Calcium soap from Palm Fatty Acid Distillate (PFAD) for ruminant feed: The effect of CaO quality on reaction temperature

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Abstract. Indonesia is the largest palm oil producer in the world and contributes to about 58% of the world’s total palm oil production in 2018. Palm fatty acid distillate (PFAD) is a palm oil refining by-product that contains lots of free fatty acids. Previous research related to the production of calcium soap has successfully found the right stoichiometry and operating conditions at the laboratory and bench scale. This research examines the influence of CaO active concentration on the reaction temperature of calcium soap production on the pilot scale. First, molten PFAD, CaO solids, and water are feed into a CSTR. The mixture is discharged from the CSTR to the screw reactor at a certain temperature, which is then released to the belt conveyor. The experimental result shows that the rate of temperature increment of the mixture using CaO with an active concentration of 79% is greater than CaO of 72%. This may be caused by the different amounts of heat released during the reaction, viscous mixture properties which then influence the mass transfer process between the reaction components. The result also shows that there is a 14% - 19% difference between the calculated and measured temperature, which is predicted due to heat loss, particularly caused by water evaporation during the reaction.

1. Introduction
Indonesia is the world’s largest producer of palm oil with the amount of 43 million tons, which is equivalent to 58% of the total world’s palm oil production in 2018 [1]. Besides palm oil, crude palm oil (CPO) refining process also produces a by-product called palm fatty acid distillate (PFAD) [2]. PFAD can be used as raw material for oleochemical and bioactive industries such as vitamin E, phytosterols, and squalene. In other countries, PFAD can be processed into animal feed supplements that can increase energy supply [3].

The calcium soap, as a form of protected fat used for ruminant feed supplement, is preferable than the free fatty acid. Unlike directly feeding free fatty acid to a ruminant, the protected fat does not interfere with fermentation in cow’s rumen [4]. Protected fat has a high energy concentration which gives benefits to dairy cows, for instance, an increased milk production [5] as well as pregnancy rate [6].
Research related to the production of calcium soap by saponifying PFAD with various CaO active levels has been done on a laboratory scale. It was found that the reaction with a lower concentration of active calcium of CaO resulted in products with a higher acid value, which indicates a lower reaction conversion [7]. Saponification is known as a spontaneous and exothermic reaction that produces heat during the reaction [7]. Meanwhile, there is also heat produced by the presence of calcium oxide and water as the result of dissolved calcium in the water. The heat involved in this reaction can be seen in the increase of the mixture temperature [8].

This study aims to determine the effect of CaO active concentration on the mixture temperature in the production of calcium soap through the saponification reaction in a pilot scale. The CaO active concentrations that are used in the experiment are 79% and 72%. The calcium soap product will be analyzed its acid number as it can indicate the amount of free fatty acid that is converted to product. The favorable calcium soap for ruminant feed is the one that has a low acid number.

The hypothesis of this research is that the saponification reaction with a higher active concentration of CaO will result in a higher rate of temperature increment of the mixture where the reaction occurs. This is because the reaction emits more heat due to the higher CaO concentration which reacts with PFAD.

2. Material and Methods

2.1. Materials
The PFAD used in this study was obtained from the crude palm oil refining plant in PT Tunas Baru Lampung Tbk. The calcium oxide came from the limestone calcination process in Padalarang. Water was also used in the reaction to accelerate the saponification rate.

2.2. Experimental set-up
The equipment used in this experiment includes a CSTR, a screw reactor, and a belt conveyor shown in Figure 1.

![Figure 1. Equipment set-up for making calcium soap](image)

First, the size of the calcium oxide chunks is reduced using a disc mill; then it is sieved on several layers to get 100 mesh CaO powder. As for the calcium soap making, PFAD is melted in the CSTR at a certain temperature. CaO is reacted with the molten PFAD with a certain stoichiometric ratio [6]. Water is then added to the homogeneous mixture. After a certain reaction temperature is reached, the mixture is released from the CSTR to the screw reactor and led to the belt conveyor.

The products are tested for the acid number using ISO 6060:2009 and evaluated to estimate the fatty acid conversion. The sample of calcium soaps (1 g) is dissolved in ethanol, heated to 60°C, and stirred for approximately 10 minutes. Phenolphthalein is added as the indicator to the mixture and then titrated by 0.01 N potassium hydroxide (KOH). The acid number is calculated as the number of KOH in milligrams required to neutralize the free fatty acids in 1 g of the sample. The CaO active
concentration is determined by using ASTM 1984 from The Schumacher Centre for Technology & Development, UK. The sample of CaO (2.5 g) is added by free-carbon-dioxide water (35 - 45 mL) and sugar solution of 50% concentration. The mixture is then stirred for around 30 minutes. Water is added to the mixture until the mixture reaches 250 mL volume in the Erlenmeyer glass. The mixture is filtrated subsequently. The first 15 – 30 mL filtrate is separated from the glass. 25 mL filtrate is titrated by 0,357 N sulphuric acid (H$_2$SO$_4$) with phenolphthalein as the indicator.

2.3. Variations
There are 2 procedures done in the experiments, making calcium soap with CaO A, which contains 79% active CaO, and CaO B, which contains 72% active CaO. The difference between the procedures lies in the variation of the CSTR discharge temperature. The mixture in CSTR using CaO grade A was released from CSTR to screw reactor at various temperatures, i.e. 84°C, 86°C, and 90°C. On the other hand, the mixture in CSTR using CaO grade B was released at temperature 72°C, 76°C, 80°C, and 86°C. This range was chosen because the saponification reaction temperature to form calcium soap starts around 78°C. From the experiments, it is observed that the 72% active CaO content produced the viscous reaction mixture. As a result, the mixture should be released at a lower temperature from the CSTR, since the reaction mixture will become more viscous at higher temperatures, so that it cannot be discharged from the CSTR into the screw reactor properly. Another variation in experiments was the use or omission of the screw reactor. The list of experiments is shown in Table 1.

| Run | CaO Level (%) | Use of Screw Reactor | T$_{outlet}$ CSTR (°C) |
|-----|---------------|----------------------|------------------------|
| 1   | 72            | No                   | 80                     |
| 2   | 72            | No                   | 76                     |
| 3   | 72            | No                   | 78                     |
| 4   | 72            | Yes                  | 72                     |
| 5   | 79            | No                   | 86                     |
| 6   | 79            | No                   | 90                     |
| 7   | 79            | No                   | 84                     |
| 8   | 79            | Yes                  | 90                     |
| 9   | 72            | Yes                  | 84                     |
| 10  | 72            | Yes                  | 78                     |
| 11  | 72            | No                   | 72                     |
| 12  | 72            | No                   | 86                     |

3. Results and Discussion
The temperature profile in the CSTR versus reaction time was recorded for each experiment, shown in Figure 2.

The reactions during the process can be divided into 2 steps, i.e. the reaction between CaO and water, and the saponification of fatty acid with hydroxide of calcium, as can be seen in Equations 1 and 2.

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$$  \hspace{1cm} (1)

$$2\text{C}_{16}\text{H}_{32}\text{O}_2 + \text{Ca(OH)}_2 \rightarrow \text{C}_{32}\text{H}_{62}\text{CaO}_4 + 2\text{H}_2\text{O}$$  \hspace{1cm} (2)

As the saponification reaction occurs at the temperature about 78°C, the temperature profile can be divided into two zones. The first zone is the temperature below 78°C, where the temperature gradient results from the heat produced by reaction 1. The second zone is above 78°C, where the temperature
gradient results from the combination of heat released by reaction 1 and reaction 2. In this work, only the temperature gradient in zone 1 is discussed.

Based on the calculation results, the enthalpy reaction between CaO and water forming Ca(OH)$_2$ at 78°C is -67.44 kJ/mol while the enthalpy reaction between Ca(OH)$_2$ and PFAD forming calcium soap and water at 78°C is -660.47 kJ/mol. This causes the saponification reaction to produce greater heat, thus the rise in the mixture temperature becomes faster after 78°C. The temperature gradient is only investigated from the experiments whose mixture temperature exceeded 78°C. Those, which did not reach 78°C show very different physical properties. The mixture became so viscous that the reaction could not take place further. From the observation during the experiments, the reaction between CaO and water took place immediately after the water was poured into the mixture, at which the initial temperature was set to 63°C for CaO A and 67°C for CaO B. Hence, the rise of mixture temperature from initial temperature to 78°C was solely caused by the heat released from the reaction of CaO and water. The temperature increase after 78°C is assumed to result from the heat released by a combination of the CaO-water reaction as well as the saponification reaction of PFAD and Ca(OH)$_2$.

Figure 2 shows that differences in the active CaO concentration affect the rate of temperature increase, as the temperature raise with CaO A is faster than with CaO B. The heat released by the reaction can be calculated using Equation 3.

\[ Q = n \cdot \Delta H \]  

(3)

With \( Q \) = reaction heat (kJ), \( n \) = reaction mole (mol), and \( \Delta H \) = reaction enthalpy (kJ/mol). It is assumed that all of the CaO active concentration perfectly reacts with water. For CaO A, the initial active mole of CaO is 5.5 mole, while CaO B is 5 mole. The reaction heat is used to calculate the rate of temperature increment using the transient heat transfer equation shown in Equation 4.

\[ Q = m \times C_p \times \Delta T \]  

(4)

The calculated temperature was then compared with the measurement to determine the effect of CaO levels on the mole that reacts. The temperature calculation of the experiments using CaO B is
based on run 1, 3, 10, and 12 of the experiments, where the temperature exceeded 78°C. The differences between the calculated and measured temperatures from run 1 and 3 are shown in Figure 3.

![Figure 3](image1.png)

**Figure 3.** Comparison between the calculated temperature and the experimental temperature (1) run 1; (2) run 3

The rate of moles that reacted and % temperature differences for the whole experiments are shown in Table 2 below.

**Table 2.** The rate of reaction and percentage of temperature differences

| Run | CaO Level | Rate of temperature rise (°C/sec) | Mole rate of reaction (mole/sec) | Difference (%) |
|-----|-----------|-----------------------------------|----------------------------------|----------------|
| 1   | 72%       | 0.03                              | 0.013                            | 13.4           |
| 3   | 72%       | 0.02                              | 0.010                            | 19.3           |
| 10  | 72%       | 0.02                              | 0.011                            | 14.3           |
| 12  | 72%       | 0.03                              | 0.014                            | 17.3           |
| 5   | 79%       | 0.16                              | 0.059                            | 19.1           |
| 6   | 79%       | 0.11                              | 0.042                            | 16.9           |
| 7   | 79%       | 0.12                              | 0.044                            | 17.6           |
| 8   | 79%       | 0.09                              | 0.034                            | 18.6           |
| 9   | 79%       | 0.07                              | 0.028                            | 17.1           |

From Table 2, the differences between the calculated temperature with the measured temperature are around 14% - 19%. It can be caused due to heat loss from the system, particularly due to water evaporation during the reaction. There is heat loss to the surroundings as well, as the water in the jacket of CSTR at the beginning of the operation was 63°C or 67°C. A higher mixture temperature also caused the heat loss rate to be larger.

From the Table, it can be seen that the rate of temperature increment using CaO A is greater than with CaO B. This is due to the lower CaO active concentration in CaO B compared to CaO A, so that less heat was released from the reaction. On the other hand, the reaction mixture using CaO B was much more viscous than using CaO A. The high viscosity of mixture affected the mass transfer rate, so that the contact between the reactants was slower or more difficult compared to the system using CaO A.

From Figure 2, it can be seen that the time needed to reach mixture temperature of 78°C using CaO A was between 2.5 – 5 minutes. Meanwhile, the runs using CaO B took between 7 – 9 minutes to
reach that temperature. From this experiment, it can be concluded that the temperature of the mixture of PFAD with CaO A raised faster than with CaO B.

The parameter that determines the quality of calcium soap produced is the acid number. In this experiment, the acid numbers obtained are between 0.4 to 5.8. This result shows that there is a certain amount of free fatty acids from PFAD that did not react with CaO, particularly in the system with CaO B, where the active CaO concentration is lower than in CaO A. During the saponification reaction, water was produced and a fraction of it vaporized due to the mixture temperature that increased with time. The amount of water vaporized affected the extent of the reaction or the degree of conversion of PFAD. This is consistent with the Le Chatelier’s Principle [10], where the reaction will shift toward the product as more water vaporizes.

4. Conclusion
The experimental result shows that the higher concentration of active CaO will produce a higher rate of temperature increment of the mixture. This could be due to differences of amount of heat released by reaction, viscous mixture properties, and mass transfer between the reaction components.

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