Preparation of unsaponifiable fraction from crude palm oil: a short review

To cite this article: N C Firsta et al 2020 IOP Conf. Ser.: Earth Environ. Sci. 475 012032

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Preparation of unsaponifiable fraction from crude palm oil: a short review

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Abstract. Crude Palm Oil (CPO) is one of vegetable oil obtained by extracting palm fruit mesocarp and has a red color because of the high content of beta carotene. Other bioactive ingredients in CPO include Vitamin E, squalene, and phytosterol found in the unsaponifiable fraction. To obtain multi-component bioactive, a saponification and extraction process is needed. Saponification generally uses strong bases, there are sodium hydroxide and potassium hydroxide. The use of sodium hydroxide as a base catalyst can produce vitamin E and phytosterol which is higher than potassium hydroxide. The use of potassium hydroxide as a base catalyst is able to produce higher yields, beta carotene, and squalene compared to sodium hydroxide.

1. Introduction
Palm oil is a commodity that play an important role in Indonesian economy. Based on data from Central Bureau of Statistics Indonesia, the area of palm (Elaeis sp.) plantations since 2013 has generally increased. In 2017, the area of its plantations reached 12.30 million hectares with crude palm oil production 31,487,986 tons [1]. Production of crude palm oil (CPO) is obtained from the mature part of the coconut mesocarp, before the refining process. Palm oil contains a large amount of oleic acid, mostly palmitic and linoleic acids so that the content of unsaturated fatty acids from palm oil is higher compared to coconut oil and palm kernel oil (PKO) [2]. The unique profile of fatty acids and the triacyl content of glycerol in palm oil is the reason why it is suitable for various food products [3]. The applications of CPO are generally used for cooking, frying, and as a source of vitamins. The main content in CPO such as palm olein, palm stearin, liquid fraction, and solid fraction are used in several foods and industrial products such as shortening, ice cream, cosmetics, toothpaste, and biodiesel [3].

Palm oil, which is a vegetable oil has several bioactive components of natural antioxidants such as vitamin E, phenolic compounds, and carotenoids. In addition, vegetable oil is a better source of lipids because it has lower saturated fat [4, 5]. The bioactive component found in the unsaponifiable fraction of palm oil and requires saponification and extraction to collect the bioactive components that have several benefits for human body.

Previous studies have shown that natural α-Tocotrienol vitamin E derived from CPO can enhance neuronal protection in the brain thereby minimizing neurodegenerative risk [6]. Tocols group also provides potential health benefits as a cardiovascular prevention agent [7]. In addition, unsaponifiable
fraction also contains carotenoids which can be applied as a food coloring. Part of carotenoids, (β-cryptoxanthin) has a stimulating effect on bone formation and homeostatic role in bone formation so it can prevent osteoporosis, especially in post-menopausal women [8]. To obtain multi-component bioactive, a saponification and extraction process is needed so that the unsaponifiable fraction (USF) is obtained [9]. Saponification generally uses strong bases: potassium hydroxide, and sodium hydroxide [10]. In this short paper, we will explain the effect of KOH and NaOH as alkaline catalysts on the CPO saponification process and its correlation to yields and some bioactive compounds from USF.

2. KOH and NaOH as a base catalyst for USF preparation
Multicomponent bioactive compounds found in the USF was obtained by saponification and extraction. Saponification is carried out using strong bases, generally KOH and NaOH [11]. Basic catalysts such as KOH and NaOH are used because the prices are relatively cheap and easy to handle [12]. The saponification process can occur if it uses a strong base, like KOH and NaOH. The strong base would react directly with esters and triglycerides so it would produce free fatty acids, glycerol, and soap. The use of KOH in saponification has a stronger and faster effect on fatty acids compared to the use of NaOH base catalysts [13, 14]. The research conducted by Ulfa [15] and Susantiyo [16] shows that the use of KOH and NaOH has an effect on the yield and multi-component bioactive compounds, such as beta carotene, vitamin e, squalene, and phytosterol in the USF of CPO. The following description illustrates the comparison between using KOH and NaOH in the saponification of these parameters.

2.1. Yield
The use of NaOH and KOH bases influences the yield [17]. NaOH as a base catalyst in CPO saponification had a higher yield than using KOH. The response of optimal results obtained by saponification using KOH is 5.004% [16]. While the optimal yield response obtained by saponification using NaOH is 5.84% [15]. Based on the research that has been done, different alkalis will tend to produce different results. Different results are shown by Singh et al. [12], saponification using KOH has a higher yield value than NaOH. The results of USF are influenced by several factors including the type of alkali used, the concentration of alkali, and the temperature of saponification [12, 17]. NaOH as a base catalyst produces more soap than KOH, this causes more triglycerides to participate compile using NaOH so that it will increase the yield value [18]. Alkaline concentrations that are too low cause the fat to break down optimally, while the excess of alkali used causes an excessive alkali reaction to triglycerides so that the resulting yield is not optimal [10]. Less reaction time causes less perfect saponification reaction, excessive reaction time causes excessive reaction between bases and fat, so that the amount of soap produced will be more and the amount of yield is less [11, 19]. The addition of alcohol to the saponification process also affects the results produced. Alcohol is a polar organic solvent. A large amount of alcohol will cause the process of dissolving fatty acids faster so that more triglycerides can dissolve with alcohol, which would increase yield.

2.2. β-carotene
β-carotene is a fat-soluble organic compound that gives the orange, red, and yellow colors and it is naturally found in plants in the seeds, flowers, and fruit [20]. β-carotene is a simple form of carotenoid, which has the molecular formula C_{40}H_{56} and has 11 double bonds [21]. In CPO, the main carotenoids in palm oil are composed of α-carotene and β-carotene [22]. Beta carotene would dissolve in hexane as a non-polar phase in liquid-liquid method extraction [20]. β-carotene in the USF of the saponification process with NaOH has obtained 544.74 ppm [15]. Whereas the USF of the saponification process with KOH obtained β-carotene 9706.35 ppm [16]. The content of β-carotene in saponification using KOH has higher levels than saponification using NaOH. This is also supported by research conducted by Toomey et al. [23], the use of KOH in saponification tends to produce higher carotene values in the USF compared to NaOH. KOH produced higher β-carotene values because KOH is more effective in
oxidizing fat than NaOH [24]. KOH saponification is the hydrolysis reaction of carboxylic acid esters in the alkaline condition. Fat will react with KOH especially triglycerides become glycerol and carboxylic acids and produce soap as a by-product [25]. KOH's ability to produce soft soap makes it easy for USF to be extracted. Whereas, beta carotene is part of USF [26]. Carotenoids have benefits in humans such as being able to be beneficial as pro-vitamin A to maintain eye health, improve lipid profiles in the blood, act as basal protection for the skin against UV irradiation [27]. In the body, β-carotene will be broken down by β-carotene dioxygenase in the mucosa of the small intestine into two retinyl molecules, which are then reduced to vitamin A (retinol) [21].

2.3. Vitamin E
In general, food sources with the highest concentrations of vitamin E are vegetable oils, followed by nuts and seeds [28]. In crude palm oil, vitamin E is contained in it and had concentrations in the range of 600-1000 ppm [29]. Vitamin E contained in the USF of CPO with NaOH saponification has a higher vitamin E compared to saponification using KOH. The use of NaOH bases in the saponification process is more effective when compared to KOH, which NaOH bases will produce higher levels of vitamin E. NaOH is a strong base used in the saponification process because it is exothermic when it reacts with water and dissolves in ethanol [30]. The amount of Vitamin E in USF with saponification using NaOH was obtained at 19372.30 ppm [16]. While total Vitamin E in USF with saponification using KOH had a total vitamin e of 10182.79 ppm [15]. Vitamin E contained in palm oil is tocopherol (74.4%) and tocotrienol (25.6%) [31]. Tocopherol has antioxidant properties, especially α-tocopherol, while tocotrienols have antioxidant properties 40-60 times more effective when compared to tocopherol. This is because the natural tocotrienols are related to the presence of unsaturated side chains that produce higher fusion into cells [32]. According to Loganthan et al. [28], α-tocopherols have strong vitamin E activity, whereas β, γ, and δ-tocopherol have strong activity outside the body, such as food products. While tocotrienols, especially β and γ-tocotrienols are nutrients that are effective in therapy in cases of high cholesterol. γ-tocotrienol affects the coenzyme for the 3-hydroxy-3-methyl glutamate (HMG) enzyme and suppresses enzyme production, which produces less cholesterol produced by liver cells [34].

2.4. Squalene
Chemically, squalene (C₃₀H₅₀) is unsaturated hydrocarbons with six double bonds, it had physical properties odorless and tasteless [35]. Squalene is synthesized by animals, bacteria, plants, and fungi as precursors for the synthesis of secondary metabolites such as sterols, hormones, or vitamins [36]. The largest concentration of squalene available in nature is found in the liver of certain fish species, especially sharks. However, the intensive arrested of sharks can potentially threaten the existence of this species, and many of them become endangered due to their long reproductive cycle and slow growth [37]. Therefore, squalene from vegetable sources is expected to be an alternative to fulfilled squalene's needs. In the results of USF analysis using NaOH, the level of squalene was obtained at 316,906.11 ppm [15], while the results of USF using KOH for saponification was 651.22 ppm [16]. According to Estiasih et al. [38] squalene levels in CPO range from 200 - 540 ppm. Based on the results of the above analysis, it can be seen that saponification using KOH had a higher level. There is an increase in squalene in USF compared to CPO because of the elimination of free fatty acids and triglycerides, as the main component of CPO, during saponification [38]. In the human body, squalene is synthesized by the liver and secreted in large quantities by the sebaceous glands [37]. Squalene has several physiological functions, such as increasing immune response, anti-aging activities, and anti-tumor. Squalene is widely used in medicine, food, cosmetics, and chemical engineering [39].
2.5. Phytosterol

Phytosterol is a natural compound that has a similar structure to cholesterol [40]. It is found in vegetable products, especially vegetable oils, seeds, and some fruits [41]. Phytosterol in CPO contains β-sitosterol, stigmasterol, and campesterol [38]. Beta-sitosterol is a type of phytosterol with abundant presence [42]. Phytosterol is found in vegetable fats and oils and can be extracted using nonpolar solvents such as hexane, iso-octane, and 2-propanol [43]. The USF of CPO which was saponified with KOH as a base catalyst had a higher amount of phytosterol than using NaOH. The amount of phytosterol in the USF using NaOH in the saponification process was 658,020.22 ppm [15]. Whereas the amount of phytosterol in the USF using KOH had total phytosterol 687,100 ppm [16]. According to Sampaio et al. [44] phytosterol in CPO ranges from 362 - 627 ppm. Phytosterol is widely used in food supplements that are enriched and added to commercial foods because of its efficacy [45]. Phytosterol has been scientifically proven to be able to reduce low-density lipoprotein (LDL) by competing with cholesterol in the digestive tract so that cholesterol absorption will be hampered, so it will be decreased cholesterol. Lower phytosterol in the blood can provide other benefits, such as reducing the risk of heart disease, stroke and heart attack [40].

3. Conclusions

CPO has several valuable bioactive compounds, including beta carotene, Vitamin E, squalene, and phytosterols found in USF. The USF is obtained through saponification by base catalysts, such as KOH and NaOH. KOH is capable to producing higher yields, beta carotene, and squalene than using NaOH. Meanwhile, NaOH can produce higher vitamin E and phytosterol.

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