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Comparative Analysis of Calcium Sources for Enhancing Protection in Coconut Fatty Acid Distillate Ca-soap Production using FTIR

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Abstract. Coconut fatty acid distillate (CFAD) is a by-product of the coconut oil process which rich medium-chain fatty acid and can be utilized in dairy ration as a protected form. Calcium soap (Ca-soap) is a protected fat method that is affordable to apply in dairy farms. This study compared the quality of Ca-soap with different calcium sources using Fourier Transform Infrared (FTIR) Spectroscopy. There were two Ca-soap of CFAD using CaO by modified fusion method and $CaCl_2$ by double decomposition process. Comparative analysis was conducted in FTIR spectra and transmittance peaks of CFAD, CaO-CFAD, and $CaCl_2$-CFAD. The results showed transmittance peak of carboxylic acids and water functional molecules were different in CFAD compared to Ca-soap. There was no peak transmittance of O-H and H-O-H on CFAD. However, the presence peak on Ca-soap products showed water production of saponification reaction. As for carboxylic acid molecules, C=O decreased after the reaction to Ca-soap. The transmission value of C=O bond showed 47.10% and 89.34% in CFAD and CaO-CFAD respectively. However, there was no peak in $CaCl_2$-CFAD. The no peak transmittance of carboxylic acids indicated higher Ca-soap conversion. In conclusion, the Ca-soap of CaC_{l2}-CFAD was of higher quality than CaO-CFAD.

1 Introduction

Indonesia is recognized for having the largest area globally dedicated to the cultivation of coconut palms, with 17.16 million metric tons in 2021 [1]. Coconut cultivation spans some provinces in Indonesia, including Riau, East Java, Central Java, North Sulawesi, North Maluku and Central Sulawesi that had about 87 industries involved in various sectors such as coconut oil production, integrated processing, desiccated coconut, and carbon industries [2]. In refinery process become coconut cooking oil, there are some processes such as degumming, bleaching, filtrating, and deodorizing. The deodorization produces two main products: coconut cooking oil and

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Coconut Fatty Acid Distillate (CFAD). The CFAD, a by-product from coconut cooking oil production, is used as a raw material in soap manufacturing. [3].

Coconut fatty acid distillated contained rich medium-chain fatty acid. It can be utilaze as dietary fat and energy supplement to dairy cows, particularly in early lactation that required high energy. During early lactation, dairy cows often face challenges in meeting their high energy demands for milk production through dietary intake. Consequently, they mobilize body reserves, potentially resulting in a negative energy balance. [4, 5]. However, unprotected fat can adversely affect rumen fermentation, leading to decreased nutrient digestibility [6]. Protected fats are capable of bypassing rumen fermentation and subsequently function as an energy source after the absorption in the small intestine [7], resulting improving nutrient digestibility [8] and tended to enhance milk production in dairy cows [9–11]. This underscores the importance of protecting CFAD for its use in dairy cattle feed.

One method of protecting fat is through the production of calcium soap, achieved via the reaction between calcium and fatty acids [12]. Several techniques for making calcium soap are the modified fusion method using CaO and the double decomposition process using $CaCl_2$. The CFAD is oil material with rich free fatty acid in form of carboxylic acid, unlike calcium soap with no existence carboxylic acids [13]. The absence or low presence of carboxylic acids in high-quality calcium soap indicates efficient conversion of fatty acids into the soap. Fourier Transform Infrared (FTIR) spectroscopy, a method using transmission spectroscopy technique which is depend on the infrared absorption at specific wavelengths of the sample, is employed to identify chemical bonds of carboxyl acids. Carboxylic acids exhibit a strong broad O–H stretching band within 3300–2500 cm^{-1} region and stretching band of C=O is detected near 1700 cm^{-1} [14]. Therefore, objective of this study was to assess calcium soap quality using FTIR by quantifying the conversion of free fatty acids into calcium soap.

2 Materials and Methods

2.1 Samples preparation

Coconut fatty acid distillate was obtained from coconut oil refining in Indonesia. There are two calcium sources consisting of calcium oxide (CaO) and calcium chloride ($CaCl_2$). Sodium hydroxide was used for saponification reaction with $CaCl_2$.

Calcium soap production was carried out using two methods depending on calcium source, including modified fusion reaction and double decomposition process. In the first method, CFAD was reacted with CaO at 60°C (initial mixture temperature), with distilled water comprising approximately 20% of the CFAD mass. The mixture of molten CFAD and CaO was heated and stirred until it became homogeneous. The saponification reaction commenced promptly upon adding hot distilled water at 60°C and stirring for less than 10 minutes, resulting in the formation of granular soap. The soap is relatively dry due to the evaporation of water [12]. The reaction of fusion process can be expressed briefly as follows [15]

$$CaO + 2RCOOH \rightarrow \text{Calcium Soap } (Ca\,(OOCR)_2) + H_2O \quad (1)$$

In double decomposition process, NaOH and $CaCl_2$ was used by Kumar et al [16] modified method. Concentration of NaOH was conducted refers to saponification

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value of CFAD (0.192 g/mL). A mixture of CFAD and NaOH solution were heated and formed a water-soluble sodium soap. The $CaCl_2$ solution was gradually added to the water-soluble soaps with continuous stirring to facilitate the formation of calcium soaps. Subsequently, an abundance of solid $CaCl_2$ was introduced to enhance the separation of the insoluble soaps. Calcium soaps were then dried in a tray. The reaction of double decomposition process can be expressed briefly as follows [15]:

$$NaOH + RCOOH \rightarrow RCOONa + H_2O$$
$$2RCOONa + CaCl_2 \rightarrow \text{Calcium soap } (Ca(OOCR)_2) + 2NaCl \qquad (2)$$

2.2 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR of Perkin Elmer Spectrum Two was used to investigate the presence of water and carboxylic acid molecules within the samples, applying an attenuated total reflection (ATR) technique. The samples comprised CFAD raw materials (oil), calcium soap 1 (CaO-CFAD) and calcium soap 2 ($CaCl_2$-CFAD). The analysis was conducted using the Pyris infrared spectrum analyzer software. The transmission values of the samples were observed across a wavenumber range of 4000–400 cm^{-1}.

2.3 Data Analysis

This experiment was analyzed descriptively to compare calcium soap quality for two methods and CFAD as raw material. Parameters were measured including wavenumber and transmittance of carboxyl and water functional groups.

3 Results

The FTIR spectra of CFAD, CaO-CFAD, and $CaCl_2$-CFAD can be shown in Figure 1, illustrating variations in transmission values and peaks between CFAD and the calcium soaps produced by the two methods. The figure shows distinct differences in transmission values and peak characteristics among CFAD, CaO-CFAD, and $CaCl_2$-CFAD.

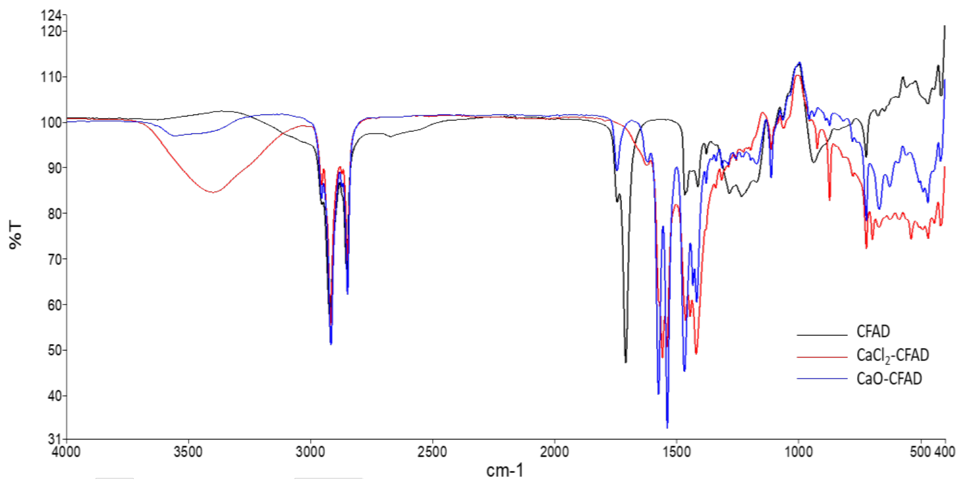

Figure 1. FTIR Spectra of CFAD, CaO-CFAD, and $CaCl_2$-CFAD

The FTIR analysis results for water and carboxylic acid functional groups wavenumbers in CFAD, CaO-CFAD, and $CaCl_2$-CFAD are showed in Table 1 and Table 2, respectively. Table 1 exhibits the absence of peak transmittance for water functional molecules (O–H and H–O–H) in CFAD, whereas peaks are observed in both calcium soap products. Regarding carboxylic acids (Table 2), the results shows a transmission value of 47.10% for the C=O bond in CFAD, 89.38% for CaO-CFAD, and no transmission peak for the C=O groups in $CaCl_2$-CFAD.

Table 1. FTIR analysis result based on water functional groups wavenumber for CFAD, CaO-CFAD, and $CaCl_2$-CFAD.

Functional Groups		Reference	CFAD	CaO-CFAD	$CaCl_2$-CFAD
O-H (stretching)	Wavenumber	3600-3200*	-	3557.49	3400.83
	Transmittance		-	97.15	84.63
H-O-H (stretching)	Wavenumber	1645*	-	1618.74	1620.37
	Transmittance		-	91.36	90.63

*Source: [17]; CFAD: Coconut Fatty Acid Distillate; CaO-CFAD: CFAD Calcium soap from Calcium Oxide; $CaCl_2$-CFAD: CFAD Calcium soap from Calcium Chloride

Table 2. FTIR analysis result based on carboxylic acids functional group wavenumber for CFAD, CaO-CFAD, and $CaCl_2$-CFAD

Functional Groups		Reference	CFAD	CaO-CFAD	$CaCl_2$-CFAD
C=O (stretching)	Wavenumber	1700*	1708.44	1744.80	-
	Transmittance		47.10	89.38	-
O-H (stretching)	Wavenumber	3300-2500*	2922.54	2956.34	2955.92
	Transmittance		57.22	83.39	86.31

*Source: [14]; CFAD: Coconut Fatty Acid Distillate; CaO-CFAD: CFAD Calcium soap from Calcium Oxide; $CaCl_2$-CFAD: CFAD Calcium soap from Calcium Chloride

4 Discussion

Coconut Fatty Acid Distillate (CFAD) can be converted as calcium soap, with saponification methods varying based on the calcium source utilized. Some methods for producing calcium soaps include the modified fusion process, where the free fatty acid reacts directly with calcium oxide (CaO) [12] and the double decomposition process, which involves the reaction of the fatty acid with sodium to form sodium soap, followed by the reaction of this intermediate with calcium chloride ($CaCl_2$) [16]. The quality of the calcium soap as protected fat can be assessed by measuring the conversion of free fatty acids to soap. The FTIR analysis was employed to identify changes in the chemical bonds of CFAD as the raw material or reactant and calcium soap as the product. Identification of organic compounds is a common application of infrared spectroscopy [14]. The different transmission value and peak between CFAD, CaO-CFAD, and $CaCl_2$-CFAD indicate there are changes the organic compounds due to the saponification process in production calcium soap of CFAD.

The primary molecules associated with calcium soap include water and free fatty acids (carboxylic acids) functional groups. During the saponification process, fatty acids are converted into soap, generating water molecules [15]. The O–H stretching bands are detected within the spectral range of 3600–3200cm^{-1}, and H–O–H bending band is observed at approximately 1645cm^{-1}[17]. The CFAD, as the raw material, contains no water, thus it shows no peaks corresponding to O–H and H–O–H in its FTIR spectrum. However, the presence of these peaks in both calcium soap products indicates the production of water during saponification [15]. This finding is supported by Handojo *et al.* [13], who reported the calcium soap products exhibit the presence of water molecules, whereas it was absent in the oil source.

The presence of free fatty acids in calcium soap products can be assessed using the acid value [18, 19] and quantified using FTIR analysis of carboxylic acid functional groups [13]. Carboxylic acids exhibit a strong broad C=O stretching band and O–H stretching band [14], which are characteristic markers for carboxylic acid groups such as free fatty acids[13] and can be characterized using FTIR [20]. The transmittance (%T) measures the percentage of light transmitted by the compound, ranging from 100% (no absorption or no transmission peak) to 0% (complete absorption) [20]. The absence of a transmission peak in $CaCl_2$-CFAD indicates a high conversion of the saponification reaction, implying that the carboxylic acids have been fully converted into soap [13]. However, the transmission value for the C=O bond in CaO-CFAD indicates that some free fatty acids remain unconverted into calcium soap.

5 Conclusion

It can be concluded that the calcium soap through the double decomposition process using $CaCl_2$ exhibited a higher conversion rate, with no presence of carboxylic acids. Therefore, it is recommended to utilize $CaCl_2$ in the production of calcium soap from CFAD.

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