Synthesis and application CTAC surfactant from palmityl alcohol in insecticide emulsifiable concentrate formulation

E N Yunira1, A Suryani1,2, Dadang2,3, S Tursiloadi4

1Graduates Program of Agroindustrial Technology, Department of Agro-industrial Technology, Bogor Agricultural University, Bogor, Indonesia
2Surfactant and Bioenergy Research Center (SBRC), Bogor, West Java, Indonesia
3Departement of Plant Protection, Faculty of Agriculture, Bogor Agricultural University, Bogor, Indonesia
4Research Center for Chemistry, Indonesian Institute of Sciences, South Tanggerang, Banten, Indonesia

Email: ekanurazmi@gmail.com, anisuryani.sbrcipb@gmail.com, dadangtea@ipb.ac.id, tursilo@gmail.com

Abstract. Surfactants become a very important component in pesticide product as they afford different properties and also make stable and homogeneous possible formulation. Surfactant usually produced from petroleum and can be harmful for environment. Palm oil is one of the most potentials resources that can derive to produce surfactant. This study aims to determine characteristic of CTAC surfactant and to get the best insecticide formulation prototype. CTAC surfactant produce from palmityl alcohol by two step process. Characteristics of this surfactant are density of 0.9968 g/cm3, surface tension of 27.47 dyne/cm, contact angle of 20.39 and pH of 9.16. Emulsifiable concentrate formulation contain of active ingredient and co-formulant. Surfactant DEA and CTAC are used as surfactant for EC formulation. Physical properties of formulation are surface tension 33.4-36.3 dyne/cm, density 0.8756-0.9098 g/cm3, particle size 1.23-4.48 µm and pH 6.86-7.44. The best formulation is with adding DEA surfactant about 5% and CTAC 1%.

1. Introduction
Surfactant is an oleo chemical product usually used as an additive material to decrease surface tension in suspension. Surfactant has hydrophilic and hydrophobic part to tied two different solutions that couldn’t blend [1]. The hydrophilic part usually interact strongly with polar materials (water) while the hydrophobic is present in the tail interact with nonpolar material (Oil) [2]. Materials that have a difference in polarity will be more difficult mixed homogeneously therefore required active ingredients that can bind both types of materials. The surfactant itself consists of several types based on the charge of anionic, cationic, nonionic and amphoteric surfactants. This surfactant is widely used in detergent, agrochemical, medicine and other products. Surfactants become a very important component in this product as they afford different properties and also make stable and homogeneous formulations possible [3]. One product that is in desperate need of surfactant in improving its performance is agrochemical products such as pesticides. The development of new surfactant-based system as bio activator for actives is a key factor to improve the cost effective performance increasing process efficiency, energy and raw material
savings. In pesticide formulation, surfactant can be used to improving active ingredient activity and very essential for its preparation and maintenance of long-term physical stability, and also essential for enhancing biological performance of the agrochemical, increasing the foliar uptake of herbicides, growth promoters and defoliants [4]. Mostly, active ingredient of pesticide cannot be dissolve in water, so it forms an unstable phase and low performance. Surfactant play as important material to make this active ingredient can be useful for the application of pesticide formulation. There are several types of surfactant such as anionic, cationic, nonionic and amphoteric surfactants. Among this surfactant that usually used in industry in anionic surfactant because good detergency, so it can be used in soap industry or petroleum industry. Beside this surfactant, cationic surfactant played as important surface agent that can be used only in applications in which they cannot be substituted by other surfactants, i.e. those which require a positive charge or a bactericide action. Cationic surfactants usually produce from petroleum oil. Indonesia actually has the largest palm oil plantation. This resource can be a material to produce cationic surfactant. Unfortunately, before using palm oil derivate, we need to know the best method to produce it. There are two types cationic surfactant that mostly used in industry such as CTAC and CTAB. CTAC can produce from palmityl alcohol [5].

Synthesis consist of two step process reaction, they are producing alkyl halide and amine quartenerization. In pesticides, this surfactants used as adjuvant. Surfactant mostly used about 230.000 ton every year, with concentration about 1-10% [6]. Surfactant as plasticizer, to increase mobility of agrochemical material and at temper wax layer of leaves.

Most pesticides must be formulated using suitable formulations to keep bioactivity and enhance efficacy, safety, and convenience of the active ingredients while spraying. There are so many formulation that can be used such as emulsifiable concentrate (EC), microemulsion (ME), suspension concentrate (SC), wettable powder (WP) and water dispersible granule (WG) [7,8]. Emulsifiable concentrate is the most formulation that used in pesticide especially insecticide. Emulsifiable concentrate formulation is a liquid formula consists of active ingredient and co-formulant (solvent and adjuvant) [9]. Surfactant as adjuvant will help formulation to disperse equally on leaves. Synthesis surfactant in insecticide formulation has to identify physical properties such as surface tension, pH, particle size and density. A good formulation can preformed a good emulsion. This research is aim to know molecular weight and purity of CTAC surfactant, characteristic surfactant and also formulation of pesticide.

2. Material and Methods

2.1 Material

The material were used such as cetyl alcohol 99% from Sigma-Aldrich, thionyl chloride from TCI, dichloromethane, pyridine, trimethylamine 45% from Sigma-Aldrich, diethanolamide surfactant from palm oil, xylene, emmamectin benzoate from Asia Foresight-Care Group Ltd, Shanghai, Cina, and APG surfactant. The tools were used such as magnetic stirrer, chemical erlenmeyer and glass, oven, 3 neck flasks, hotplate, molecular sieve and condenser.

2.2 Methods

2.2.1 Synthesis CTAC

CTAC synthesized from palmitic acid C16 (Cetyl alcohol) by two step process. First step was produce alkyl halide. Alkyl halide synthesized by reacted cetyl alcohol with thionyl chloride and pyridine with molar ratio of 1:3 at temperature 80°C. This reaction last for 24 hours. This process will
produce cetyl chloride. The second step was produce CTAC. CTAC synthesized by reacted cetyl chloride with trimethylamine. The ratio molar of this material was 1:3. This process last for 6 hours at temperatures 50°C. Cetyl alcohol and CTAC molecular weight will be measured with LCMS to aim CTAC formation.

2.2.2 Application surfactant in pesticide formulation

Pesticide formulation was developed by adding cationic and nonionic surfactant. The formulation called emulsifiable concentrate (EC). The process of formulation was mixing active ingredient and co-formulant. Emmamectin benzoate used as active ingredient and the co-formulant contain of xylene as solvent, surfactant nonionic (APG and DEA with molar ratio of 60:40) and cationic surfactant (CTAC). Emmamectin benzoate mixed with solvent until dissolved properly. Then, surfactant was adding and mixed with the first solution. This formulation will be form emulsion and CMC will be measurement by surface tension. Pesticide characterization will be determine by pH, surface tension and particle size.

3. Result and Discussion

3.1 Synthesized CTAC

Surfactants have the ability to reduce surface tension of a medium and reduce interfacial tension between two different phases of polarity degree such as liquid with liquid, solid with liquid, or gas with liquid [10]. Surfactant from palm oil has been developed previously, DEA surfactants is one of them which are widely used in cosmetic and soap products [11], methyl ester sulphonate (MES) and sodium dodecyl sulphate (SDS) surfactants [12] and APG surfactants [13]. Most of surfactants that can usually use in pesticide formulation such as nonionic and cationic surfactant. Nonionic surfactant is a surfactant with hydrophilic and hydrophobic properties which generated by the presence of oxygen ester groups and hydrocarbon groups. Cationic surfactants also dissociate in water into a negatively charged ion and a positively charged ion and the hydrophilic head is positively charged (cation). Due to the positive charge of the head group, cationic surfactants strongly adsorb onto negatively charged surfaces such as fabric, hair and cell membrane of bacteria.

Cationic surfactant usually used in pesticide formulation such as CTAB or CTAC. CTAC can be produce by two step process. The first step is producing alkyl halide by reacted cetyl alcohol (palmityl alcohol) with thionyl chloride and pyridine at 80°C for 24 hours [5]. Cetyl alcohol converted cetyl chloride because substitution bimolecular nucleophilic. The nucleophilic substitution is a selective chain sequence of positively charged carbon chains by the nucleophile, so the position of the leaving group will be replaced by the nucleophile. Nucleophiles are ions that have free electron pairs, so they will bind selectively to the positive charge of the substrate. SN₂ will produce an inversion configuration that takes place in one stage through the transition stage [14]. The second step is amine quartenerization. Cetyl chloride will be reacted with trimethylamine. Quartenerization of trimethylamine occurs because of SN2. Carbon ions in cetyl chloride have a positive partial charge because chloride ions are more electronegative. While nitrogen ions in trimethylamine have free electron pairs, this causes trimethylamine to attack cetyl chloride and replace the chlorine ion position [5].
### Table 1. Molecular weight changes

| Material                                | Molecular weight |
|-----------------------------------------|------------------|
| Cetyl Alcohol (Palmityl Alcohol)        | 242.44 g/mol     |
| CTAC                                    | 284.6 g/mol      |

Conversion of cetyl alcohol into cetyl trimethylammonium chloride, can be seen from increasing of molecular weight of cetyl alcohol (242.44 g/mol) in to CTAC molecular weight (284.6 g/mol (Table 1). This reaction will be producing CTAC by exchanged ion of hydroxyl ion with chloride and ammonium. From this molecular weight, it will be determined the purity of this material. Based on LC/MS measurement, purity of CTAC is about 92% (Figure 1).

![Weight Molecular Spectrum of Cationic Surfactant](image)

**Figure 1. Weight Molecular Spectrum of Cationic Surfactant**

#### 3.2 Characteristic of Surfactant

There is two types of surfactant that can be used in insecticide formulation, there are nonionic and cationic surfactant. The surfactant that were used in this formulation is diethanolamide and CTAC. DEA is actually a surfactant that synthesis from palm oil derivate. Before both of surfactant used in formulation, it is important to know physical properties of both of surfactant in water. The color of diethanolamide surfactant was yellow a little brown, and CTAC was white.

### Table 2. Surfactant properties of DEA and CTAC

| Surfactant Properties | DEA           | CTAC           |
|-----------------------|---------------|----------------|
| Density               | 0.9762 g/cm³  | 0.9968 g/cm³  |
| Surface Tension       | 27.16 dyne/cm | 27.47 dyne/cm |<br>27.16 dyne/cm | 27.47 dyne/cm |
| Contact Angel         | 18.18°        | 20.39°        |
| pH                    | 11.1          | 9.16          |
| Viscosity             | 257.35 cP     | -             | 257.35 cP       |

Table 2 show surfactant properties in water. As an agent to help active ingredient to disperse in water, surfactant DEA and CTAC can decrease surface tension of oil and water about 27.16 dyne/cm and 27.37 dyne/cm. Density of DEA based on palm oil is actually similar with DEA comersial is about 0.9762 g/cm³, and for CTAC is about 0.9968 g/cm³. Viscosity of DEA shown 257.35 cP shown there is no differences from 242.27 cP [15], pH of DEA and CTAC is also important for insecticide formulation. pH of DEA and CTAC 11.1 and 9.16 is actually in bases phase. Contact angel of the surfactant shown 18.18° and 20.39°. This shown that surfactant can decrease the angle of pesticide in leaves, and this also means that active ingredient can spread equally on the leaves.
3.3 Pesticide Formulation

3.3.1 Surface Tension

Pesticide formulation that developed in this research is emulsifiable concentrate (EC). EC formulation contains active ingredient and co-formulant. Surfactant, solvent, and any additional material that need in formulation called co-formulant. In this research formulation, emamamectin benzoate choose as active ingredient. Emmamectin is actually has low solubility in water, it is about 24 mg/L [16]. Emamectine can soluble in some solvent like xylene, dichloromethane, methanol and many other organic solvent. Because this mixed material will need another material to help it soluble in water. Surfactant can be the agent for this formulation. DEA and CTAC will help formulation to easily soluble in water. Non-ionic surfactants are surfactants whose molecules are not charged. The hydrophilic and hydrophobic properties are generated by the presence of oxygen ester groups and hydrocarbon groups. The hydrocarbon group consists of carbon–carbon and carbon–hydrogen bonds [1]. Cationic surfactants also dissociate in water into a negatively charged ion and a positively charged ion and the hydrophilic head is positively charged (cation). Cationic surfactants strongly adsorb onto negatively charged surfaces.

![Figure 2. Surface tension of surfactant DEA and Cationic in insecticide formulation](image)

Surfactant will help to decrease surface tension of the formulation. Figure 2 shown surface tension of formulation decrease from 1-5% of adding nonionic surfactant. Adding 5% nonionic surfactant show the minimum surface tension, it was about 33.40 dyne/cm, this is lower than surface tension of formulation without surfactant, based on umam 2016 research, it was about 34.69 dyne/cm. Adding surfactant will cause decrease surface tension in the solution. After reaching a certain concentration, surface tension will be constant. When surfactant is added above this concentration then the surfactant aggregates forming a micelle. The concentration of the formation of this micelle is called Critical Micelle Concentration (CMC) [10]. The critical micelle concentration (CMC) is the concentration at which self-association of surfactant monomers occurs to form micelles. This
aggregation behavior is a function of electrostatic interaction between the polar heads (hydrophilic segment of surfactant molecule) and the interaction between the hydrocarbon chains (hydrophobic segment of surfactant molecule) [17]. This CMC measurement, surfactant concentration can be determined. The highest concentration of DEA surfactant is used in this formulation about 6%. In the future measurement of insecticide formulation, DEA concentration of formulation is about 1-6% and CTAC surfactant is about 1%.

3.3.2 Density

Density is an important parameter to be analyzed because density value related to surface tension value which is one of emulsion stability factor. Density defined as the ratio of the weight of a material to the total volume of the constituent materials [18]. Density of formulations, measured with density meters. Data shown the density of formulation is in range of 0.8756-0.9098 g/cm$^3$ (Table 3). Data shown that additional of surfactant will increase the density. It means that, the molecular weight of surfactant will also increase. Measurement density will also help to determined insecticide’s trade name. Increasing density of formulation will be affected to the surface tension and contact angle, because in the point of increased surfactant weight molecular and will be affected to the emulsion that is formed. The emulsion will be demulsion if additional surfactant is too much.

| Table 3. Density of Insecticide Formulation |
|-----------------|-----------------|
| Sample          | Density (g/cm$^3$) |
| DEA 1% + CTAC 1%| 0.8956 ± 4,8E-04 |
| DEA 2% + CTAC 1%| 0.8969 ± 8,5 E-05|
| DEA 3% + CTAC 1%| 0.8987 ± 5,7E-05 |
| DEA 4% + CTAC 1%| 0.9008 ± 9,9E-05 |
| DEA 5% + CTAC 1%| 0.9031 ± 1,6E-04 |
| DEA 6% + CTAC 1%| 0.9042 ± 2,7E-04 |
| DEA 7% + CTAC 1%| 0.9055 ± 2,8E-05 |
| DEA 8% + CTAC 1%| 0.9078 ± 2,8E-05 |
| DEA 9% + CTAC 1%| 0.9072 ± 8,5E-05 |
| DEA 10% + CTAC 1%| 0.9098 ± 4,3E-05 |

3.3.3 Particle size

In the conventional formulations, the content of surfactants and co-surfactants is generally 10–20 times of emamectin benzoate weight, and the content of organic solvents and co-solvents is generally 10–30 times of emamectin benzoate weight [16]. The most effective emulsifiers are nonionic surfactants that can be used to emulsify O/W or W/O [19]. Surfactant mixtures, for example, ionic and nonionic, or mixtures of nonionic surfactants can be more effective in emulsification and stabilization of the emulsion. Surfactant will help to perform a good emulsion, and can be identified with particle size measurement. Particle size measuredin micrometers unit. The range of droplet size is about 1.23-4.48 µm (Table 4). Droplet size will be increase if surfactant is adding in the formulation. This particle size showed a micelle that formed emulsion equally in formulation. From particle size can be seen how the emulsion spread equally by coated the active ingredient and solvent (Figure 3). Solution of solvent and active ingredient formed an oil, surfactant will help it disperse in water by coated it. This
particle size will also effect to surface tension. Data shown in 5% adding DEA, can be decreased particle size to 1.8 µm.

| Table 4. Particle Size of Formulation |
|--------------------------------------|
| Sample                        | Particle size (µm) |
| DEA 1% + CTAC 1%       | 1.23 ± 0.34        |
| DEA 2% + CTAC 1%       | 1.43 ± 0.20        |
| DEA 3% + CTAC 1%       | 2.56 ± 0.69        |
| DEA 4% + CTAC 1%       | 2.99 ± 1.48        |
| DEA 5% + CTAC 1%       | 1.80 ± 0.36        |
| DEA 6% + CTAC 1%       | 4.84 ± 2.74        |

The developed formulation then tested for its emulsion in water. Figure 3 shows the dispersion of emulsion that formed between formula and water. If particle size become smaller after additional some surfactants, it means the better emulsion formed. Tests were carried out at 3-6% of surfactants concentration. Data showed that additional surfactant of 4% will form larger particle size, about 6.55 µm. Meanwhile the addition of surfactant about 6% will be formed smaller particle size about 4.38 µm. This shows the stability of the emulsion will be formed by the addition of surfactants.

Figure 3. Particle Size Distribution of Formulation in Water

3.3.4 pH Formulation

| Table 5. Value of pH Formulation in Water |
|------------------------------------------|
| Sample                        | pH              |
| DEA 1% + CTAC 1%       | 6.86 ± 0.026 |
| DEA 2% + CTAC 1%       | 6.80 ± 0.032 |
| DEA 3% + CTAC 1%       | 6.80 ± 0.014 |
| DEA 4% + CTAC 1%       | 6.82 ± 0.021 |
| DEA 5% + CTAC 1%       | 7.02 ± 0.000 |
| DEA 6% + CTAC 1%       | 7.44 ± 0.156 |

Value of pH involves a single ion quantity, the activity of the hydrogen ion, which is immeasurable by any thermodynamically valid method and requires a convention for its evaluation.
pH is a simplest method to measured acidity of formulation. Insecticide formulation has to be more bases than acid. It actually can cause rusty on the leaves. Data shown, Formulation in water have pH in range of 6.86-7.44 (Table 5). Additional of surfactant can also increasing pH value. From the data, it also shown that pH of this formulation is actually neutral. So this formulation is more save to be used in application on leaves.

4 Conclusion
CTAC synthesis from cetyl alchol by two step reaction, they are produce alkyl halide and amine quartenerization. CTAC identified by increasing molecular weight from cetyl alcohol about 242.44 to 284.6 g/mol. Characteristic of nonionic and cationic surfactant that used in insecticide formulation show can decrease surface tension and contact angle. Insecticide formulation formed from mixing active ingredient, solvent and surfactant. Characteristics of insecticide formulation are surface tension 33.4-36.3 dyne/cm, density 0.8756-0.9098 g/cm^3, particle size 1.23-4.48 µm and pH 6.86-7.44. The best formulation is with additional DEA surfactant about 5% and CTAC 1%.

5 References
[1] Karsa DR 2006 What are surfactants? In: Richard D Fan (ed) Chemistry and Technology of Surfactant (Oxford : Balckwell publishing) pg 2.
[2] Schramm LL, Marangoni DG 2000 Surfactant and their solution: Basic Principles. in Schramm LL. Surfactant: Fundamentals and Applications in the Petroleum Industry (Australia: Cambridge University Press) pp 5.
[3] Terol A, Gomez-Mingot M, Maestre SE, Prats S, Todoli JL, Paredes E 2009 Simple and rapid analytical method for the simultaneous determination of cetrimonium chloride and alkyl alcohols in hair conditioners Int. J. Cos. Sci. 32: 65-72.
[4] Castro MJL, Ojeda C, Cirelli AF 2013 Advances in surfactants for agrochemicals J Environ Chem Lett doi 10.1007/s10311-013-0432-4.
[5] Tsany FA 2017 Pengembangan Metode Sintesis Surfaktan Kationik Setil Trimetil Amonium Klorida (Bogor: Institut Pertanian Bogor) Skripsi.
[6] Edser C 2007 Multifaceted role for surfactants in agrochemicals Focus Surfact 2007(3):1-2.
[7] Qian L, Li T 2005 Review of reproductive toxicity of environmental chemical pollutants J Env and Occ Med 22(2): 167–171.
[8] Chen L, Yu X, Chen J, Ye Q, Fang H 2003 Preliminary application of new formulation of pesticides in safety production of Jiaobai Acta Agr Zhejiangensis 15(3): 177–180.
[9] Knowles DA 1998 Chemistry and Technology of Agrochemical Formulations (Netherland : Kluwer Academic Publisher).
[10] Indrawijaya B 2016 Formulasi Pestisida Nabati Minyak Mimba Menggunakan Surfaktan Dietanolamida untuk Pengendalian Hama Ulat Grayak pada Tanaman Kedelai (Bogor: Institut Pertanian Bogor) Tesis
[11] Laura 2004 Pengaruh Rasio Mol Reaktan dan Lama Reaksi dalam Pembuatan Dietanolamida sebagai Surfaktan Berbasis Minyak Inti Sawit (Bogor: Institut Pertanian Bogor) Skripsi.
[12] Septiyannii 2013 Karakterisasi Sifat Adsorspi Surfaktan Metil Ester Sulfonat (MES) dan Surfaktan Sodium Dodesil Sulfat (SDS) pada Core Sintetik (Bogor: Institut Pertanian Bogor) Skripsi.
[13] Suryani A, Dadang, Styadjit, Tjokrowardojo AS, Mochamad NNK 2009 Rekayasa proses produksi, karakterisasi dan aplikasi Alkil poliglikosa (apg) berbasis Alkohol lemak C12 (dodecanol) dan pati sagu sebagai surfaktan dalam Formulasi herbisida Prosiding seminar hasil-hasil penelitian IPB.

[14] Afrianti R. 2012. Reaksi substitusi nukleofilik menggunakan katalis [BMIM]PF₆ silika gel serta studi awal hidrolisis produk reaksi (Jakarta: Universitas Indonesia) Skripsi.

[15] Dora 2017. Penggandaan Skala Produksi Surfactan DEA Pada Reaktor 25 Liter dan Pemanfaatannya dalam Insektisida Nabati Minyak Mimba (Bogor: Institut Pertanian Bogor) Tesis.

[16] Zheng CH 2012 Development of a 1.0% emamectin benzoate microemulsion Anhui Chem Ind 38(3): 49-51.

[17] Almoazen H, Simonelli P 2008 determining the critical micelle concentration in o/w emulsion using the rate constant of hydrolysis for benzyl acetate J Dis Sci and Tech 29:958-965.

[18] Dewi HS, Rahayuningsih M, Hambali E 2017 Formulation of insecticide profenofos using surfactant diethanolamide (DEA) based on palm olein IOP Conf. Series: Earth and Env Sci 65 : doi 10.1088/1755-1315/65/1/012022.

[19] Tadros TF 2013 Emulsion Formation and Stability (Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA).