Potential and Characteristics Identification of Nanoemulsions Production from CPO using Sonication Method

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Abstract
Emulsions are colloidal dispersions of liquids/phases/droplets that do not mix with other liquids, which generally consist of an oil phase and an aqueous phase. Based on the dispersed phase particle size, stability, and appearance emulsions are divided into three categories: conventional emulsions, microemulsions, and nanoemulsions. Sonication is one of the most widely developed methods as it is proven to be more effective in producing nano-sized particles when compared to conventional methods. This research is a preliminary research to determine the best formulation for the preparation of emulsion from CPO using sonication method and to determine the characteristics of CPO emulsion as well as to develop the potential usefulness and economic value of CPO. The variations were 1, 3, 5, 7, 9% (v/v) CPO with distilled water and 5 ml of tween 80 as surfactant. The smallest particle size was obtained in the variation with the amount of CPO 1 ml, which was 188.4 nm and the PDI (Polydispersity Index) value was 0.663, indicating that the particles produced were heterogeneous. Thus, the emulsion produced had a pH between 4-5, a viscosity of about 1 cp, and had good stability during the 14 days of observation.

Keywords**:** *CPO, Emulsion, Sonication*.

Abstrak
Emulsi merupakan dispersi koloid dari cairan/fase/tetesan yang tidak bercampur dengan cairan lainnya, dimana pada umumnya terdiri dari fase minyak dan fase air. Berdasarkan ukuran partikel fase terdispersi, stabilitas, dan kenampakannya emulsi dibagi menjadi tiga kategori yaitu emulsi konvensional, mikroemulsi, dan nanoemulsi. Metode sonikasi adalah salah satu metode yang sedang banyak dikembangkan karena terbukti lebih efektif dalam menghasilkan partikel berukuran nano jika dibandingkan dengan metode konvensional. Penelitian ini merupakan penelitian pendahuluan untuk mengetahui formulasi terbaik dalam pembuatan emulsi dari CPO menggunakan metode sonikasi dan mengetahui karakteristik emulsi CPO serta mengembangkan potensi kegunaan dan nilai ekonomis CPO.

Variasi yang dilakukan yaitu CPO 1, 3, 5, 7, 9 % (v/v) dengan aquadest dan menggunakan tween 80 sebagai surfaktan sebanyak 5 ml. Ukuran partikel terkecil diperoleh pada variasi dengan jumlah CPO 1 ml yaitu 188,4 nm dan nilai Polydispersity Index (PDI) 0,663 yang menunjukkan bahwa partikel yang dihasilkan heterogen. Emulsi yang dihasilkan memiliki pH antara 4-5, viskositas sekitar 1 cp, dan memiliki stabilitas yang baik selama 14 hari pengamatan.

Keywords*: *CPO, Emulsi, Sonikasi.

1. Introduction

Emulsions are colloidal dispersions of liquids/phases/droplets that do not mix with other liquids, which generally consist of an oil phase and an aqueous phase. This oil-in-water (o/w) based emulsion acts as a delivery system necessary to facilitate the dispersion of lipophilic bioactive components and hydrophilic systems (McClements, Decker and Weiss, 2007). Based on the dispersed phase particle size, stability, and appearance emulsions are divided into three categories: conventional emulsions, microemulsions, and nanoemulsions. Based on its appearance, nanoemulsions tend to be transparent or slightly turbid in contrast to conventional emulsions that have a turbid appearance (McClements and Rao, 2011). Nanoemulsion is one of the products of nano technology that has a particle size between 10-100 nm. When compared to conventional emulsions, nano emulsions have several advantages such as high physical stability, high biovailability, and low turbidity making its more promising new alternative in various industries (Ghosh, Mukherjee and Chandrasekaran, 2013). Nanoemulsions have been used widely in industries such as pharmaceutical, healthcare, food, agriculture, and cosmetics (Walia et al., 2022).

Currently, the application of nanotechnology in the world is growing rapidly and is both a challenge and an opportunity for Indonesia to contribute to the world market as a producer. Nano technology is a technology based on materials with particle sizes around 1 per billion (10 9 m) which at this size the properties of the material can change so that nano materials can increase the effectiveness of the material. Over the past decade, nano technology has become a lot of attention for researchers. This nano technology has been widely applied in various industrial sectors such as agriculture, cosmetics, food, pharmaceuticals, textiles, environment, and so on. Some of the products resulting from the development of nano technology are nano sensors, nano emulsions, nano pesticides, nano capsules, and others.

The preparation of nanoemulsions can be divided into two categories of methods: high-energy methods: Highpressure homohenization, microfluidization, and sonication. The second is low-energy methods: spontaneous emulsification, phase inversion technique, membrane emulsification, emulsion inversion, and solvent displacement (Aswathanarayan and Vittal, 2019). Sonication is one of the most widely developed methods as it is proven to be more effective in producing nano-sized particles when compared to conventional methods. The components of a nano-emulsion are mixed by sonication methods that utilize ultrasonic waves and high vibration energy to break up the particles (Tahir et al., 2023). In common, the ultrasonic homogenizer produces high-intensity strengths by acoustic cavitation, characterized as the implosive collapse, expedient improvement, and fast development of vapor bubbles, coming about in capable shear powers and shockwave in a fluid medium and droplet destruction (Rodrigues et al., 2016). The basic principle is that sonication utilizes the phenomenon of cavitation formed when ultrasonic waves penetrate a liquid, causing the formation of bubbles in the liquid that expand and contract rapidly and explode instantly breaking particles into nanoparticles (Ampofo & Ngadi., 2022; Dheyab et al., 2020).

Nanoemulsions consist of several main components, including the water phase, oil phase, surfactants, and cosurfactants. Several oil phase formulations commonly used are daiclyglycerols (DAG), triacyglycerols (TAG), monoacylglycerols, essentian oils, mineral oils, fat substitutes, free fatty acids (FFA), weighting agents, waxes, vitamins, and lipophilic compounds (Pavoni et al., 2020). Common surfactants used are Tween-80, tween-60, and span-60 while cosurfactants include glycerin, ethylene glycol, ethanol, propanol, and so on (Aswathanarayan and Vittal, 2019). Essentially, all oils and fats have a TAG Structure containing fatty acids. One of the oils that contains fatty acids is palm oil with a saturated fatty acids close to 50% and unsaturated fatty acids of 50% composition. The composition of fatty acids is generally palmitic and staric acids which can be varied from country to another. Crude Palm Oil (CPO) is a refined production product, which is primary production that is processed and is one of the most consumed and produced oils in the world, including as a basic ingredient for cooking oil production. CPO contains more than 95% TAG, DAG, FFA, and minor components of almost 1%. Therefore, CPO has criteria that can be used as an oil phase in nanoemulsion formulation. While In 2021, Indonesia is listed as the world's largest palm oil producer with a plantation area of 14.62 hectares and is expected to produce 45.12 million tons of CPO per year (Statistics, 2021). Therefore, based on its availability and economic value, this CPO has great potential to be used in producing nanoemulsions as an oil component.

One of the derivative products of palm oil industry that has been utilized for the preparation of nanoemusions is Red Palm Oil (RPO). Nanoemulsions can be produced from RPO using the High Pressure Homogenizer (HPH) method with droplet sizes ranging from 105 - 125 nm and high stability with a shelf life of 15 weeks at 10^{o}C (Yuliasari et al., 2014). RPO is the result of refining CPO. Based on previous research, it can be used as a reference for the production of nanoemulsions using various methods. However, no research has been conducted on the formulation and characterization of CPO emulsion using sonication method. The purpose of this study is to determine the potential usefulness and economic value of CPO in the production of nanoemulsions using the sonication method and to determine the characteristics of the resulting CPO emulsion.

2. Method

This research was done in the Laboratory of Research and Basic Chemistry, Department of Chemical Engineering, Politeknik Negeri Samarinda. The raw materials used in this research was CPO, tween 80, and distilled water. Particle size and Polydispersity Index (PDI) tests of CPO emulsion was conducted at the nanoscience and nanotechnology research center of ITB.

2.1 Sample Preparation

The research preparation began by transforming the phase of the thickened CPO at room temperature by heating 60^{o}C until the phase changed to liquid

2.2 Pulp Making Process with Delignification

Mixed CPO (1 ml, 3 ml, 5 ml, 7 ml, and 9 ml) with distilled water to a volume of 100 ml and added surfactant tween 80 as much as 5% (v/v). Then homogenize with a magnetic stirrer (2000 rpm) for 25 minutes and then put in a sonicator for 10 minutes. Then the physical characterization of nanoemulsion preparation was carried out.

2.3 Particle Size Test and Polydispersity Index (PDI)

This test uses the assistance of a Particle Size Analyzer (PSA) tool with Dynamic Light Scattering type. Then as much as 10ml of sample was put in a previously cleaned cuvette. then put into the sample holder and analyzed by the instrument. The data obtained are particle size, polydispersibility index polydispersibility value which indicates the diversity of droplet size.

2.4 pH Test

Measurement of the pH value of nanoemulsion preparations was carried out using a pH meter. Before use, it was necessary to carry out a calibration or verification process using a buffer solution pH 7.01 and pH 4.01 until the device showed the pH value.

2.5 Viscosity Test

The viscosity of the nanoemulsion was measured using an Oswald viscometer. A total of 4 ml of nanoemulsion preparation was pipetted into the viscometer. Then the fluid was sucked using a bulp until it passed the upper line after which it was calculated the time required for the fluid to pass the lower limit line.

2.6 Turbidity Test

Turbidity measurements were carried out using a colorimeter tool which aims to determine the level of turbidity of the nanoemulsion preparation, The test was preceded by reading the turbidity value of the blank (distilled water) then continued with the reading of the nanoemulsion preparation.

2.7 Stability Test

The stability test was carried out by using a centrifuge. A total of 15 ml of nanoemulsion preparation was put into the tube and then the centrifuge process was carried out at a speed of 4000 rpm for 20 minutes. This test was conducted to determine the stability of nanoemulsion preparations by observing the presence of phase separation or creaming, precipitation, and turbidity after centrifugation.

3. Result and Discussion

3.1 Emulsion Size and PDI

In this study, the variation used was the concentration of CPO in water to obtain the best formulation in making emulsions with small particle sizes. The results of particle size and particle size distribution (PDI) tests of emulsion formulations from CPO can be seen in Table

1. Samples A, B, C, D, and E represent the variation of using 1, 3, 5, 7, and 9 (mL) CPO respectively.

Table 1. Particle Size and PDI Test Result

Sampel	CPO (ml)	*Z-average* (nm)	PDI
A	1	188.4	0.663
B	3	649.9	0.500
C	5	735.7	0.746
D	7	1328.5	0.560
E	9	610	0.641

Based on the results of emulsion particle measurements, the smallest particle size obtained from the variation with the amount of CPO 1 ml is 188.4 nm. Based on Table 1, increasing the volume of CPO causes an increase in the mean diameter of the droplets, but there was no significant relationship in PDI to the addition of CPO volume. This result could be related with research conducted by Manjesh (2022) who found that decreasing the concentration of essential oil and lipid-soluble extract decreased the droplet size of nanoemulsions and oil concentration had no impact on PDI. According to Jose (2022) emulsions depending on their stability and droplet size can be divided into several types: nanoemulsions, microemulsions and macroemulsions or coarse emulsions. Macroemulsions or also called conventional emulsions have a particle size > 100 nm, nanoemulsions are < 100 nm, while microemulsions are < 25 nm. However, several studies revealed emulsions of droplet size less than 500 nm can be categorized as nanoemulsions (Han et al., 2024; Zhao et al., 2022). Furthermore, Sugumar (2024) suggested that nanoemulsions have extremely small size between 20 – 200 nm. In fact, some authors have a different parametrization of nanoemulsion size, with sizes less than 100 nm, 200 nm, and 500 nm. There are several factors that affect the droplet size of the resulting emulsion, which include the type of homogenizer used, energy intensity and time, oil concentration used, type of surfactant (emulsifier) and physicochemical properties of the sample such as interfacial tension and viscosity (Lee & McClements, 2010).

Meanwhile, based on the PDI results, it shows that the resulting particle size was heterogeneous. A PDI value of less than 0.3 indicates a homogeneous particle size, otherwise if the PDI value is above 0.3 then the resulting particles are heterogeneous (Pegi et al., 2011). The heterogeneous droplet size can be caused by the insufficient sonication time resulting in inadequate distribution of wave energy throughout the media. Sonication time was proven to have an influence on droplet size, increasing sonication time could reduce the droplet size (Ghosh et al., 2013). The energy supply in the form of pressure and microfluidization was inadequate to homogenously reduce the droplet distribution and size, which resulted in larger PDI values were obtained (Ricaurte et al., 2016).

3.2 Characteristics Emulsion

Viscosity was tested to determine the viscosity of the nanoemulsion produced, the higher the viscosity value, the more difficult the emulsion flows. The results of the emulsion viscosity test are shown in Table 2.

Table 2. pH and Viscosity Test Results

Sampel	pH	Viskositas (cp)	Turbidity (FTU)
A	5.06	1.0282	45
B	5.01	1.1349	146
C	4.92	1.1494	177
D	4.83	1.1876	197
E	4.5	1.1845	251

In this study, the viscosity of the emulsion was linearly related to the particle size. Viscosity tends to increase as the amount of CPO used in making the emulsion increases. According to Tahir et al (2023), by its properties, emulsion viscosity was influenced by particle size. This viscosity indicates the thickness of the dispersed medium in the nanoemulsion system.

The results of the emulsion pH test are shown in Table 2. The pH value of the emulsion decreased. The test results of the emulsion pH value show that the higher the concentration of CPO used in the production of emulsions, the lower the pH of the emulsion produced.

The resulting turbidity shows an increase in value as the CPO used in the formulation increases. Emulsion preparations that have turbidity values close to 0 FTU (blank value) will have a visual appearance that is increasingly clear and transparent. The turbidity of the emulsion produced is due to the physical properties of the CPO it carries, which is reddish-orange in color derived from carotene compounds.

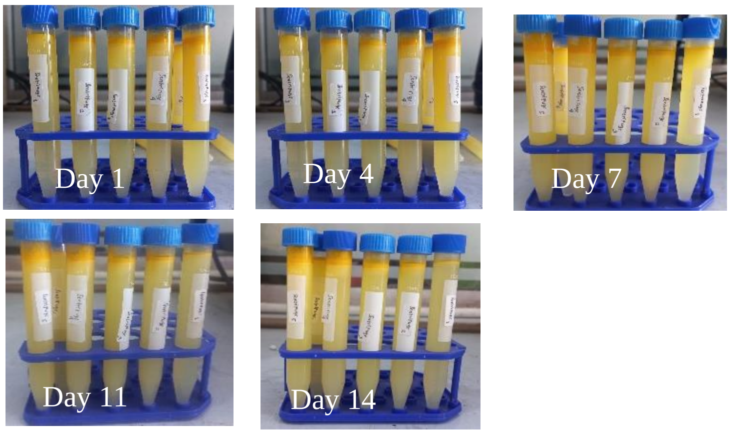

Figure 1. Stability Test for 14 Days

Furthermore, the emulsion preparation was tested for stability for 14 days as shown in Figure 1. The test results showed that the emulsion was quite stable because there was no phase separation after centrifugation and no sediment formed from day 1 to day 14. The layer that appears at the top was a characteristic carried by CPO, namely stearin. Stearin is one of the by-products produced from palm oil processing that contains fatty acids and is composed of saturated triglycerides (Aisyah and Winardi, 2023). At room temperature CPO will freeze and liquefy when heated at 65 ^{o}C, and if allowed to stand it will form two layers, namely the oil layer (olein) which is generally red and the solid layer (stearin) which is yellow (Yamin, 2021).

4. Conclusion

Based on the research conducted, the best formula for emulsion preparation with a mixture of 1 ml of CPO produced a nanoemulsion with a particle size of 188.4 nm and a PDI value of 0.663. The nanoemulsion produced had a pH between 4.5-5 and was quite stable. Based on the results obtained, CPO has the potential to be one of the materials for nanoemulsion production. Furthermore, emulsion production can be developed by increasing the stirring speed and sonication time to obtain smaller and more homogeneous particle sizes.

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