Calcium Soap from Palm Fatty Acid Distillate for Ruminant Feed: Reaction Method

Lienda A. Handojo, Antonius Indarto, Daniel Pramudita, Dian Shofinita, Anggina Meitha, Rakhmawati Nabila, Harry Triharyogi

ABSTRACT--- Palm fatty acid distillate (PFAD) is a by-product of crude palm oil (CPO) refining, which contains free fatty acid as the main component and can be used as a raw material to produce calcium soap. The supplementation of calcium soap to the feed of ruminant gives benefits to their health as well as to increase the quality and quantity of milk production. This research examined the various methods of calcium soap production i.e. modified fusion reaction using two different calcium sources and double decomposition process using two different calcium sources. The result showed that at the same mole ratio of Ca source to PFAD, the production of calcium soap using modified fusion method had better performance compared to double decomposition process. CaO showed to be the better source of calcium for modified fusion method of calcium soap production.

Keywords: calcium soap, PFAD, modified fusion process, double decomposition process

INTRODUCTION

The world production of palm oil was estimated to reach 62.8 million metric tons per year in 2017 (Global Palm Oil Production, 2017). Beside palm oil, CPO refining process also generates side product, the so called palm fatty acid distillate (PFAD). Indonesia produced 34 million tons of palm oil (USDA, 2016). Between January-May 2017 about 289 thousand tons of PFAD were resulted from the refining process in Indonesia (Indonesia Central Bureau of Statistics, 2017). Although it shows to be major product, the utilization of PFAD in Indonesia is currently rather limited. PFAD with its high content of fatty acid can also be used as a source material for animal feed (Top, 2010).

The calcium soap, as a form of protected fat used for ruminant feed supplement, is preferable than the free fatty acid called unprotected fat. Unlike directly feeding free fatty acid to ruminant, the protected fat does not interfere with fermentation in cow's rumen (Chalupa et al., 1984). The consumption of calcium soap by ruminants increases the quality and quantity of milk. It has been reported that the milk quantity increases by 3-8% with the intake of 0.45 kg of calcium soap daily. Furthermore, the fat content of the milk increases by 0.2-0.3% and the cow's fertilization success rate increases by 20% (Suksombat, 2009). Following FAO data (2016), milk productivity in Indonesia was still low at 1.8 tons of milk/Cow/year.

PFAD can be converted into calcium soap through saponification reaction with calcium source. There are three methods in producing metal soaps, namely with double decomposition process, fusion reaction including modified fusion process and metal acid reaction methods (Rogers, et al 1959). The double decomposition process comprises the reaction between the fatty acid and the sodium continued by the reaction of the intermediate sodium soap with another metal salt (Rogers et al 1959). The fusion method occurred by reacting free fatty acid source directly with metal source in the form of oxide, hydroxide or salt compound (Perez, 2007). The metal-acid reaction method involves the reaction between the free metal in the form of a powder and a fatty acid to form a polyvalent metal soap (Rogers et al., 1959).

PROBLEM STATEMENT

In order to obtain a successful approach for industrialization of animal feed from PFAD, a simple, efficient, and less-expensive reaction method has to be determined. Two different reaction methods and two sources of calcium have been investigated and discussed in this study.

THE AIM OF RESEARCH

The purpose of this study was to observe the process of calcium soap production as an animal feed made from PFAD using various methods.

METHOD OF RESEARCH

Materials

Materials used in this research were CaO, $Ca(OH)_2$, $CaCl_2$, and NaOH with technical grade concentration. PFAD as source of fatty acid was obtained from CPO refining without any further treatment (PT. Tunas Baru, Lampung Tbk. Indonesia).

Revised Manuscript Received on 14 February, 2019.

Lienda A. Handojo, Department of Chemical Engineering, Institut Teknologi Bandung
Antonius Indarto, Department of Chemical Engineering, Institut Teknologi Bandung
Daniel Pramudita, Department of Chemical Engineering, Institut Teknologi Bandung
Dian Shofinita, Department of Chemical Engineering, Institut Teknologi Bandung
Anggina Meitha, Department of Chemical Engineering, Institut Teknologi Bandung
Rakhmawati Nabila, Department of Chemical Engineering, Institut Teknologi Bandung
Harry Triharyogi Department of Chemical Engineering, Institut Teknologi Bandung

Methodology

The synthesis of feed animal calcium soap was conducted using a modified fusion reaction and double decomposition process. The modified fusion reaction occurred by reacting PFAD with $Ca(OH)_2$ or CaO at the initial mixture temperature of 60°C, above the melting point of PFAD. While the double decomposition method reacted PFAD with NaOH continued by reacting the product, i.e. sodium soap with $CaCl_2$ at a temperature of 70-80°C.

For all experiments, the analysis of the reaction was focused on acid value determination of the calcium soap product. The characterization of PFAD was conducted at the beginning of experiment by using Gas Chromatography (Shimadzu 2010 plus with FID detector, Rtx-5 column, and helium and hydrogen as gas carrier). The PFAD was converted into fatty acid methyl ester by esterification prior to transesterification process using strong acid. The acid value was determined following ISO 660: 1990, by dissolving one gram of calcium soap in ethanol heated at 60°C for 10 minutes then titrated with 0.01 N potassium hydroxide using phenolphthalein indicator (FSSAI, 2012).

ANALYSIS AND DISCUSSION

Characterization of PFAD

The composition of PFAD obtained from industrial CPO refining in Sidoarjo is shown in table 1 while the typical GC spectra data of feed were shown in figure 1.

Table 1 Composition of fatty acids in PFAD.

Fatty acid composition (wt%)	This study	Hamidin (1983)
C12; Lauric	0-0.2	0.1-0.3
C14; Myrstic	1.2-1.4	0.9-1.5
C16; Palmitic	45.2-53.7	42.9-51.5
C18; Stearic	2.8-7.1	4.1-4.9
C18:1; Oleic	32.7-50.6	32.8-39.8
C18:2; Linoleic	0-3.7	8.6-11.3

The result shows that the PFAD composition had been dominated by palmitic acid and oleic acid compared to other fatty acids. The average of acid and soap values of the PFAD were 191 mg KOH/g and 231 mg KOH/g, respectively. The percentage of free fatty acid of feed calculated as palmitic acid reached 87.1%. Top (2010) showed that PFAD used as a raw material for calcium soap production usually contained 81.7% of fatty acid as palmitic acid and typically consisted of palmitic acid and oleic acid as the major components. Besides, it was preferable to use the naturally source of fatty acids as raw material for producing calcium soap (McAskie, 1989)

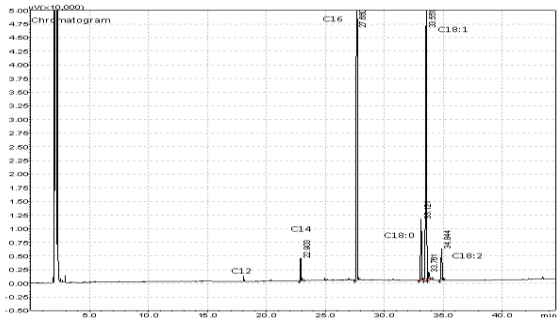

Figure 1. Gas Chromatography analysis of fatty acid composition

The fusion reaction was conducted by reacting PFAD and calcium source as the reactants. In this study, two calcium sources were applied, which were CaO and $Ca(OH)_2$. The result of using CaO as calcium source to produce calcium soap from PFAD is shown in figure 2. The acid value of the product represents the amount of fatty acid left in the product, or was not converted into calcium soap. The lower acid value of the soap means that the conversion of the reaction was higher.

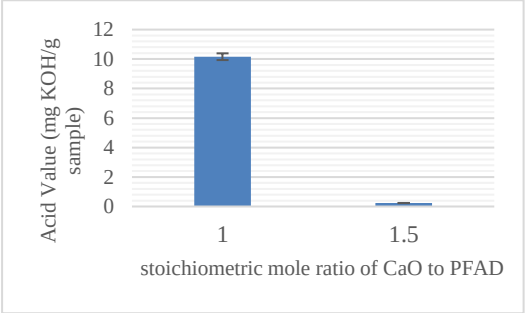

Figure 2. Acid value of the calcium soap produced from PFAD and CaO with fusion reaction (initial temperature 60ºC, water addition 20% mass of PFAD mass)

Figure 2 shows the effect of reactant mole ratio on the acid value of the product. The result shows that at higher stoichiometric mole ratio of CaO to PFAD, the lower acid values of the product was obtained at the same initial mixture temperature. This indicated that the use of higher CaO to PFAD mole ratio was preferable due to the higher conversion of the saponification reaction. The desirable acid value of the calcium soap for animal feed is as low as possible to prevent feeding free fatty acid to ruminant. Meanwhile, feeding excess calcium to dairy cattle may interfere with trace mineral absorption especially zinc (NRC, 2001). Therefore, the mole ratio of calcium oxide to PFAD in calcium soap production should not be too high too.

The calcium requirement for dairy cattle weighing of ± 450 kg according to NRC (2001) is 50.7 g/day. Thus, based on theoretical calculation, the amount of calcium in products is 75.74 g using a mole ratio of 1.5 per 600 g of calcium soap. The value is higher than the limit calcium intake. Therefore, the stoichiometric mol ratio should be reduced to

suit the required calcium level. This should occur after taking the calcium intake from other feeds such as cassava waste, grass, and corn silage in account.

During this saponification reaction of PFAD and CaO, water was added as reaction catalyst to initiate the saponification reaction. In general, the fusion process was carried out under steam pressure at high temperature about 150-200°C and for about 3-5 hours (Scott, 1974), the presence of water as catalyst made the reaction occurred rapidly at low temperature. McAskie (1989) suggested to add water in the range of 15%-25% of PFAD mass. In this experiment, the amount of water added was maintained at 20% of PFAD mass in order to give sufficient amount of water to act as the reaction catalyst, yet not excessive to disturb the saponification reaction. The addition of excessive water may shift the reaction towards the saponification reactants and may reduce the conversion level, which is undesirable.

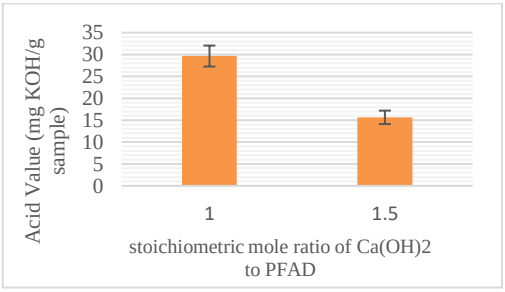

Figure 3. Acid value of the calcium soap produced from PFAD and $Ca(OH)_2$ with fusion reaction (initial temperature 60°C, water addition 20% mass of PFAD mass)

Figure 3 shows the acid values of products from saponification reaction of PFAD and $Ca(OH)_2$. The same trend can be observed here, as the use of higher stoichiometric mole ratio of $Ca(OH)_2$ to PFAD may result in a decrease in the acid values of the product. However, the result implies that the conversion level of the saponification reaction with $Ca(OH)_2$ was lower when compared to the reaction with CaO as the calcium source. The use of stoichiometric mole ratio of $Ca(OH)_2$ to PFAD of 1.5 resulted in an acid value of 15 mg KOH/g sample, which was still much higher than the acid value of the commercial soap (below 1 mg KOH/g sample). This result suggests that the use of CaO as the calcium source for this reaction may be preferable compared to $Ca(OH)_2$ due to its lower acid values of the products that indicates higher conversion level.

Double Decomposition Process

In this process, excess NaOH and $CaCl_2$ were used with a stoichiometric mole ratio to PFAD of 1.2 for each. A small stoichiometric mole ratio was selected for a double decomposition process using $CaCl_2$ as a Ca source comparable to a modified fusion method with Ca source of CaO and $Ca(OH)_2$. The alkali soap process prior to calcium soap production took place for about 2 hours for each stage with temperature maintained at 70-80°C. A 10% NaOH solution added to the molten PFAD-water mixture formed a water soluble sodium soap, after which a 30% $CaCl_2$ solution was added and an instantaneous precipitation was formed. After stirring for about two hours, the fine suspension was formed.

After washing with water and filtering using a filter cloth, the desired calcium soap could not be obtained. On the other hand, Lide (1994) mentioned calcium soaps should be formed rapidly from sodium soaps and a calcium compound, moreover the conversion reaction was quite good (96.8%). The calcium soap is insoluble in water. Meanwhile, the byproduct, sodium chloride, and excess reactants are highly soluble in water.

Figure 3. The appearance of unseparated water-calcium soap and dry calcium soap

In subsequent experiments under the same conditions, the fine suspension was formed at room temperature and atmospheric pressure for approximately 24 hours. After two times of water washing, calcium soap was obtained though the filtrate colour was still white indicated the presence of inseparable calcium soap. The calcium soap filtered was then dried and its acid value was measured. The acid value was closed to 0 mg KOH/g performing the high purity of product. In contrary, the yield was very low, i.e. 12.48g of calcium soap produced from 50 g PFAD, while from modified fusion reaction the yield reached about 60g from the same amount of PFAD.

Compared to the double decomposition process conducted by Garg (1997), Yoshizawa et.al (1992), and Zhou et al. Al (2000), the use of the mole of $CaCl_2$ in this experiment was less. Among the variations already performed, the stoichiometric mole ratio between $CaCl_2$ and Na soap of 2.76 resulted in a saponification degree of 80% (Garg, 1997). While in Yoshizawa et.al (1992), mole ratio of $CaCl_2$ and Na soaps operated in the range 1.9-2.1 and mixing temperature was about 75-95°C. The higher the temperature and the duration of Na soap mixing and $CaCl_2$ solution, the larger the size of the calcium soap particles (Yoshizawa, 1992).

A small stoichiometric mole ratio cannot produce the desired calcium soap in double decomposition process. In addition, the process of double decomposition is considered uneconomical and requires further drying process (Scott 1974) and more difficult to conduct since the possibility of side reactions to form gel and occlusion of inorganic salt and alkaline soaps. This side product could only be removed by water washing (Roger et al., 1959).

CONLUSIONS

The two methods for producing calcium soap were observed resulting modified fusion method as the best method due to the fastest process, higher yield, as well as less energy and raw material needed. In addition, calcium oxide as calcium source resulted the better result compared with calcium hydroxide through acid value.

ACKNOWLEDGEMENT

The authors would like to extend their sincere gratitude to BPDPKS Indonesia for providing the research grant and PT Tunas Baru Lampung Tbk for providing PFAD for this research.

REFERENCES

1. Chalupa, W. et. al., 1984. Rumen fermentation in vitro as influenced by long chain fatty acid, J. Dairy Sci. 67, 1439-1444.
2. Export Statistic Subdirectory 2017 *Export Trading Bulletin According to Harmonized System March-May 2017* (Jakarta: Indonesia Central Bureau of Statistics)
3. Lide, D. R., 1993-1994. Ed. CRC Handbook of Chemistry and Physics, 74th ed.; CRC press: Boca Raton, FL.
4. FAOSTAT, 2016. Yearly Production of Palm Oil in Countries and Regions, Retrieved 10 April 2017, from http://faostat3.fao.org/
5. FSSAI, 2012. Manual of Methods of Analysis of Foods Oils and Fats.
6. Garg, M. R., 1997. Bypass Fat Production Using Acid Oil, Its Effect on *In Vitro* Rumen Fermentation and Effect of Its Feeding on *In Sacco* DM Disappearance in Sheep. AJAS. 10 (6): 571-574.
7. Global Palm Oil Production, 2017. United States Department of Agriculture Estimation, Retrieved 15 10 May 2017, from http://www.globalpalmoilproduction.com
8. Hamirin K. 1983. Survey on characteristics of Malaysian palm fatty acid distillate (pfad) and palm oil (soap-stock). PORIM Report PO (59) 83 General. Pal Oil Research Institute of Malaysia.
9. McAskie, W., 1989. Ruminant Feedstuff, their production and apparatus for use therein. US Patent 485 323 33.
10. NRC, 2001. Nutrient Requirement of Dairy Cattle, 7th rev. ed. National Academic Press, Washington, D. C.
11. Perez, E.P., 2007. Method of producing calcium, sodium or magnesium soaps from fatty acids or oleins from animal or vegetable fats and use thereof as nutrients in monogastric animal feed. EP Patent 800 546.
12. Rogers, R.H., Blew, W.R., 1959. Manufacture of metal soaps. US Patent 2 890 232.
13. Scott, L.F., Monrovia, Strachan, H. D., et.al., 1974. Manufacture of Metallic Soap. US Patent 3 803 188.
14. Suksombat, W., 2009. Improving the Productivity of Lactating Dairy Cows through Suplementation. International Dairy Topics. 8 (1): 7-11.
15. Top, Ab Gapor Md, 2010. Production and utilization of palm fatty acid distillate (PFAD). Lipid Technology. 22 (1).
16. US Department of Agriculture, 2016. Oilseeds: world markets and trade. Foreign Agricultural Service, United State.
17. Zhou, C, et. al., 2000. Plastics Manufacture and Processing CA:37.
18. Yoshizawa, et. al., 1992. Continues Process for Preparing Metallic Soaps. US Patent 5 175 322.