MATEC Web of Conferences **268**, 03001 (2019) https://doi.org/10.1051/matecconf/201926803001
*RSCE 2018*

# Calcium soap from palm fatty acid distillate for ruminant feed: Calcium oxide particles size

*Lienda* Handojo[1,*], *Antonius* Indarto[1], *Dian* Shofinita[1], *Muhammad* Saadi[1], *Dea* Yulistia[1] and *Fathinah* Hasyyati[1]

[1]Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung, 40132, Indonesia

**Abstract.** High production of crude palm oil has led Indonesia to become one of the countries that have a large number of palm fatty acid distillate (PFAD) in the world. As a source of fatty acid, PFAD has wide range of uses, including as a fat supplement in the ruminant feed when reacted with a calcium source such as calcium oxide (CaO). At the working temperature above PFAD's melting point, those reactants form a homogeneous phase with the help of intensive stirring. By the presence of a small amount of water, the mixture will be saponified and become the calcium soap. This research studied how different particles sizes of CaO could influence the reaction conversions based on the acid value of the product. The CaO solid particles were sieved and separated into the different fraction of sizes (<177 μm, 177-320 μm, and 320-640 μm). Smaller particle resulted in a lower acid value which indicates a high conversion of free fatty acid and lower moisture content which is preferable for the product.

## 1 Introduction

A large number of palm fatty acid distillate (PFAD) is produced in Indonesia as a result of the massive production of crude palm oil (CPO). Based on Indonesia Palm Oil Producers Association, in 2016 Indonesia produces 32.5 million tons of palm oil, or equal to 54% of the world's total palm oil production [**1**]. Even now, in 2018 the quantities increase to 40.5 million tons [**2**]. For edible purposes, CPO is refined to eliminate unwanted components, including free fatty acid (FFA), colored, and odorous compounds [**3**]. PFAD has a relatively high FFA concentration, vary by 65-95% depends on the refining process [**4**]. Therefore, PFAD has been used in some developed countries as the raw materials of oleochemical, biofuel, laundry soap, and feed industries [**5**].

Saponification reaction between the FFA in PFAD and metals oxide such as calcium oxide (CaO) produce calcium soap, which can be used as ruminant feed. This feed acts as rumen bypass fat supplement [**6**] and has a high energy concentration known to give benefits to dairy cows, for instance, increase milk production [**7**] and increase pregnancy rate [**8**]. The calcium in the feed also help the cows to maintain calcium balance during lactation period [**9**].

The soap making process was studied physically and chemically to get the desired product. Product preferably doesn't have any free fatty acid or calcium left, because such unreacted mixture is unstable when coming in contact with water [**10**]. Unreacted FFA can also cause the product's shelf life to be shorter. One of the factors that affect the reaction is how well the calcium oxide get in contact with PFAD, which is related to the mixing process and the particle size of CaO powder. This study evaluated the effect of different particle sizes of CaO to the acid value of the product that reflects the reaction conversion.

## 2 Material and methods

### 2.1 Materials and reagents

PFAD in this study obtained from two different crude palm oil refining plant in Java. The calcium oxide comes from the limestone calcination process in Padalarang. Water was also used in the reaction to accelerate the saponification rate.

### 2.2 Experimental set-up

First, the size of calcium oxide was reduced by using a ball mill, then sieved to fractions to get different particle sizes of CaO powder. As for the soap making, CaO was reacted with the molten PFAD in a certain stoichiometric ratio. After the mixture was well stirred, water was added immediately and the mixing was kept going until the reaction is complete [**11**]. The particle size of CaO powder was the independent variable, whereas the other reaction parameters such as the amount of CaO, the working temperature, and the number of water added to the mixture remained as the controlled variables.

The water content of the PFAD is measured according to the official AOCS Aa 3-38 method [**12**]. The acid value of the samples measured using ISO 660:2009 and calculated as the number of KOH in milligrams required

* Corresponding author: lienda@che.itb.ac.id

to neutralize the free fatty acids in 1 g of sample. The percentage of acid value difference between PFAD and calcium soap is calculated to get the percentage of reacted free fatty acids.

For the analysis of fatty acid composition in PFAD, the sample is prepared before analyzed using gas chromatography. First, the esterification process of fatty acids into fatty acid methyl esters (FAME) is carried out according to the method in the Compendium of Food Additive Specifications [**13**]. Then FAME is injected into a set of gas chromatography mass spectrometer (GCMS) QP2010 with Direct Sample Injection (DI) from Shimadzu. The type of column used is the Rtx-5MS capillary column from Restek. The relative percentage of fatty acids in the portion of fatty acids in the sample is determined by the normalization technique.

## 3 Results and discussion

### 3.1 PFAD characterization

There are two PFAD sources used in this study. PFAD is semisolid in golden yellow color at room temperature and melts into a gold liquid when heated. PFAD was characterized by physicochemical properties such as water content and the amount of FFA. The results of the analysis on the two PFADs are shown in **Table 1**.

**Table 1**. Physicochemical properties of PFAD

| Property | PFAD-1 | PFAD-2 |
|---|---|---|
| Water content (%) | 0.54 | 0.56 |
| FFA (%) | 87.99 | 90.96 |

The water content in PFAD-1 and PFAD-2 is 0.54% and 0.56% respectively. These values are in accordance with the Palm Oil Research Institute of Malaysia (PORIM) standard for PFAD with a maximum of 1% [**13**]. The number of FFA in PFAD-1 is 87.99% and PFAD-2 is 90.96%. This value is in accordance with the PORIM standard for PFAD with the content of FFA as palmitic acid must be at least 70% [**14**]. The amount of FFA in PFAD is an important parameter because it shows how much free fatty acid can be reacted with calcium oxide in the production of calcium soap.

The results of calculations on both PFAD are shown in **Table 2**. Palmitic acid (C16:0) dominates fatty acids in both PFAD, with the value around 45%, followed by oleic acid (C18:1 n9) with the value around 36%. The fatty acid composition in PFAD shows the possibility of its use in the industry, especially in producing calcium soap. Some studies shows that the saturated fat with a higher C16 to C18 ratio is more digestible by cows [**5**] and fatty acid from natural sources are preferable for the raw material of calcium soap [**15**].

**Table 2**. Fatty acids composition in PFAD

| Fatty Acid | PFAD-1 (%) | PFAD-2 (%) |
|---|---|---|
| Lauric, C12:0 | 0.17 | 0.17 |
| Myristic, C14:0 | 1.72 | 1.46 |
| Palmitic, C16:0 | 45.58 | 45.16 |
| Palmitoleic, C16:1 n9 | 0.20 | 0.15 |
| Stearic, C18:0 | 5.44 | 6.28 |
| Oleic, C18:1 n9 | 36.01 | 35.99 |
| Oleic, C18:1 n11 | n/a | 1.83 |
| Linoleic, C18:2 n9,12 | 10.47 | 10.27 |
| Arachidic, C20:0 | 0.40 | 0.51 |

### 3.2 Product's acid value

Calcium oxide powder was sieved into several sizes and used as the reactants with the same stoichiometric ratio. All various CaO sizes resulting in similar results with a slight difference in the acid value, so only two data of particle size are showed. **Fig. 1** represents the acid value of calcium soap using CaO with the particle size of <177 μm, 177-320 μm, and 320-640 μm by using two different PFADs.

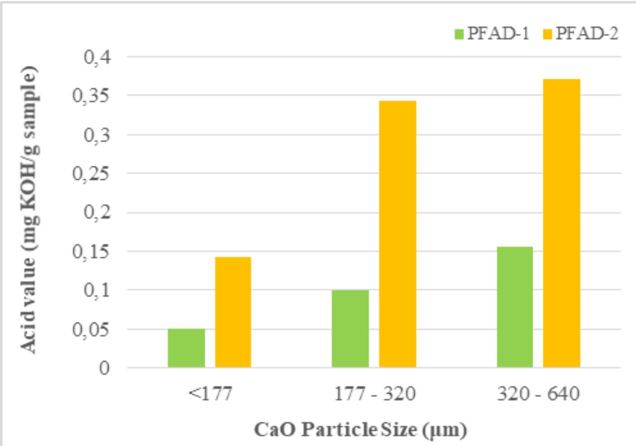


**Figure 1**. The effect of CaO particles size to product's acid value.

At the same size of CaO particles, calcium soaps from PFAD-1 has lower acid value compared to the one using PFAD-2 because %FFA in PFAD-1 is lower than PFAD-2. All variation of CaO particle sizes in both PFAD produced low acid value in the products (<1.0 mg KOH/g sample) which indicate a good FFA conversion of more than 99%. Based on the data, the smaller the size of CaO, the lower the acid value of calcium soap, which means more FFA is reacted.

In the reaction between solid particles and liquid, the dispersion of solid is the important thing in mass transfer between solid and liquid, especially in agitated vessel system which is used in this experiment. The effective mass transfer relies on physical processes such as mixing which affect the intensity of turbulence in the system [**16**]. The molten PFAD and solid particles of CaO basically form a solid-liquid suspension. The reaction is held in intensive mixing to keep the presence of turbulences in the system and suspend the solids, so there are no particles rested on the tank bottom. The turbulent liquid motion will drive the particles so the space between the particles is filled with the suspended fluid [**16**], to form a homogenous suspension.

Generally, the diffusional mass transfer (M) is expressed using **Eq. 1** as followed:

$$M = k_{SL} a_p (C_S - C_L) \tag{1}$$

where $k_{SL}$ is the solid-liquid mass transfer coefficient, $a_p$ is the interfacial area for mass transfer per unit volume of suspension, $C_S$ is the solid concentration on the solid surface and $C_L$ is the solid concentration in the liquid's bulk. Therefore ($C_S$ – $C_L$) is the solid concentration driving force. While $a_p$ is defined as **Eq. 2** as followed:

$$a_p = \frac{6\alpha}{d_s} \tag{2}$$

where α is the void fraction or volumetric fraction of solid in liquid's volume and $d_s$ is the diameter of a solid particle. Based on those equations, solid particles size affect the diffusional mass transfer which affects the reaction. The rate of diffusion also increases as the flow becomes more turbulent [**17**].

### 3.3 Mixture temperature over time

Saponification is known as a spontaneous and exothermic reaction that produces heat during the reaction [**18**]. Meanwhile, there is also heat produced by the presence of calcium oxide and water as the result of dissolved calcium in the water [**19**]. The heat involved in this reaction can be seen in the increase of mixture temperature. Parameters related to the reaction (moisture content, peak temperature, and the time to reach the peak temperature) by using PFAD-2 are shown in **Table 3**.

**Table 3**. Peak temperature and moisture content of calcium soap

| Parameter | CaO Particle Size (µm) | | |
|---|---|---|---|
| | <177 | 177 - 320 | 320 - 640 |
| Peak temperature (°C) | 93 | 93 | 90 |
| Time to reach peak temperature (s) | 344 | 424 | 548 |
| Moisture content (%) | 8.50 | 10.50 | 11.00 |

The temperature profile of mixtures over the time is shown in **Fig. 2**. Both PFADs are resulting in similar results in temperature profile, so there is only one profile (using PFAD-2) presented here.

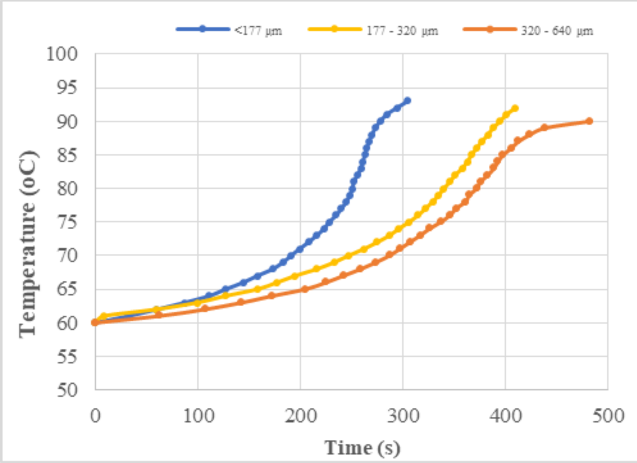


**Figure 2**. The mixture's temperature over the time using PFAD-2.

Reaction time is calculated since the water added to the mixture (t = 0 s), until they reach the peak temperature. The mixture of PFAD and CaO is kept in a constant temperature before the addition of water. After adding the water, there is a slight decrease of temperature in the mixture, then the temperature slowly increase during the reaction. The increased temperature considered as the result of the heat released by the reaction.

The data shows that the finer size of CaO resulted in a higher peak temperature and shorter time of reaction. Although the FFA conversion is relatively the same (>99%), the time to reach peak temperature is different. The time needed to reach the peak temperature can reflects the reaction rate, which means that the larger the surface area of CaO particles the slower the reaction rate will be. This is related to the likelihood of collision between the reactants, the small particle increase the number of collisions per second thus increases the reaction rate.

The high temperature of reaction also related to the average value of calcium soap's moisture content. The released heat during the reaction causes the water to evaporate from the mixture. The smaller the particle size of CaO, more heat released in a shorter time, therefore the moisture content is lower.

## 4 Conclusion

This study shows that the particles size of CaO in an adequate mixing process affect several parameters related to the reaction. Finer CaO particles size is preferable because it gives higher FFA conversion, shorter time to complete the reaction, and lower moisture content. Further study related to the physical process of making calcium soap is required to achieve an efficient process and good results in the product.

Sincere gratitude is extended to BPDPKS Indonesia for providing the research grant and supporting this study.

## References

1. Handojo, L.A., Indarto, A., Shofinita, D., Meitha, A., Nabila, R., Triharyogi, H., Hakim, M.G.A. and Saadi, M.R. Calcium soap from palm fatty acid distillate for ruminant feed: $Ca(OH)_2$ as calcium source, MATEC Web of Conferences, 2018, 159, 02062.
2. Available online at www.indexmundi.com/agriculture/?country=id&commodity=palm-oil&graph=production
3. Verhe, R., Verleyen, T., Huyghebaert, A., Dewettinck, K., De Greyt, W. Tocopherol oxidation during deodorization, Proc. of the New Trends in Edible Oil Refining, January, Gent, Belgium, 2000.
4. Chang, A.S., Sherazi, S.T.H., Kandhro, A.A., Mahesar, S.A., Chang, F., Shah, S.N., Laghari, A.S. and Pahnwar, T. Characterization of palm fatty acid distillate of different oil processing industries of Pakistan, Journal of Oleo Science 65(11), 2016, 897-901.
5. Top, A.G.M. Production and utilization of palm fatty acid distillate (PFAD), Lipid Technology Journal 22(1), 2010, 11–13.
6. Luchini, D. N., Strohmaier, G. K., Frederiksen, E. D., Hawkes, J. G., Dull, B. J., Polyunsaturated fatty acid monovalent and divalent metal salt synthesis, US Patent 007820842B2, 2007.
7. Purushothaman, Sajith, Kumar, Anil, Tiwari, D.P. Effect of feeding calcium salts of palm oil fatty acids on performance of lactating crossbred cows, Asian-Aust. J. Anim. Sci. 21(3), 2008, 376-385.
8. Suksombat, W. Improve the productivity of lactating dairy cows through supplementation. International Dairy Topics. 8(1), 2009, 7-11.
9. NRC, Nutrient Requirement of Dairy Cattle, 7th rev. ed. National Academic Press, Washington, D. C., 2001.
10. Burgos, A., Balley, W., Apparatus for use in making ruminant feedstuff. US Patent 20070092617A1, 2007.
11. Handojo, L., The process of ruminant feed supplements production enriched with calcium fat. Indonesia Patent S00201803641, 2018 (registered).
12. AOCS Firestone, D. (6th Edition), Official Methods of Analysis, Association of Analytical Chemistry, Inc. Arlington, USA, 2013.
13. Food and Agriculture Organization of the United Nations; World Health Organization, Compendium of Food Additive Specifications, *Joint FAO/WHO Expert Committee on Food Additives*; $80^{th}$ meeting 2015.
14. Hamirin, K. Survey on characteristics of Malaysian palm fatty acid distillate (PFAD) and palm acid oil (soapstock). PORIM Report PO (59) 83, 1983.
15. McAskie, W., Ruminant Feedstuff, their production and apparatus for use therein. US Patent 485 323 33, 1989.
16. Bong, E.Y., Parthasarathy, R., Eshtiaghi, N., Wu, J., Solid-liquid effects on solid-liquid mass transfer in an agitated vessel. International Symposium on Mixing in Industrial Processes 7, Beijing, China, 2011.
17. Sterbacek, Z., Tausk, P., Mixing in the chemical industry. Pergamon Press, 1965.
18. Handojo, L.A., Indarto, A., Shofinita, D., Meitha, A., Nabila, R. and Triharyogi, H. Calcium soap from palm fatty acid distillate (PFAD) for ruminant feed: quality of calcium source, MATEC Web of Conferences, 2018, 156 02007.
19. Handojo, L.A., Indarto, A., Shofinita, D., Meitha, A., Nabila, R., Triharyogi, H. and Kevin, L. Calcium soap from palm fatty acid distillate for ruminant feed: the influence of water temperature, IOP Conf. Series: Earth and Environment Science, 2018, 141 012010.