functional groups. The difference in the FTIR spectrum of oil and ADEA was observed as an indicator of the success of the formation of ADEA surfactant.

HLB (Hydrophilic Lipophilic Balance) Value Analysis

The hydrophilic-lipophilic balance (HLB) value can be determined based on the surfactant critical micelle concentration (CMC) value. This value is obtained from the lowest surface tension value based on equation 1 [24]:

$$HLB = 7 - 0.36 \ln \left(\frac{Co}{Cw}\right). \qquad (1)$$

Description:

Cw = CMC value (Concentration value at the lowest tension surface)

Co = 100-Cw

HLB = *Hydrophilic-Lipophilic Balance*

Table 1. Addition of ADEA to the formulation of Herbicide.

Formulation (%)	Alkyldiethanolamide (g)	Herbicide 48% (g)	Water (g)
1	0.5	24	25.5
2	1	24	25
3	1.5	24	24.5
4	2	24	24
5	2.5	24	23.5
6	3	24	23
7	3.5	24	22.5
8	4	24	22
9	4.5	24	21.5

Formulation Herbicide

The herbicide formulation consists of a soluble liquid formulation with the active ingredient isopropylamine 48% (w/w) (commercial herbicide). The formulation concentrates range from 25-65% with an optimum concentration of 48%, and it is easy for the dissolution process [1]. The inclusion of ADEA surfactant ranges from 1 to 9% by weight. This variation in concentration is based on the results of previous research [8], which states that a concentration of 5% has excellent characteristics, so it is used as a benchmark or midpoint concentration. Furthermore, the formulation adds water as a solvent. The quantity specified for each treatment is 50 g. The formulation was blended utilizing a homogenizer at a stirring rate ranging between 2000 to 3,000 rpm for a duration of 10 to 15 minutes.

RESULTS AND DISCUSSION

Extraction and Purification Ketapang Seed Oil

The extraction method used is soxhlation because this method is faster and more efficient in terms of time, and the solvent obtained can be reused [25]. The selection of n-hexane as a solvent is because it is a nonpolar solvent, so it can dissolve ketapang seed oil, which is also nonpolar. Ketapang seed oil resulting from the soxhlation process is purified using vacuum column chromatography, which aims to separate the oil from its impurity compounds. This compound has a polar group and will be attracted by a polar stationary phase, such as silica gel. Meanwhile, nonpolar triglycerides will pass through the column first. This purification process uses n-hexane as an eluent. From this research, pure Ketapang seed oil (triglycerides) was obtained, which was yellow in color and clearer compared to before purification. This can be caused by impurities that have been retained in the silica gel. Then, the Ketapang seed oil is separated from the solvent using a rotary evaporator. Based on calculations, the oil content obtained an average of 59.08%. The percentage of oil content obtained was lower by 60% than the research by [10]. This can be influenced by water content, fruit maturity, or the geographical location where the ketapang tree grows. Meanwhile, [26] compared the results of Ketapang seed oil extraction using two methods, soxhlation, and maceration. The yield of oil extraction using 22 hlet extraction is higher (57.5%) compared to the maceration method (51%).

Synthesis and Purification Alkyldiethanolamide

ADEA is synthesized from ketapang seed oil or triglycerides, and diethanolamine 1 M uses a catalyst immobilized (Lipozyme TL. IM) and n-hexane p.a as a solvent. The n-hexane p.a solvent was chosen since it has high purity and can dissolve the product well. Diethanolamine is alkaline, but the synthesis reaction uses an enzyme catalyst, where the appropriate pH condition is pH 7. This is because a very high (alkaline) or low (acid) pH will reduce or even damage the performance of the enzyme. [27] stated that immobilized enzymes are more active than free enzymes in the pH range (5-10). An immobilized enzyme refers to a system or formulation in which the enzyme molecule is enclosed within a chamber, preserving its catalytic activity. This results in enhanced stability and the ability to be reused [28]. The objective of enzyme immobilization is to enhance its economic efficiency by enabling the repeated utilization of the immobilized enzyme over an extended duration. Additionally, the biocatalyst can be effortlessly separated from the product mixture. Immobilized enzymes are efficient, environmentally friendly, and selective bio-catalysts that facilitate the catalysis of reactions even in challenging environmental conditions [29][30]. The synthesis process was reacted in a water bath stirrer for 1 hour 13 minutes, with a stirring speed of 40 rpm. The reaction results suggest a change in turbidity; this indicates that a reaction has occurred in the reactant. Furthermore, the ADEA purification process is carried out. The ADEA surfactant produced from 10 g of oil is 0.58 g of ADEA in solid form and 5.54 g of ADEA in liquid (gel) form. The total amount of ADEA conversions produced was 61.2%. This result is not ery different from the results obtained by [31], which is 60%.

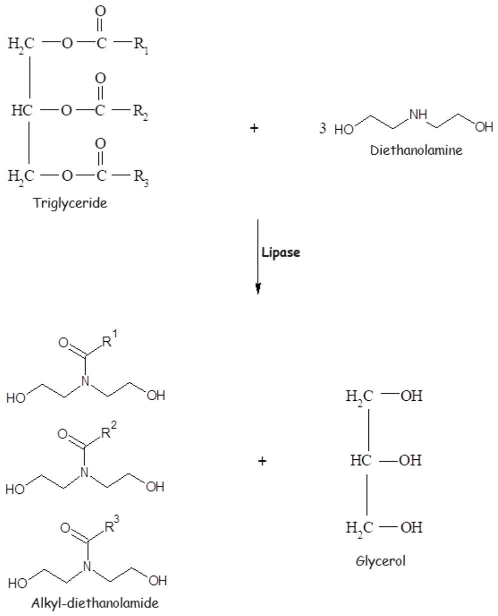

Figure 1. Amidolysis reaction of Triglyceride of Ketapang Seed Oil

Acid Value (AV) and Saponification Value (SV)

The acid number test aims to state the amount of free fatty acids contained in a material. The acid number provides a parameter for the level of rancidity based on the amount of free fatty acid content [32]. Based on the research results, the average number before refining was 3.46 mg NaOH/g oil, while the acid number obtained after refining was 1.2 mg NaOH/g oil. There are differences in the value of the acid number before and after purification. This is because there are still impurities in the oil, so it needs to be separated using KKV. The acid number of the refined oil obtained is in accordance with the standard acid number according to SNI [33]. The acid number value of Ketapang is almost similar to the acid number of nyamplung oil (1.17) [13] but lower when compared to the acid number of other non-edible oils, such as castor oil (1.97) [34]. The synthesized ADEA product exhibited an average acid number of 72.62 mg NaOH/g ADEA. There was a fairly high increase in the acid number between the oil acid number and ADEA. This suggests that triglycerides from Ketapang oil have undergone amidolysis and discontinuity reactions to become fatty acids and form ADEA (Figure 1).

The saponification value test is carried out to determine the molecular weight of a material. The measurement results revealed that the saponification value was 106.59 mg KOH/g oil. Certain plant-based oils, like palm and coconut oils, have short-chain fatty acids in large quantities, resulting in high saponification value (235-260 mg KOH/g oil) [35]. In line with this statement, it can be concluded that Ketapang oil is composed of long carbon chain fatty acids with a high molecular weight and will produce a lower saponification value. Based on the research results, the ADEA saponification value was 177.82 mg KOH/g. The saponification value has an inverse relation with molecular weight. The saponification value of ADEA is greater than that of Ketapang oil triglycerides. This is because ADEA has a smaller molecular weight (397 g/mol) compared to Ketapang oil triglycerides (940 g/mol). This indicates that most of the ester groups in triglycerides have changed to amides.

Determination of Total Alkyldiethanolamide Nitrogen Content

Analysis of total nitrogen levels is a quantitative analysis using the Semi Macro Kjeldhal method. The Kjeldahl method represents a simple technique used to analyze the overall nitrogen content present in amino acids, proteins, and nitrogen-based compounds. The principle of this method is the formation of ammonium through a destruction process using an acid catalyst. Including a catalyst in the Kjeldahl method will speed up oxidation and potentially lead to rapid ammonium formation [36]. Based on the results of the analysis, the ADEA sample exhibited a nitrogen content of 0.07%. This means that there is 0.005 mmol of nitrogen in 1 g of ADEA sample. This indicates that ADEA was successfully synthesized from ketapang seed oil.

FTIR of Ketapang Seed Oil and Alkyldiethanolamide

FTIR analysis of Ketapang seed oil is displayed in Figure 2. Wavenumbers of 2,854.09 cm^{-1} and 2,924.67

cm^{-1} indicate the presence of C-H bonds. The detected wavenumber of 1,746.68 cm^{-1} indicates the presence of C=O ester bonds in triglycerides. The wavenumber of 1,163.39 cm^{-1} suggests that there is a bond between C-O and absorption for C-C at a wavenumber of 722.34 cm^{-1}. These results are in accordance with the research results of [10] for Ketapang seed oil.

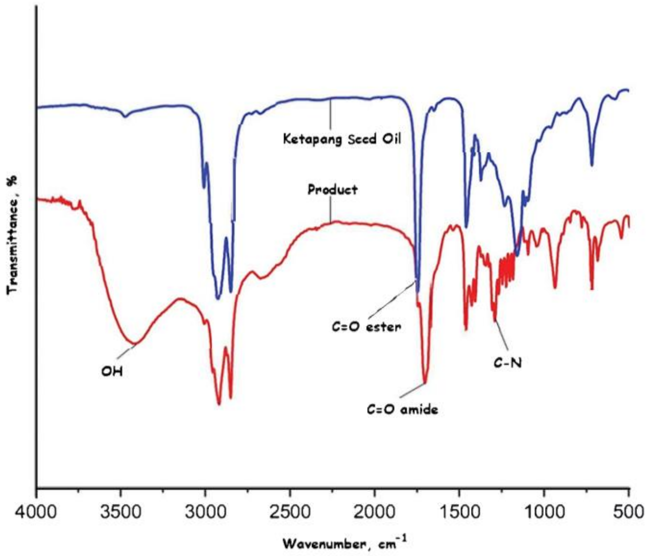

Figure 2. FTIR spectrum of ketapang seed oil and ADEA.

Table 2. Wavenumber of ketapang seed oil and ADEA.

Function Group	Wavenumber (cm^{-1})	
	Triglycerides	ADEA
C-C	722.34	720.58
C-O	1163.39	-
C=O	1746.66	1702.64
C-N	-	1295.63
C-H	2924.67	2917.97
N-H	-	-
O-H	-	3428.55

For the ADEA spectra, the absorption at wave number 3,428.55 cm^{-1} was detected as an O-H group, which is not found in oil. The absorption of the C=O amide group shifted from C=O ester, 1,746.66 cm^{-1} to 1,702 cm^{-1}. The spectrum exhibits no peak visible in the absorption area of the N-H group because the N in ADEA is N-tertiary. Absorption for the C-N group was detected at a wave number of 1,295.63 cm^{-1}. The presence of this functional group suggests the success of ADEA synthesis. This is in accordance with research by [31] and [37]. A comparison of the wave number absorption areas of Ketapang seed oil and ADEA is provided in Table 2.

HLB Value of Alkyldiethanolamide

Determination of the HLB value is carried out using the CMC value method, which is obtained from the results of the lowest surface tension concentration of the surfactant. Knowledge of CMC is very important when using surfactants because surface tension does not decrease further above CMC. The CMC value is a chemical-physical parameter for pure surfactants in terms of surface activity [38]. The CMC value of the surfactant was found to be 2.5. The HLB results obtained were 5.68. This value is included in water-in-oil or W/O emulsions. These results indicate that ADEA surfactant is lipophilic and has a tendency to interact with oil more strongly. This leads to a reduction in the oil's surface tension [39]. ADEA surfactant does not yet have an ideal wetting HLB value of 7-9 [40]. However, this emulsion (W/O) is able to increase the effectiveness of herbicide absorption into the leaf layer, which has a lipophilic cuticle.

Density, Viscosity, and pH of Alkyldiethanolamide

The density of a quantity is expressed in terms of the weight of the liquid per unit volume. The average density value is 0.942 g/mL. This value is not much different from the ADEA density synthesized by [8] using palm oil methyl ester of 0.9762 g/mL. ADEA viscosity testing uses an Ostwald viscometer. The average flow time is 50.49 seconds. The flow time obtained is then compared with the water standard. Meanwhile, the viscosity value of water is 0.889 cP, so the viscosity value from ADEA is 6.328 cP.

The pH measurement aims to determine the acidity condition of the ADEA surfactant. The ADEA pH is 6.2. This pH also corresponds to the effectiveness of surfactant work, which is around 5-7 [41]. The pH measurement indicator is quite essential as it will determine the toxicity of the formulation. A very acidic pH value or alkaline cannot be used, considering that ADEA will be a mixture of formulations that are applied to plants and have an impact on soil conditions. Table 3 provides the characteristics of ADEA.

Analysis Formulation Herbicide

Analysis of herbicide formulations was carried out to observe the effect of adding surfactants on the variations in formulations used. The observed characteristics are related to viscosity, density, and surface tension changes. The ADEA surfactant used is the liquid phase ADEA since the liquid phase is more soluble and homogeneous than the commercial herbicide formulation used.

Density Value of Formulation Herbicide

Surfactant density refers to the amount of surfactant liquid in relation to the volume of the herbicide formulation. The study findings indicate that increased surfactant concentration leads to a decrease in the formulation's density value. The density of commercial herbicides has a value of 1.118 g/mL but increases when the surfactant concentration is added to 1%, and the density decreases further when the concentration is added. Based on density calculations, the 1% surfactant formulation produces a density of 1.124 g/mL, while the 9% formulation has a density value of 1.108 g/mL. This is because the water mixture in the 1% formulation is larger (25.5 g) while the surfactant concentration is less (0.5 g). The 9% formulation contains less water (21.5 g) and a greater surfactant concentration (4.5 g). In herbicide formulations, if the amount of surfactant is higher and the amount of water is lower, this will cause the density value to decrease, and vice versa. The water density value (0.997 g/mL) also influences the density test results of the herbicide formulation. The density value of water exceeds that of ADEA, which measures 0.941 g/mL. The density value is directly proportional to the surface tension value. The lower the density, the lower the surface tension of the liquid, and vice versa [42]. This indicates that ADEA surfactant works well in herbicide formulas since it can reduce surface tension. The density value of each formulation can be observed in Figure 3.

Table 3. Characteristics of Alkyldiethanolamide.

No.	Parameter	Value
1	Acid Number, mg KOH/g	72.62
2	Safonification value, mg KOH/g	103.79 ADEA
3	HLB	5.68
4	pH	6.2
5	Density, g/mL	0.941
6	Viscosity, cP	6.328

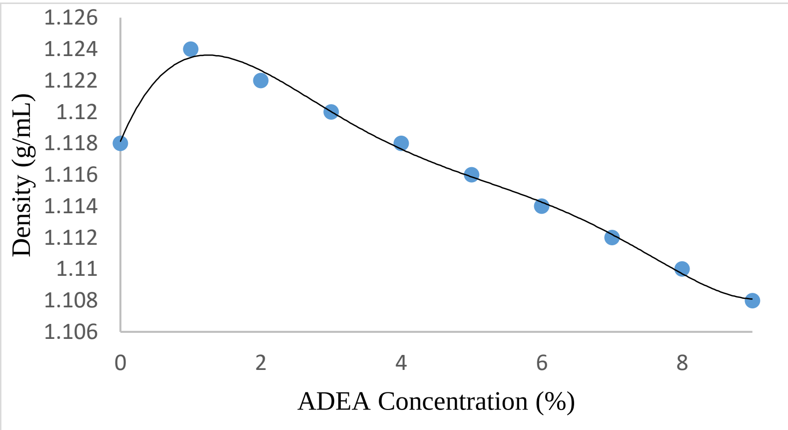

Figure 3. Interaction of ADEA density and percentage in formulation herbicide

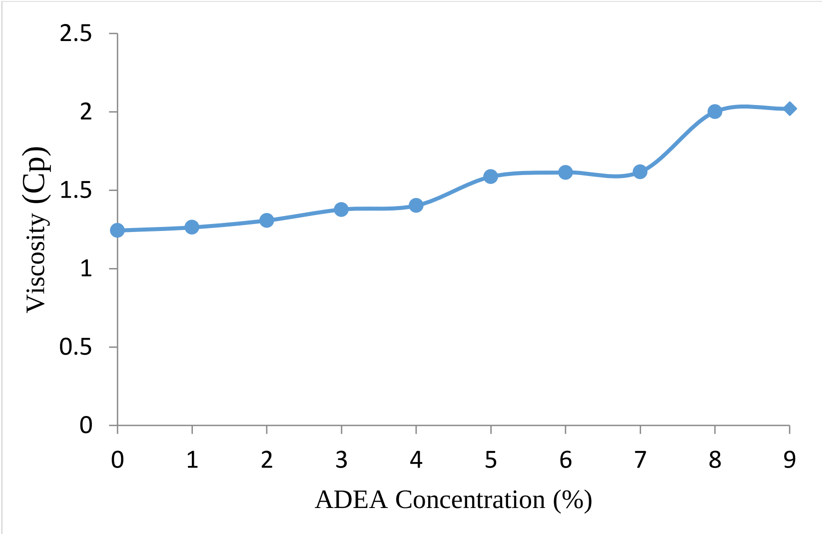

Figure 4. Viscosity of variation of ADEA percentage in formulation herbicide

Viscosity Value of Formulation Herbicide

A viscosity test is carried out to determine changes in the viscosity level of several herbicide formulations. The results of viscosity testing on commercial herbicides or without the addition of surfactants were found to be 1.243 Cp. Based on the research results, it can be seen that with increasing surfactant concentration, the viscosity level of the herbicide formulation also increases (Figure 4). In the 1% formulation, the viscosity value starts to increase slightly to 1.259 cP until the 5% to 9% formulation increases. This is related to the viscosity of the ADEA surfactant itself and the formation of micelles from the surfactant with
26 oncentration above 5%, making the formulation flow rate require quite a long time. This aligns with findings from [43], indicating that as the surfactant concentration rises within a formulation, the viscosity also increases. As the concentration of the surfactant increases, the solubilization process will increase since the concentration of micelles formed will be greater [44].

Surface Tension Value of Formulation Herbicide

Surface tension is an indicator of the efficiency of adding surfactants to commercial herbicides. Low voltage indicates good emulsion. In herbicide formulations, there are two phases that are difficult to homogenize. The herbicide formulation is in the oil phase, and the water phase is in the solvent. The addition of surfactant is very influential in the formation of the emulsion in the herbicide so that the solution becomes homogeneous.

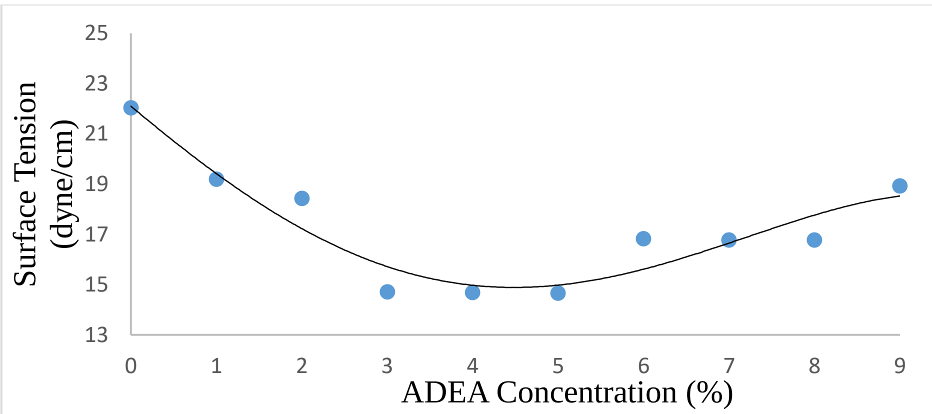

Figure 5. Effect of ADEA percentage in formulation herbicide to surface tension.

The findings indicated that incorporating ADEA surfactant at a concentration of 1-3% led to a decline in surface tension measurements from 19.19 dyne/cm to 14.709 dyne/cm. The presence of water solvent in the herbicide formulation also affects the surface tension value because ADEA surfactant has more polar properties and tends to dissolve in water. Hence, the hydrophilic groups become longer, and the hydrophobic groups become shorter. The distribution of bond energy among liquid molecules results in a reduction of the cohesive energy between these molecules in the liquid [8]. This leads to a reduction in the value of surface tension. The 5% formulation represents an equilibrium state among the surface molecules of the liquid, thereby contributing to a decrease in the optimal surface tension value. Between concentrations of 3-5%, surface tension tends to remain consistent. The lowest surface tension was observed at an ADEA concentration of 5% (14,656 dyne/cm). This 5% formulation represents an equilibrium state among the liquid's surface molecules, leading to a decline in the ideal surface tension value. This happens because, at that point, the CMC value (2.5) has been reached. The CMC value indicates the critical concentration of surfactant in forming micelles, and surfactant added to the system will spontaneously change into micelles [7, 8].

The inclusion of 5-6% ADEA resulted in elevated surface tension values. This happens because the formulation has reached a threshold CMC value, so if excess surfactant is added, back emulsion will occur, which will cause the surface tension value to increase. This is in accordance with the observations of [45] that the surface tension value for solutions that add surfactants will continue to decrease before the solution reaches the CMC point. After the CMC value reaches the minimum point (saturation point), then changes occur. This figure is commonly termed as the maximum achievable surface tension value attainable through surfactant addition. The lower this limit, the higher the efficacy of the surfactant, as noted in reference [46]. Upon incorporating ADEA at concentrations ranging from 6-8%, there was still an increase in surface tension, but the increase was not significant. Greater changes in surface tension occurred at ADEA concentrations of 8-9%. This is thought to occur because it is related to the size of the micelles formed during CMC.

The surface tension in commercial herbicides or without the addition of surfactant is 22.023 dyne/cm. Based on Figure 4, it can be seen that the lowest decrease in surface tension occurred in the 5% formulation. The surface tension value decreased to 14.656 dyne/cm. A small surface tension value and an HLB value of 5.68 (W/O) will increase the ability of herbicides containing the active compound IPA glyphosate to absorb into the tissues of weed plants. This has the potential to make the herbicide work more effectively and efficiently.

CONCLUSION

Alkyldiethanolamide (ADEA) based on ketapang seed oil triglycerides has several distinctive characteristics so that it can be used as a surfactant. The application of ADEA surfactant in a herbicide formulation has the potential to reduce surface tension.

ACKNOWLEDGEMENTS

This research was funded by the Institute for Research and Community Service (LPPM) at the University of Mataram through PNBP funds.

REFERENCES

1. Tominack, R. L. (2000) Herbicide Formulations. *Journal of Toxicology*, **38(2)**, 129–135. http://doi.org/10.1081/CLT-100100927.

2. Mesnage, R., Defarge, N., Spiroux, D. J., Seralini, G. E. (2015) Potential Toxic Effect of Glyphosate and Its Commercial Formulation Below Regulatory Limits. *Food and Chemical Toxicology*, **84(1)**, 133–153. https://doi.org/10.1016/j.fct.2015.08.012.

3. Gitsopoulus, T. K. I., Damalas, C. A., Georgoulas, I. (2014) Improving diquat efficacy on grasses by adding adjuvants to the spray solution before use. *Planta Daninha*, **32(2)**, 355–360. https://doi.org/10.1590/S0100-83582014000200013.

4. Gosh, V., Mukherjee, A., Chandrasekaran, N. (2014) Ultrasonic Emulsification Reduces Droplet Diameter and Enhances Stability. *International Journal of Drug Delivery*, **3(1)**, 13–16. https://doi.org/10.1016/j.ultsonch.2012.08.010.

5. Pawignya, H., Fanilla, N, Melinia, A. P. (2023) Synthesis of Diethanolamide Surfactant from Palm Oil by Esterification and Amidation Processes. *MEST* 2022, AER 2023, 88–89. https://doi.org/10.2991/ 978-94-6463-134-0_9.

6. Hall, L. (2014) How Herbicides Work, Biology to Application, Edmonton: Alberta Agriculture and Development.

7. Yusriah, Hambali, E., Dadang (2017) Botanical Insecticide Formulation of Neem Cake Oil with Dea Surfactant. *Jurnal Teknologi Industri Pertanian*, **27(3)**, 310–317. https://doi.org/10.24961/j.tek.ind.pert.2017.27.3.310.

8. Rusdiana, I. A., Hambali, E., Rahayuningsih, M. (2020) Utilization of Diethanolamide Surfactant from Methyl Esters of Palm Oil in Herbicide Formulation with Active Isopropylamine Glyphosate. *Jurnal Agrosscience*, **8(1)**, 44–53. https://doi.org/10.18196/pt.2020.113.

9. Nisya, F., Hambali, E., Rahmini, Rivai, M., Nobel, CS, Ari, IS, Ainun, (2015), Effects of Palm-DEA Non-Ionic Surfactant as An Additive in Buprofezin Insecticide on the Efficacy of it

in Controlling Brown Planthopper Rice Pest. Presented at *ICAIA*, Bogor, 3–4 August 2015.

10. Suhendra, D., Gunawan, E. R., Hajidi (2019) Synthesis and Characterization of N-Methyl Fatty Hydroxamic Acids from Ketapang Seed Oil Catalyzed by Lipase. *Molecules*, **24(21)**, 1–7. https://doi.org/ 10.3390/molecules24213895.

11. Ravensca, I., Saleh, C., Daniel (2017) Making Surfactant Oil Based Ketapang seeds (*Terminalia catappa L.*) with Triethanolamine. *Journal Atomics*, **2(2)**, 183–189.

12. Anand, A. V., Divya, N., Kotti, P. P. (2015) An updated review of Terminalia catappa. *Pharmacogn Review*, **9(18)**, 93–8. https://doi.org/ 10.4103/0973-7847.162103.

13. Gunawan, E. R., Suhendra, D., Arimanda, P., Asnawati, D., Murniati (2023) Epoxidation of Terminalia catappa L. Seed Oil; Optimization Reaction. *South African Journal of Chemical Engineering*, **43**, 128–134. https://doi.org/10. 1016/j.sajce.2022.10.011.

14. Gunawan, E. R., Suhendra, D., Windari, B. A. N., Kurniawati, L. (2019) Enzymatic synthesis of palmitoylethanolamide from ketapang kernel oil. *Jurnal of Physic Conference Series*, **1321**, 1–6.

15. AOCS Official Method Cd 3–25

16. AOCS Official Method Cd 1d–92

17. AOCS Official Method Ca 5a–40

18. AOCS Official Method Cd 3d–63

19. AOCS Official Method Ac 4–91

20. AOCS Official Method Ea 7–95

21. Allam, A. Y., Wani, S. A., Chen, T. W., Khan, Z. S., Mohmad, S. R. (2023) Chemical, Physical, and Technological Characteristics of Palm Olein and Canola Oil Blends. *Journal of Food Quality*, **20(23)**, 1–17. https://doi.org/10.1155/2023/6503667.

22. AOACS Official Methods of Analysis 18th edition (2005) Association of Official Analitycal Chemist, Washington DC, USA.

23. Wardana, D., Ramadhan, A., Amne, D. P. F., Eddiyanto (2019) Utilization of Glycerol from Used Oil as An Ester Glycerol Surfactant. *Indonesian Journal of Chemical Science and Technology*, **2(2)**, 111–120. https://doi.org/10. 24114/ijcst.v2i2.13999.

24. Wirtanto, E., Lim, M., Masyithah (2012) Study of Purity and Effect of Reagent Ratio, Initial Reaction pH and Reaction Temperature on CMC and HLB Values of Sodium Lignosulfonate. *Jurnal Teknik Kimia USU*, **1(1)**, 15–19. https://doi.org/10. 32734/jtk.v1i1.1400.

25. Uahomo, P. O., Daniel, C., Kpaduwa, S., Ezerioha, C. E. (2023) Characterization and Comparative Assessment of the Essential Oil from Lime (Citrus aurantifolia) Exocarp Using Maceration and Soxhlet Extraction Methods. *Scholars International Journal of Chemistry and Material Sciences*, **6(6)**, 126–134. July 2023, DOI: 10.36348/sijcms.2023.v06i06.002.

26. Janporn, S., Chi-Tang Ho, Chavasit, V., Pan, Min-Hsiung, Chittrakorn, S., Ruttarattanamongkol, K., Weerawatanakorn, M. (2015) Physicochemical properties of Terminalia catappa seed oil as a novel dietary lipid source. *Journal of Food and Drug Analysis*, **23(2)**, 201–209. https://doi.org/ 10.1016/j.jfda.2014.06.007.

27. Moreira, K. S. Oliveira, A. L. B, Junior, L. S. M., Monteiro, R. R. C. (2020) Lipase From Rhizomucor miehei Immobilized on Magnetic Nanoparticles: Performance in Fatty Acid Ethyl Ester (FAEE) Optimized Production by the Taguchi Method. *Frontiers in Bioengineering and Biotechnology*, **8**, 693. https://doi.org/10.3389/fbio.2020.00693.

28. Gupta, S., Bhattacharya, A., Murthy, C. N. (2013) Tune to immobilize lipases on polymer membranes: techniques, factors and prospects. *Biocatalyst Agriculture Biotechnolology*, **2**, 171–190. https://doi.org/ 10.1016/j.bcab.2013.04.006.

29. Xia, H., Zhong, X., Li, Z., X., Jiang, Y. B. (2019) Palladium-mediated hybrid biocatalysts with enhanced enzymatic catalytic performance via allosteric effects. *Journal of Colloid Interface Science*, **533**, 1–8. https://doi.org/10.1016/j.jcis. 2018.08.052.

30. Zheng, J., Wei, W., Wang, S., Li, X., Zhang, Y., Wang, Z. (2020) Immobilization of Lipozyme TL 100L for methyl esterification of soybean oil deodorizer distillate. *Biotechonology*, **10(2)**, 51. https://doi.org/10.1007/s13205-019-2028-6.

31. Gunawan, E. R., Suhendra, D., Trisnasari, Kurniawati, L. (2018) Optimization of the Enzymatic Ammonolysis of Alkanolamide from Ketapang Kernel Oil. *Journal of Physics. Conference series*, **1095(012014)**, 1–6. https://doi. org/10.1088/1742-6596/1095/1/012014.

32. Nwacoko, N., Akuru, U. B., Green, I. A. (2023) Physicochemical Properties and Fatty Acid Composition of Freshly Prepared Palm oil. *African Journal of Biochemistry Research*, **17(2)**, 9–14. https://doi.org/10.5897/AJBR2023.1167.

33. SNI 01-3555-1998, How to Test Oil and Fat, Jakarta.

34. Omari, A., Mgani, Q. A., Mubofu, E. B. (2015) Fatty Acid Profile and Physico-Chemical Parameters of Castor Oils in Tanzania. *Green Sustainable Chemistry*, 154–163. http://doi.org/10.4236/gsc.2015.54019.

35. Ivanova, M., Hanganu, A, Dimitri R. (2022) Saponification value of Fats and Oils as determined from H-NMR Data: The Case of Dairy Fats. *Foods*, **11(10)**, 1466. https://doi.org/10.3390/foods11101466.

36. Sáez-Plaza, P., Michałowski, T., Navas, M. J., Wybraniec, S. (2013) An Overview of the Kjeldahl Method of Nitrogen Determination. Part I. Early History, Chemistry of the Procedure, and Titrimetric Finish. *Critical Reviews in Analytical Chemistry*, **43(4)**. https://doi.org/10.1080/10408347.2012.751786.

37. Wahyuningsih, T. D., Kurniawan, Y. S., Ceristrisani, N., Suryanti, A. D. (2020) Evaluation of ethanolamide based nonionic biosurfactant materials from chemically modified castor oil and used palm oil waste. *Indian Journal of Chemical Technology*, **27**, 326–332. https://doi.org/10.56042/ijct.v27i4.28822.

38. Perinelli, D. R., Cespi, M., Lorusso, N., Palmieri, G. F., Bonacucina, G., Blasi, P. (2020) Surfactant Self-Assembling and Critical Micelle Concentration: One Approach Fits All? *Langmuir*. **36**, 5745−5753, https://doi.org/10.1021/acs.langmuir.0c00420.

39. Tang, M., Suendo, V. (2011) The Effect of Adding Organic Solvents on the Surface Tension of Soap Solutions. *Presented in SNIPS*, Bandung, 22–23, Juni 2011.

40. Swasono, A. W. P., Sianturi, P. D. E., Masyithah (2012) Synthesis Alkyl Polyglycoside Surfactant from Glucose and Dodecanol with Acid Catalysis. *Journal of Chemical Engineering*, **1(1)**, 5–9. https://doi.org/10.32734/jtk.v1i1.1398

41. Cloyd, R. A. (2016) Effect of pH on Pesticides. https://gpnmag.com/article/effects-of-ph-on-pesticides/

42. Janku, L., Bartovska, L., Soukup, J., Jursík, M., Hamouzova, K. (2012) Density and surface tension of aqueous solutions of adjuvants used for tank-mixes with pesticides. *Plant Soil Environment*, **58(12)**, 568–572. https://doi.org/10.17221/556/2012-pse.

43. Esteves, R., Onukwuba, N., Dikici, B. (2016) Determination of Surfactant Solution Viscosities with a Rotational Viscometer. *Beyond: Undergraduate Research Journal*, **1(2)**, 12–19.

44. Lachman, L., Herbert, A., Liberman, Joseph, L., Kanig (1987) The Theory and Practice of Industrial Pharmacy 3rd edition. *Bombay: Varghese Publication House*.

45. Charlena, Mas'ud, Z. A., Syahreza, A., Purwadayu, A. S. (2009) Solubility Profile of Petroleum Waste in Water as Effect of Nonionic Surfactant and Stirring Rate. *Chemistry Progress*, **2(2)**, 69–78.

46. Burlatsky, S. F., Atrazhev, V. A., Dmitriev, D. V., Sultanov, V. I., Timokhina, E. N., Ugolkova, E. A., Tulyani, S., Vincitore, A. (2013) Surface tension model for surfactant solutions at the critical micelle concentration. *Journal of Colloid and Interface Science*, **393**, 151–60. https://doi.org/10.1016/j.jcis.2012.10.020.