Calcium soap from palm fatty acid distillate (PFAD) for ruminant feed: quality of calcium source

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Abstract. Calcium soap is potentially used as fat supplements for ruminants since it contains high concentration of fat and calcium that are useful for ruminants. The consumption of calcium soap may increase the yield and the fat content of milk, as well as increase the ruminant's fertility. Calcium soap can be produced from palm fatty acid distillate (PFAD), which is a by-product of crude palm oil (CPO) refining process, and calcium oxide (CaO). In this study, the effect of CaO quality on the acid value of the product has been observed. It was found that the reaction with lower concentration of active calcium of CaO resulted in products with a higher acid value, which indicates a lower reaction conversion. Thus, the produced calcium soap requires further treatment in order to remove the unreacted calcium and free fatty acid. Washing with hexane followed by either vacuum or convection drying has been found to be able to reduce the acid value of the product significantly.

1 Introduction

Calcium soap can be used as supplement for ruminants since it contains high concentrations of fat and calcium that are useful for ruminants. The calcium soap gives benefits for ruminants, particularly regarding the milk productivity and fertility increase. Calcium soap is produced from the reaction between fatty acid and calcium source.

Previous study reported that it was preferable to use the naturally source of fatty acids as raw material to produce calcium soap, such as beef or mutton tallow, palm oil, or lard [1]. Palm fatty acid distillate (PFAD) can be potentially used as raw material for the production of calcium soap since the fat content in PFAD can reach 81.7% [2]. Usage of PFAD with 87.1% free fatty acid content for calcium soap production has been reported [3]. Furthermore, PFAD is a by-product from crude palm oil (CPO) refining process, therefore the utilization of PFAD may add cost benefit for the industry. The product of CPO refining process usually consists of 5% PFAD and 95% refined, bleached, and deodorized (RBD) palm oil [4]. Considering that Indonesia is the largest producer of palm oil with a contribution of approximately 54% to the world total palm oil production in 2016 [5], the study regarding the utilization of PFAD will be interesting.

There are several calcium sources that can be used as raw materials for the calcium soap production. A previous study compared the possibility of using $Ca(OH)_2$ and CaO as calcium sources, and concluded that the use of CaO resulted in a higher reaction conversion [6]. However, the quality of CaO produced from several sources in Indonesia may vary. The production of CaO depends on the effectivity of the $CaCO_3$ combustion, on the condition during transport and storage since CaO is hygroscopic. This study discusses the effect of CaO quality on the acid value of the product, which reflects the reaction conversion. In addition, possible additional treatments, such as washing and drying, to decrease acid value of the product after reaction have also been explored.

2 Methods of research

2.1 Materials

Materials used in this study were CaO (Stone Garden and Padalarang Company) and PFAD (PT Tunas Baru Lampung Tbk).

2.2 Methodology

2.2.1 Actual CaO determination

Calcium oxide used was obtained from the ignition of quick lime as calcium carbonate. The actual amount of CaO should be determined by dissolving it in sucrose solution from ASTM rapid sugar test. The solution of calcium oxide was boiled and cooled at room temperature, then it was added 50% sucrose solution and

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shaken for 30 minutes. Water was added until 250 mL mark in erlenmeyer was reached and filtered through whattman paper no. 1, discharging the first 15-30 mL. Then sulfuric acid titrated the solution. The available lime was calculated as 4 times the volume of 0.357 N sulfuric acid [7].

2.2.2 Saponification reaction

The saponification reaction was carried out using modified reaction method followed by washing and drying process as shown in Fig. 1.

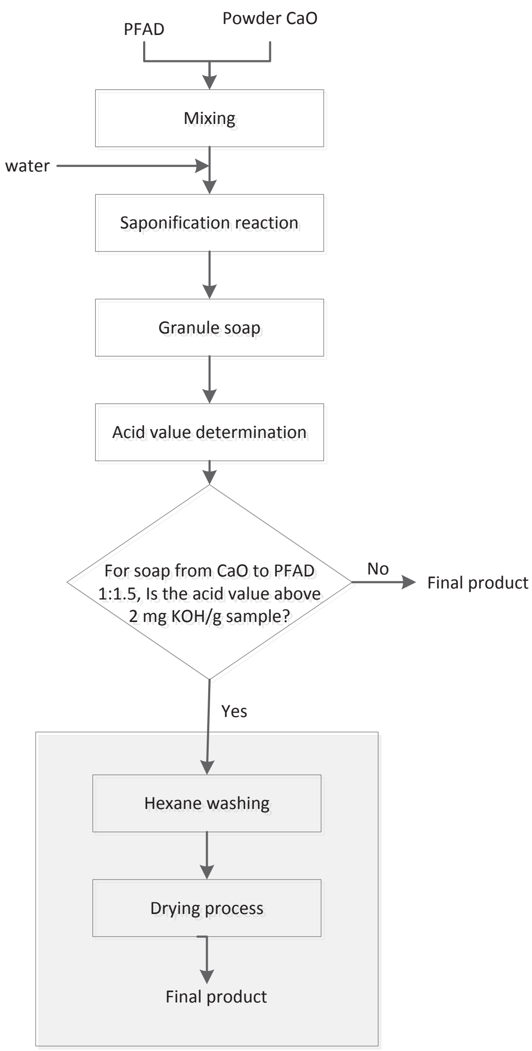

Fig. 1. Block flow diagram of the experiment methodology

The method was chosen since it needs less time for the reaction [8]. In this study, the stoichiometric mole ratio of CaO to PFAD was varied from 1 to 2, the initial temperature of PFAD in the process was 60°C, and percentage of mass of water was about 20% of PFAD. The mixture of molten PFAD and CaO was heated and stirred homogenously. Saponification reaction took place immediately after a certain amount of 60°C hot water was added and stirred for less than 10 minutes, during which the granule soap formed. The soap was relatively dry since the water evaporated as the mixture temperature raised due to the exothermic process of saponification.

2.2.3 Washing and drying process

Since the ruminants requires limited fatty acid content in their feed, the washing process was conducted to remove residual fatty acid present in calcium soap. The washing process was carried out by mixing nonpolar solvent, hexane, and product with ratio 3:1 and stirred it at 60°C for 30 minutes. The calcium soap filtrate obtained was dried in vacuum oven at 40°C, 0.4 atm and another was dried under convection dryer at 50°C for 3-4 hours.

2.2.4 Acid value determination

Acid value was determined by ISO 660: 1990. One gram of calcium soap sample was taken and dissolved in ethanol, the mixture was then heated for 10 minutes. The solution was titrated by 0.01 N potassium hydroxide using phenolphthalein indicator [9].

3 Results and analysis

3.1 The effect of CaO quality on acid value of the products

Two different sources of CaO were used in this experiment. Based on the CaO analysis the result showed that the CaO content was about 40% (CaO 1) and 75% (CaO 2). The CaO production process has a significant influence on the quality of CaO produced. Some factors affecting the quality of CaO are the natural limestone, the calcination process, the method of storage, and the method of transport [10]. The quality of CaO which may vary due to source of production can be determined with titration method using sulfuric acid after CaO is dissolved in a solution of sucrose to calculate the amount of calcium in the form of oxide.

The quality of CaO used as the main raw material is essential and is directly proportional to the quality of the products. Figure 2 shows that the CaO content used had a very significant effect on product quality. The CaO quality in this research may be affected by the storage method that could convert the CaO to $Ca(OH)_2$ due to moisture in the environment. The use of $Ca(OH)_2$ for making calcium soap had lower quality than the product using CaO as calcium source [11]. Another strong factor was likely the presence of calcium carbonate in quicklime used regarding the incomplete combustion process.

A lower acid number was preferred and indicated a higher reaction conversion. In the stoichiometric mole ratio of CaO to PFAD of 1, the CaO 1 (40%) acid value was much higher than that of CaO 2 (75%) which are 31.51 and 10 mg KOH/g sample and are proportional to 14.35% and 4.5% fatty acids as palmitate, respectively.

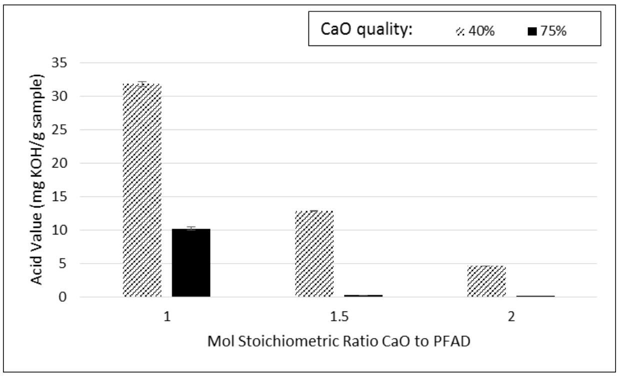

Fig. 2. The acid value of products vs. mol stoichiometric ratio at different CaO quality.

The higher the mole ratio of stoichiometry, the acid value will decrease. In the three variations of the CaO mole ratio, all the acid values of the product of CaO 1 are still above 4 indicating the product was still below the commercial product standard. As for the product of CaO 2, starting from the ratio of CaO to PFAD 1.5, the acid product number has been very low reaching 0.23 mg KOH/g sample. This value was already below to the free fatty acid content claimed by the commercial product [11].

3.2 The effect of washing and drying process on Acid value of the products

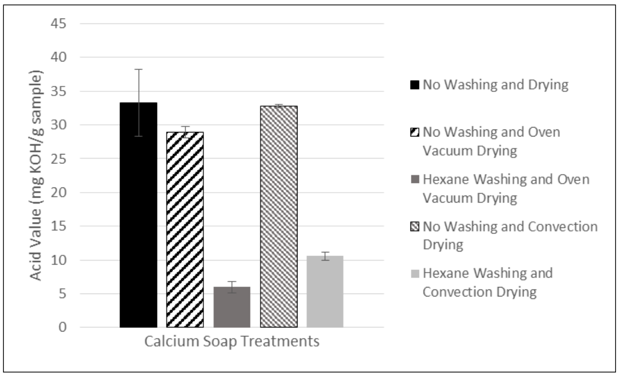

Fig. 3. The acid value of the products after washing and drying process.

The poor quality of CaO leads to a product which requires further processing to reach the desired quality. Figure 3 provides the effect of washing and drying process on the acid value of calcium soap. The soap was obtained from the reaction with a stoichiometric mole ratio of CaO to PFAD 1.5. The hexane wash treatment could reduce the acid value up to 68-82%. The drying process was then necessary to remove hexane in the final product. Hexane was used to extract fatty acids or unsaponified material. Based on Akers and Peters (1984) the organic solvent used to extract the unsaponifiable matter is hydrocarbon with 4-14 C atoms in molecular compounds like hexane [12].

The high decrease in acid value was obtained from hexane washing followed by drying using a vacuum oven, which have an end product acid number of 6 mg KOH/g, compared to hexane leaching and convection drying with an acid number of 10.6 mg KOH / g sample. The convection drying could not remove hexane as good as vacuum oven drying. As a result, hexane left in the product which still carry some unreacted free fatty acid, increases the acid value. The drying process was carried out to remove the hexane from the final product. However, the final acid value was still higher than in the commercial products. Besides, the additional processes required more energy and additional materials, therefore it was relatively uneconomical.

4 Conclusions

CaO utilized as a raw material needs to be analyzed before reacted with fatty acids to produce calcium soap. Higher CaO content yields better calcium soap product which has lower acid value. The washing process followed by drying has an effect on the quality improvement of calcium soap products. The high quality CaO still has a greater effect on the product, compared to the additional treatment applied to the product resulted from low quality CaO.

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