Calcium Soap from Palm Fatty Acid Distillate for Ruminant Feed: Analysis of Product Quality (FTIR)

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Abstract: As a lactating dairy cattle feed supplement, calcium soap gives energy in the form of protected fat and can increase milk production in dairy cattle. This well-known supplement can be produced using the modified fusion method by reacting PFAD with a calcium source. One procedure to measure the product quality is by quantifying the reaction conversion or the amount of unreacted free fatty acids. In this research, Fourier Transform Infrared (FTIR) spectroscopy analysis was used to identify the changes in chemical bonds of reactant (PFAD) and the product (calcium soap). FTIR results showed that the transmittance of the peak absorbance of water and free fatty acids (carboxylic acids) molecules were different in reactant compared to the product. For water molecules, O-H (wavenumber 3396-3411cm^{-1}) and H-O-H (wavenumber 1616.88cm^{-1}) functional groups were found in the product, but not in reactant. As for carboxylic acids molecules, C=O (wavenumber 1698.36cm^{-1}) functional groups were found decreasing after the reaction. The transmission value for the C=O bond in the PFAD is 48%. Meanwhile, there is no transmission peak in product sample 2 (CS-2) and only 95% of transmission value for product sample 1 (CS-1). The lower transmittance of carboxylic acids functional groups was correlated with the higher calcium soap reaction conversion.

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1. Introduction

Palm Fatty Acid Distillate (PFAD) is a byproduct from the distillation of crude palm oil. As the largest producer with 58.72% of the total world palm oil [1], Indonesia exports most of its PFAD without further processing [2]. In fact, PFAD contains about 81.7% of free fatty acid [3] which can be utilized as a raw material of ruminant feed. Calcium soap is a well-known lactating dairy cattle feed supplement, yet it is not commonly used in Indonesia. Calcium soap is produced by reacting PFAD with a calcium source. Previous research concluded that the use of high-quality calcium oxide as calcium source yields better calcium soap product which has a lower acid value [4].

The utilization of PFAD to calcium soap becomes more important as Indonesia has the lowest milk consumption in Southeast Asia with 11.8 liters/capita/year [5]. This may be caused by the poor productivity of dairy cows in Indonesia (1.6 tons/cow/year) which is quite low compared to other ASEAN countries, for example, Thailand (4.6 tons/cow/year) [6]. Feeding calcium soap to the dairy cattle can solve this problem. As they need high energy diets for producing milk, calcium soap gives energy in the form of protected fat. Calcium soap passes through the rumen intact and is then broken in the abomasum into fatty acids that can be absorbed and used for milk production or as an energy source [7].

This research aims to evaluate the reaction conversion of calcium soap which produced by two different operating variables: PFAD temperature and reactants mole ratio. Reaction conversion is selected as the quantitative parameter to determine the amount of fatty acids left unreacted in the product, which is conventionally stated by the acid value. Another way to specify the reaction conversion of such product is by identifying chemical bonds of the remaining reactant in the product with Fourier transform infrared (FTIR) spectroscopy analysis. One of the most common applications of infrared spectroscopy is the identification of organic compounds, such as carboxylic acids [8]. The reactant used is rich in free fatty acids in the form of carboxylic acids, unlike its product which is in the form of soap. Aside from the changes in chemical bonds of reactant, there is also a byproduct being observed from the reaction which is water. The product was evaluated using transmission spectroscopy technique which is based upon the absorption of infrared radiation at specific wavelengths as it passes through the sample [8]. Specifically, this research focuses on the changes in chemical bonds of the reactant and product by FTIR spectroscopy analysis using transmittance value of carboxylic acids functional groups and correlate the result with calcium soap reaction conversion.

2. Materials and Methods

2.1. Preparation of Experimental Samples

This research used PFAD as the source of free fatty acids and technical grade calcium oxide as the calcium source. PFAD obtained without any further treatment from PT Tunas Baru Lampung Tbk, a CPO refining plant in Sidoarjo, Indonesia. Several calcium soap samples were prepared using a modified fusion method with two different operating variables, PFAD temperature and reactants mole ratio. The PFAD was melted to various temperatures 60-90°C, then CaO powder with a mole ratio of CaO/PFAD that ranged from 1 to 1.4 was added. Hot water was added to the mixture immediately after the homogeneous phase was achieved.

2.2. Fourier Transform Infrared (FTIR) Spectroscopy

Electromagnetic radiation that interacts with a substance can be absorbed, transmitted, reflected, scattered, or have photoluminescence (PL), which provides significant information on the molecular structure and the energy level transition of that substance [9]. Calcium soap samples which are placed in the path of an infrared beam will absorb and transmit light. The light signal will penetrate the samples to the detector which measures the radiation intensities in a sample and through a sample. Its output as a function of time is converted into a plot of absorption against wavenumber by a computer using a Fourier transform method [9]. In this experiment, the application of an ALPHA FTIR spectrometer by Bruker was used to measure infrared spectra of the functional groups in calcium soap. FTIR using an attenuated total reflection (ATR) technique was used in this experiment to investigate the water molecules and carboxylic acids molecules in the samples. This measurement only needed small samples of calcium soap. Samples were analyzed using FTIR spectrometer with the help of infrared spectrum analyzer software OPUS 7.5 by Bruker. Each sample was measured twice to ensure the infrared spectra of the investigated samples. The setup measurement parameters are a resolution of 4 cm^{-1} and absorbance as result spectrum. The observed spectra are the transmission value of the different samples versus the wavenumber ranging from 4000–400 cm^{-1}. The evaluation was conducted using peak peaking OPUS Wizard tool.

3. Results and Discussion

All samples produced with different PFAD temperatures and reactants mole ratios give similar FTIR analysis results. Therefore, only two data samples were selected to be presented. The first sample (CS-1) was prepared with a mole ratio of CaO/PFAD 1 and PFAD temperature 60°C. Meanwhile, the second sample (CS-2) was prepared with a mole ratio of CaO/PFAD 1.4 and PFAD temperature 90°C. PFAD, as the raw material, were also analyzed as a threshold of the product sample measurement.

In this research, Fourier Transform Infrared (FTIR) spectroscopy analysis was used to identify changes in the chemical bonds of reactant (PFAD) and the product (calcium soap). The molecules in this focus of discussion were water and free fatty acids (carboxylic acids) functional groups. Both functional groups are typical of reactant and product of the reaction. However, those functional groups appear differently in the reactant compared to the product. Water molecules, O-H and H-O-H functional groups, were found in the product but not in the reactant. As for carboxylic acids molecules, C=O and C-O-H were found in a smaller concentration/amount after the reaction. The lower transmittance of carboxylic acids functional groups was correlated with the higher calcium soap reaction conversion. The FTIR spectra of PFAD is depicted in Figure 1, while the FTIR spectra of CS-1 and CS-2 are depicted in Figure 2 and Figure 3 respectively.

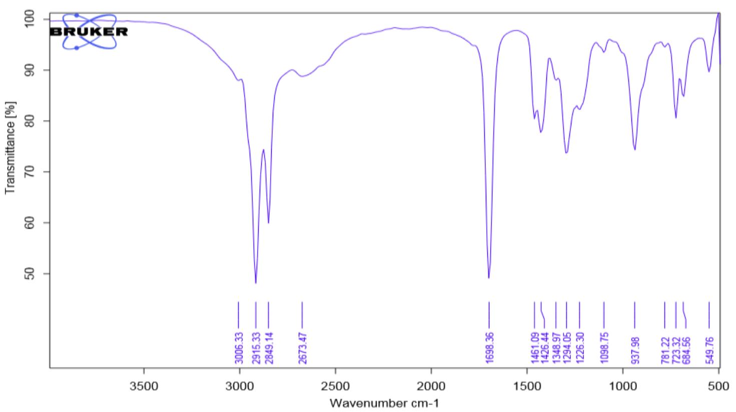

Figure 1. FTIR spectra of PFAD.

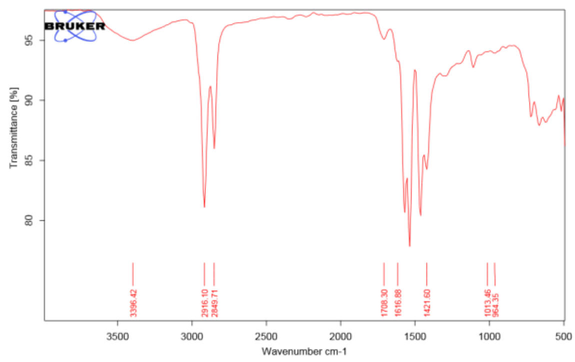

Figure 2. FTIR spectra of CS-1.

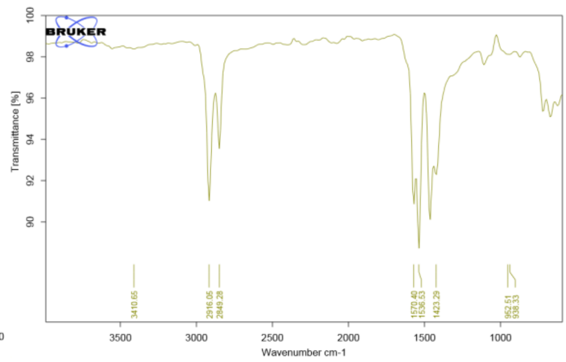

Figure 3. FTIR spectra of CS-2.

The combined FTIR spectra of PFAD, CS-1, and CS-2 is depicted in Figure 4. Table 1 and Table 2 shows FT-IR analysis results for PFAD, CS-1, and CS-2 based on carboxylic acids and water functional groups wavenumber respectively.

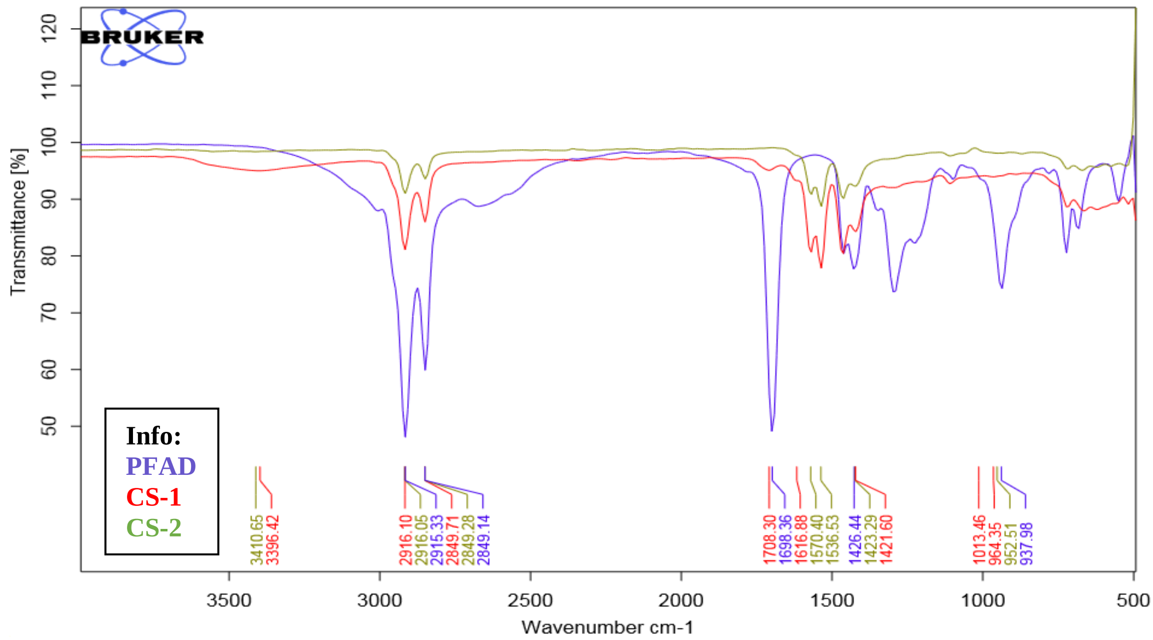

Figure 4. FTIR spectra of PFAD, CS-1, and CS-2.

Table 1. FT-IR analysis results based on carboxylic acids functional groups wavenumber for PFAD, CS-1, and CS-2.

Functional groups		Ref.	PFAD	CS-1	CS-2
O-H (stretching)	Wavenumber (cm^{-1})	3300-2500*	2915.33	2916.10	2916.05
	Transmittance (%)	-	48	81	91
C=O (stretching)	Wavenumber (cm^{-1})	1700*	1698.36	1708.30	-
	Transmittance (%)	-	48	95	-
C-O-H (in plane bending)	Wavenumber (cm^{-1})	1430*	1426.44	1421.60	1423.29
	Transmittance (%)	-	78	84	93
C-O-H (out of plane bending)	Wavenumber (cm^{-1})	930*	937.98	-	-
	Transmittance (%)	-	74	-	-

Reference: *[8]

Table 2. FT-IR analysis results based on water functional groups wavenumber for PFAD, CS-1, and CS-2.

Functional groups		Ref.	PFAD	CS-1	CS-2
O-H (stretching)	Wavenumber (cm^{-1})	3600-3200**	-	3396.42	3410.65
	Transmittance (%)	-	-	95	98
H-O-H (stretching)	Wavenumber (cm^{-1})	1650**	-	1616.88	-
	Transmittance (%)	-	-	93	-

Reference: *[10]

The results show the difference between wavenumber peaks and transmission values of water functional groups. The transmission value indicates the existence of functional groups. The differences in the characterization of the O-H water groups in the three samples indicated that PFAD has no peak transmission of O-H water functional groups, unlike the experimental calcium soap (CS-1 and CS-2), which had the O-H stretching (wavenumber: 3396-3411 cm^{-1}) and H-O-H stretching (wavenumber: 1616.88 cm^{-1}) transmission peak. The different result of the three samples corresponds to the extent of saponification reaction by modified fusion method itself which produced water during the reaction.

The C=O functional groups (wavenumber 1698.36 cm^{-1}) is typical evidence of carboxylic acids groups such as free fatty acids in PFAD. The transmission value for the C=O bond in the PFAD is 48%, while there is no transmission peak of the C=O groups in the CS-2 sample. In a high conversion of saponification reaction, the functional groups are already part of the soap compound and not in the form of carboxylic acids, the transmission peak of the C=O groups (wavenumber 1708.30 cm^{-1}) found in the CS-1 sample with 95% transmission value. These results for CS-1 indicate that not all free fatty acids are converted into calcium soap.

4. Conclusions

The best operating condition for producing calcium soap is required to achieve the highest reaction conversion. So far, this successful goal can be proven by the nonexistence of carboxylic acids groups in the product using FTIR spectrometer. Thus, it can be concluded that the CS-2 sample was made with better conditions of operation than the CS-1 sample. CS-2 was prepared with a mole ratio of CaO/PFAD 1.4 and PFAD temperature 90°C, while CS-1 was prepared with a mole ratio of CaO/PFAD 1 and PFAD temperature 60°C. Further research is necessary to find the most suitable method to quantify the reaction conversion of calcium soap production.

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