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Effect of Neutralization Pre-treatment for the Production of Magnesium Salt from Palm Fatty Acid Distillate (PFAD)

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Abstract. Palm Fatty Acid Distillate (PFAD) was used as raw material to produce magnesium salt of palm fatty acid distillate (Mg-PFAD), which can be used as a solid lubricant, emulsifier, and antioxidant in food and nutraceutical products. PFAD is composed of approximately 85–95% wt of free fatty acids (FFA) and 10–15% wt of triglycerides as impurities. To enhance the conversion of fatty acids into Mg-PFAD salt, the synthesis of Mg-PFAD salt was carried out by neutralizing or saponifying PFAD using magnesium oxide. Several pre-treatment methods prior to neutralization were investigated, such as hydrolysis, homogenization of PFAD in water, or direct neutralization. This research aimed to determine the effect of neutralization pre-treatment on the acid number, degree of FFA conversion, and concentration of total tocopherol. The homogenization-assisted neutralization process reduces the acid number by 15 times from the initial PFAD, or 6.97 mg total tocopherol/g Mg-PFAD, and results in a conversion of 94%.

Keywords: *homogenization; Mg-PFAD salt; neutralization pre-treatment; PFAD.*

1 Introduction

Refined crude palm oil (CPO) produces a by-product known as palm fatty acid distillate (PFAD), which contains 81.7% free fatty acids (FFA), 14.4% glycerides, 0.8% squalene, 0.5% vitamin E, 0.4% sterols, and 2.2% other substances [1]. Based on these components, Vitamin E is one of the essential phytonutrients beneficial to the body and functions as an antioxidant, preventing cancer [2], lowering cholesterol, increasing immunity, and having high economic value [3]. However, vitamin E tends to combine with the other components of PFAD. Because of this, to isolate vitamin E from the different parts of PFAD, it is necessary to separate the saponified components, such as FFA and glycerides, and then isolate the unsaponifiable components, such as squalene, vitamin E, and sterols.

The main products of isolating vitamin E from PFAD are Mg-PFAD salts and antioxidant concentrates. Mg-PFAD salt is a product of the neutralization reaction of fatty acids in PFAD with base oxides such as magnesium oxide (MgO) to form magnesium salts or Mg-PFAD salts. The industry uses Mg-PFAD salt as a waterproofing, thickening, suspending, filler, anti-foaming agent [4], emulsifier, lubricant, and anticaking agent [5]. Mg-PFAD salt also possesses the same quality as magnesium stearate as a solid lubricant [6] and is used in pharmaceutical products.

A variety of approaches, such as double decomposition [7], the fusion process [8], and modified fusion [9], have accomplished the production of magnesium salts and antioxidant concentrate. For example, Lestari et al. [5], [6], and Sari et al. [10] used the modified fusion approach in several studies. This process adds a certain quantity of water to a combination of fatty acids and metal oxides; specifically, the amount of water added ranges from 0.3 to 5 moles of water per mol of MgO [9]. However, this study produced magnesium salts with high FFA levels and hard solids. One way to overcome this problem is to pre-treat neutralization by adding excess water and homogenizing PFAD and water before the neutralization stage. The addition of excess water follows the method of Rieber and Scott Patent [11], [12] to produce magnesium salts in granular form. Therefore, this study aims to determine the effect of neutralization pre-treatment on the acid number, degree of FFA conversion, and concentration of total tocopherol.

2 Materials and methods

2.1 Materials

PT Tunas Baru Lampung Tbk, Lampung, Indonesia, provided PFAD with an acid number of 198 ± 0.4 mg KOH/g and a melting point of 45 – 50oC. Magnesium oxide and ethanol solvents use technical materials, while the materials for analysis are analytical grade.

2.2 Methods

2.2.1 Homogenization and Neutralization of PFAD

This research uses the methods of the Rieber Patent [11], Scott Patent [12], and Rogers Patent [9] to produce magnesium salts of fatty acids from PFAD. First, mix the melted PFAD with water, and the molar ratio of water to PFAD used in the mixture is 40 moles per mol of PFAD [11], [12]. Then homogenize the mixture with a time of 10 minutes and a speed of 8000 rpm. The addition of excess water in the homogenization process before the neutralization stage aims to produce a smaller size of PFAD dispersion in water to increase the contact area of PFAD droplets with water and produce salt in the form of granules. The dispersed PFAD was reacted with MgO for 7 minutes to produce Mg-PFAD salt. The processes of homogenization and neutralization take place at 60°C.

Homogenization time and speed affect the stability of the dispersed salt produced. The longer and higher the homogenization speed, the smaller and more stabilized the droplet size of PFAD in water, so the contact area of PFAD with water increases, and the conversion reaction between PFAD and MgO also increases. The time variation and homogenization speed have been determined based on earlier research, which found that the optimal circumstances for homogenization occurred at rates ranging from 6000 to 15000 rpm and for durations ranging from 4 to 10 minutes [13]–[19].

2.3 Analysis

The analysis used was the acid number and total tocopherol concentration. Analysis of the acid number, or FFA, using the titration method of Bockish (1988) [20] with KOH as titrant. Procedures and experimental calculations follow the Lestari method [21]. The reaction conversion formula is Eq. (1).

$$\text{Conversion} = \frac{AV_{PFAD} - AV_{sample}}{AV_{PFAD}} \times 100\% \quad (1)$$

The analysis of the total tocopherol concentration expressed the concentration of vitamin E in the sample. The analysis was carried out following the method of Wong (1988) [22] using spectrophotometry at a wavelength of 520 nm, with the calculation using Eq. (2).

$$\text{The concentration of total tocopherol (ppm)} = \frac{A_s - A_o}{M \times m_{sample}} \quad (2)$$

3 Results and discussion

3.1 Effect of pre-neutralization on acid number and conversion

The neutralization process is the process of reacting fatty acids with magnesium oxide (MgO) to remove saponified components, such as free fatty acids, and unsaponifiable components, such as vitamin E, phytosterols, squalene, and other components contained in PFAD. Pre-neutralization reduced FFA and increased conversion. The homogenization-assisted neutralization process aims to disperse PFAD in water to increase the contact area of PFAD with water. In the neutralization stage, the dispersed PFAD will react with magnesium oxide (MgO) to produce Mg-PFAD granules. The neutralization reaction will take place well if the mixture is homogenized. **Error! Reference source not found.** describes the manufacturing process for Mg-PFAD salt.

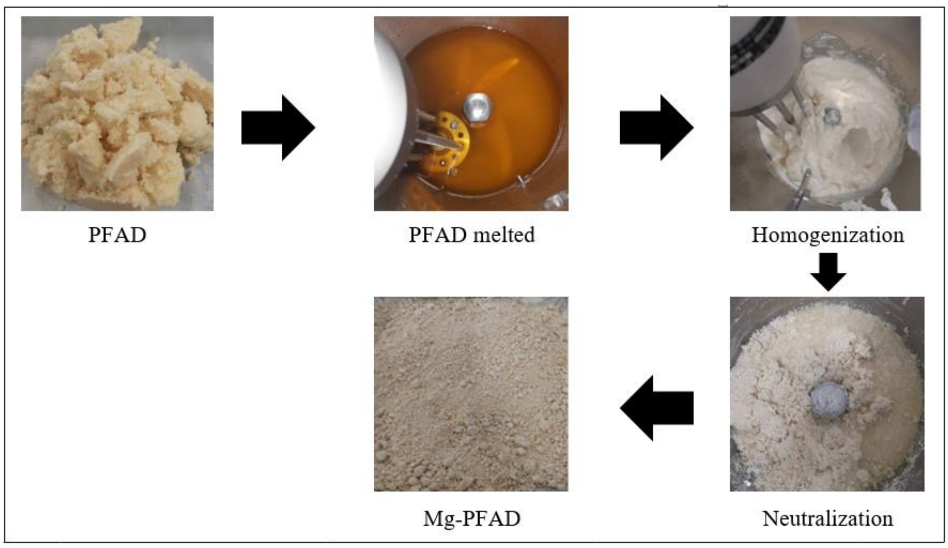

Figure 1 Production process of Mg-PFAD salt

The acid number states the KOH needed to neutralize the free fatty acids (FFA) in one gram of fat. **Error! Reference source not found.** shows the acid numbers of Mg-PFAD salt from various methods. The data show significant differences in acid numbers because the methods used differ. For example, the research results by Sari et al. [10] have the highest acid number, whereas the homogenization method has the lowest acid number. According to research by Sari et al. [10], PFAD and MgO directly reacted at the neutralization stage; meanwhile, the neutralization pre-treatment in this research occurred by adding a homogenization process. Homogenization occurs to disperse PFAD in water, thereby increasing the contact area between PFAD and water. Thus, when a neutralization reaction occurs, the contact between the fatty acids and the base oxide also increases. The outcome of the conversion proves the accuracy of these data. The conversion of the resulting Mg-PFAD salt is 94%, while the process without homogenization is 87% [10] up to 89%. Because the reaction conversion is greater when the acid number reduces, the amount of free fatty acids in the Mg-PFAD salt also gets smaller. Therefore, low FFA indicates that the quality of Mg-PFAD salts is improving.

Yuniarti produces Mg-PFAD salt using a combination of enzymatic hydrolysis and neutralization stages [23]. The neutralization process removes the saponified components (fatty acids and glycerol) by mixing HPFAD (PFAD resulting from enzymatic hydrolysis) and MgO with less water. This method resulted in a conversion rate of 92%. Compared to the process that did not involve hydrolysis and homogenization, the result has a higher conversion because the combination has already reached its maximum neutralization reaction when MgO reacts, which shows in a mixture that hardens quickly. The mixture hardens faster because the remaining water content in the HPFAD has reacted with MgO, so the remaining MgO cannot mix properly [23].

Table 1 Acid number (mg KOH/g product) of various methods

Methods	Acid Number (mg KOH/g product)		Conversion (%)
	PFAD	Mg-PFAD	
Yuniarti (2019) [23]	198 ± 0,4	15 ± 0,5	92
Sari, et al. (2021) [10]	209.87 ± 1,52	25.84 ± 0,03	87
*Using Homogenization	183.42 ± 0,39	12.17 ± 0,06	94
*Without Homogenization	183.42 ± 0,39	19.62 ± 2,15	89

*This research

Table 1 shows that the existence of neutralization pre-treatment, such as hydrolysis or homogenization, can reduce the acid number. Homogenization and neutralization pre-treatment are more effective than the combination process of hydrolysis and neutralization. The homogenization-assisted neutralization method is a simple process that is more cost-effective than enzymatic hydrolysis. It has a higher conversion rate and does not require enzymes.

Homogenization-assisted neutralization has the potential to decrease the acid number 15 times from the initial PFAD and improve reaction conversion. However, fatty acids and water are phases that do not dissolve each other, so that homogenization can affect the effectiveness of the neutralization reaction between PFAD and MgO due to collision reactions [24]. It additionally causes a reduction in the droplet size [25] so that the Mg-PFAD salt yield is high, the acid number decreases, and the unsaponifiable component at the neutralization stage will decrease [26].

Various factors can affect the level of acidity and the conversion process, including the amount and order of water added. In the studies of Yuniarti [23] and Sari et al. [10], water was added to the reactor as a catalyst after adding MgO. In contrast, before homogenization, water was added to PFAD in a 40:1 mole ratio so that the fatty acids in PFAD would mix with water, and then it was homogenized to increase dispersion and the contact area of PFAD with water. When neutralized by feeding MgO, the mixture becomes more homogeneous, which can increase the reaction conversion. In contrast to the previous research, the mixture has reached its maximum neutralization time. It indicates that the mixture solidifies rapidly due to the reaction of MgO and fatty acids.

3.2 Effect of neutralization pre-treatment on the concentration of total tocopherol

Error! Reference source not found. shows the PFAD and Mg-PFAD salt concentrations from neutralization pre-treatment. The total concentration of tocopherol in the Mg-PFAD salt of the two treatments did not change significantly. These data indicate that vitamin E was not degraded or oxidized during the process.

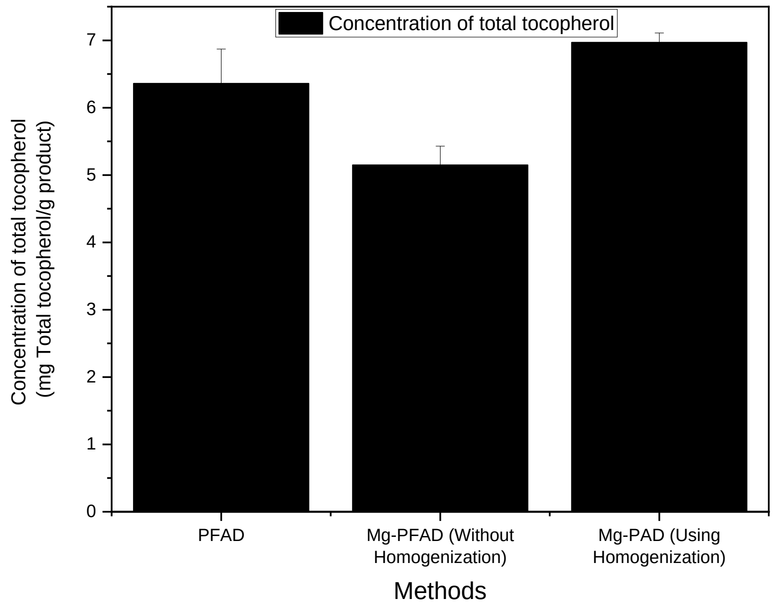

Figure 2 Concentration of total tocopherol PFAD and Mg-PFAD salt

4 Conclusion

According to the research findings, the neutralization pre-treatment, which removes unsaponifiable components such as free fatty acids, effectively lowers the acid number and increases the conversion of the neutralization to the Mg-PFAD salt. Therefore, homogenization-assisted neutralization is more effective, simple, and economical than the enzymatic hydrolysis method and direct neutralization. The Mg-PFAD salt produced from a combination of homogenization and neutralization processes can reduce the acid number by 15 times from the initial PFAD, or 12 mg KOH/g Mg-PFAD, 6.97 mg total tocopherol/g Mg-PFAD, and have a conversion of 94%.

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Nomenclature

AV	= acid value
A_s	= Absorbance of the sample solution
A_o	= Absorbance of the blank solution
FFA	= Free fatty acid
HPFAD	= Hydrolized palm fatty acid distillate
M	= Gradient
m_{sample}	= Mass of the sample
Mg-PFAD	= Magnesium – Palm Fatty Acid Distillate
MgO	= Magnesium Oxide

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