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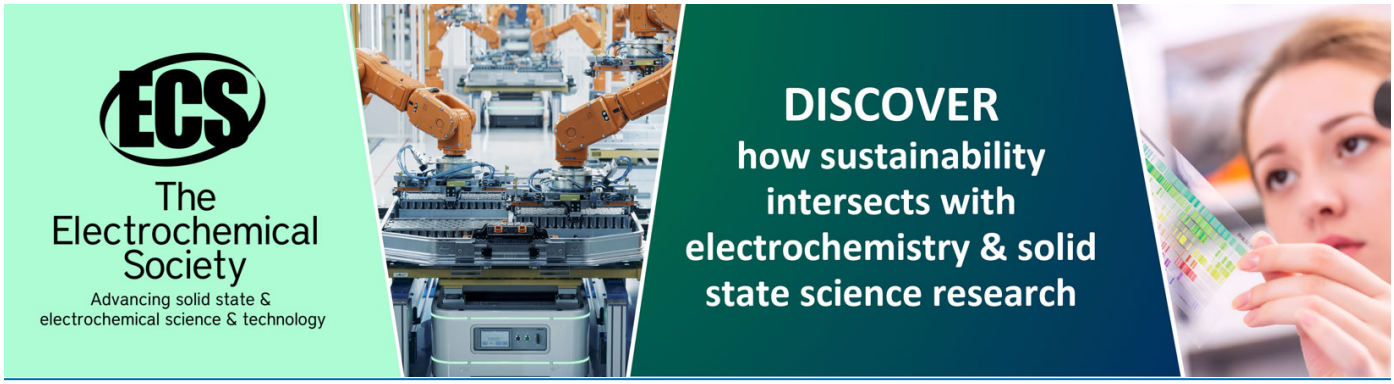

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Calcium Soap from Palm Fatty Acid Distillate for Ruminant Feed: The Influence of Initial Mixing Temperature

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Abstract. The breastfeeding dairy cows often go through metabolic disturbances and low milk production due to the use of stored body fat and minerals to assist milk production. Those problems can be solved by feeding feed supplement to the dairy lactating cows. Calcium soap is a well-known lactating dairy cattle feed supplement, which gives energy in the form of protected fat so it can increase milk productivity of dairy cattle. This research studied the use of PFAD (Palm Fatty Acid Distillate) as the free fatty acids source and calcium oxide as a calcium source to produce calcium soap using modified fusion method with water as the reaction catalyst. This study evaluated the initial mixing temperature of PFAD as the parameter affecting the conversion of PFAD, which was determined by the product acid value. The result showed that, at the same mole ratio of calcium source to PFAD, the lower initial mixing temperature gave higher reaction conversion of PFAD. The recommended initial temperature for mixing was found to be 60 ^{o}C, which gave the acid value of the product in the range of 2.96 – 3.14 mg KOH/g sample for mole ratio of CaO/PFAD 1 – 1.15.

1. Introduction

In the early days of breastfeeding, dairy cows are often malnourished because of insufficient feed intake. In this condition, dairy cows have to use stored body fat and minerals from the body to support milk production. This often leads to metabolic disturbances and low milk production [1]. The addition of fat supplements directly to the cows can increase the energy density of feed, but high-fat content of feed can create the decrease of fiber digestibility and milk fat percentage [2]. According to Chalupa et al. [3], to avoid such adverse effects, the salt of long chain fatty acids (such as calcium soap) as an animal feed supplement is a good alternative. The addition of calcium soap as a mixture of dairy cattle feed can increase the yield of milk, the composition of fat in milk, as well as the gross energy of cow's milk [4]. In Indonesia, this supplement can be used to solve the problem of low milk production, especially in fulfilling the projected consumption of cow milk for consumption which tends to increase by an average of 4.1% per year in 2017 – 2020 [5].

Crude Palm Oil (CPO) contains unwanted impurity components. CPO is generally purified for sale as Refined Bleached Deodorized Palm Oil (RBDPO). RBDPO is palm oil which has undergone a purification process to eliminate free fatty acids and purification to remove color and odor. The elimination of free fatty acids (FFA) may be performed in industrial practice using different units for neutralization with caustic, washing and drying of the fuel. The method of dry washing has been done by using modified potato and cassava starch as adsorbents [6]. The side product of the process is Palm Fatty Acid Distillate (PFAD) which is obtained as much as 5 % of the weight of palm oil. The main component of PFAD is free fatty acids that can reach around 80 % [7].

Many types of research are focusing on utilizing this by-product to increase its value. One of them is further processing through an esterification reaction with glycerol and lipase catalyst to produce

monoacylglycerol and diacylglycerol, then monoacylglycerol and diacylglycerol can be used as emulsifiers in food or non-food products such as cosmetics and drugs [8]. The utilization of PFAD also has great potential in biodiesel industries [9]. PFAD can also be utilized as raw material for producing calcium soap, a kind of ruminant feed supplement [10]. The production of calcium soap from PFAD is expected to be profitable in the palm oil industry.

There are three basic methods used in the manufacturing process of calcium soap from fatty acids, namely the double decomposition method, the modified fusion method, and the metal-acid reaction method. Modified fusion methods are generally chosen for the production of calcium soap. Calcium oxide is reacted directly by melting free fatty acids using a catalyst in the form of water [11]. This method is more economical than other methods and has been used in the manufacture of industrial-scale calcium soap. The chemical reaction involved in the modified fusion method is as follow.

$$MeO+2RCOOH \rightarrow Me(OOCR)_2+H_2O$$
or
$$Me(OH)_2+2RCOOH \rightarrow Me(OOCR)_2+2H_2O$$

The "Me" in the chemical reaction above can be replaced by any divalent metals in the modified fusion method. Certain divalent metals such as calcium, copper, magnesium, and zinc have long been recognized as beneficial mineral nutrients for humans and certain companion animals and livestock, such as ruminants, horses, dogs, cats, rabbits, hamsters, birds, fish, and the like. For example, the mineral calcium not only builds and strengthens bones and teeth, but it also maintains a normal heartbeat and regulates blood pressure. It is also essential for the healthy functioning of the nervous system. [12]

This study aims to evaluate the production of calcium soap from PFAD and a certain calcium source for ruminants feed, specifically the effect of initial mixing temperature on the conversion of the reaction. The acid value of the calcium soap was chosen as the quantitative parameter to be observed. In addition, the effect of initial mixing temperature on saponification reaction time was also observed.

2. Experimental section

2.1. Materials

Materials used in this study were technical grade calcium source and PFAD as the source of fatty acid. The PFAD was obtained without any further treatment from PT Tunas Baru Lampung Tbk – Sidoarjo, a CPO refining plant in Indonesia.

2.2. Calcium soap preparation

Several calcium soap samples were prepared using the modified fusion method with two different operating variables, initial mixing temperature, and reactants mole ratio. The PFAD was melted to various temperatures (60-90 °C), then calcium source powder was added with the mole ratio of CaO/PFAD that ranged from 1 to 1.4. Hot water was added to the mixture immediately after the homogeneous phase was achieved.

2.3. Acid value determination

For all experiments, the analysis of reaction conversion was focused on acid value determination of the calcium soap product. The analysis was done according to the standard method described in ISO 660:1990. One gram of calcium soap was dissolved in ethanol at 60 °C for 10 min. The resulting mixture was titrated with 0.01 N potassium hydroxide using phenolphthalein as an indicator. The acid value in the product was calculated with the following equation:

$$\text{Acid value} = \frac{56.1 \cdot c \cdot V}{m}$$

Where c is the exact concentration of the potassium hydroxide solution used (mol/L), V is the volume of the potassium hydroxide solution (mL), and m is the mass of the test portion (grams).

3. Results and discussion

The modified fusion method is similar to that of the fusion method, except the addition of a small amount of water to the mixture of molten fatty acid and oxide or metal hydroxide. The added water acts as a catalyst and causes reactions to occur at lower temperatures and faster reaction [13]. In the modified fusion

reaction, the usually high reaction temperature can be reduced up to 90-100 °C [14]. However, in the production of calcium soap, the lowest initial mixing temperature may be the same as molten PFAD temperature, which seems to be 60 °C [15]. The reaction can reach the saponification temperature with the help of the exothermic reaction between calcium oxide and water, which produces heat. Therefore, the reaction mixture in the modified fusion reaction does not need energy as much as the usual saponification reaction.

The experiment in this study varied the stoichiometry reactant mole ratio of CaO/PFAD in stoichiometry and the initial mixing temperature. All saponification reaction with different initial mixing temperatures and reactants mole ratios gave similar trends. Therefore, only two sets of data samples were selected to be presented, the variation of the mole ratio of reactants 1 and 1.15. The change of reaction temperature with respect to reaction time was plotted for each initial mixing temperature, as shown in Figure 1 and 2 for mole ratio 1 and 1.15 respectively. The plot was terminated as the temperature reached its peak.

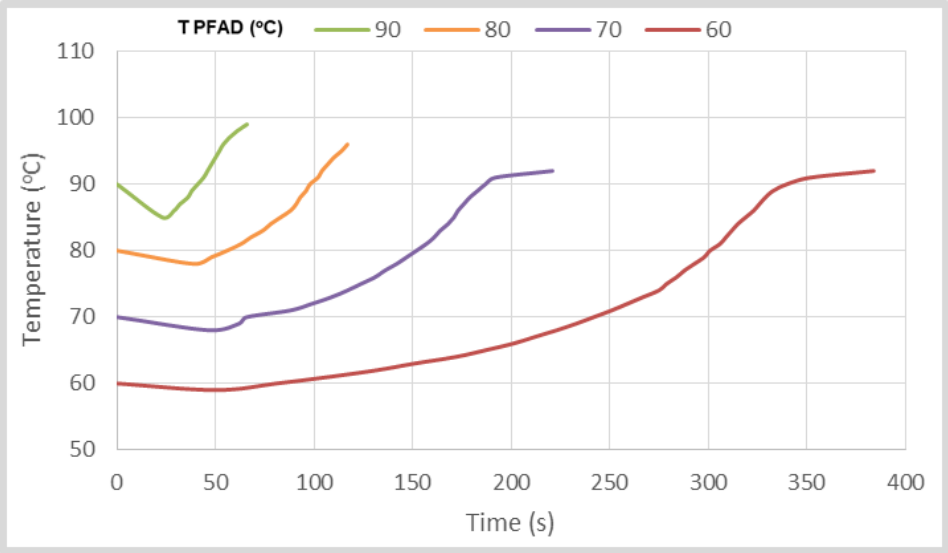

Figure 1. Reaction temperature profile as a function of reaction time at various initial mixing temperature and the mole ratio of calcium source to PFAD = 1

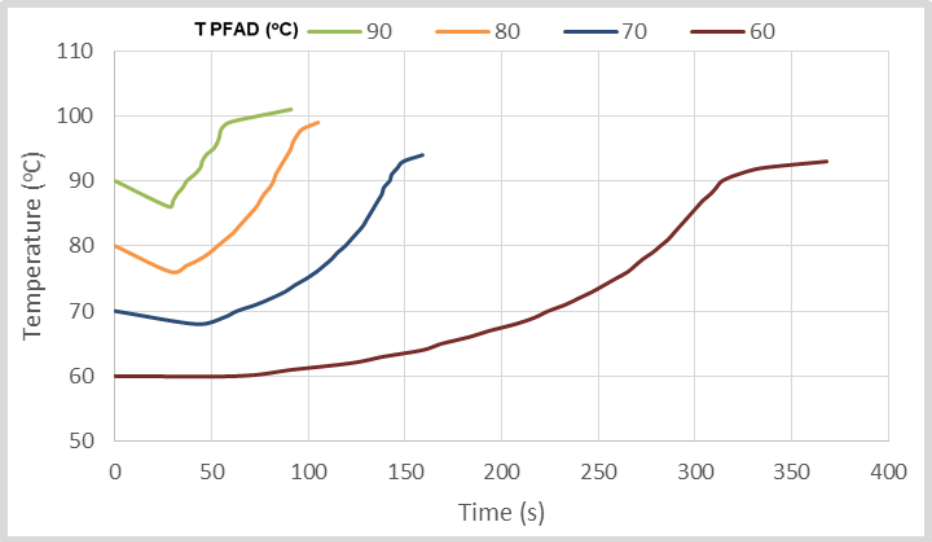

Figure 2. Reaction temperature profile as a function of reaction time at various initial mixing temperature and the mole ratio of calcium source to PFAD = 1.5

From Figure 1 and 2, the effect of various initial mixing temperature on the time needed for the system to reach the peak temperature can be observed. The peak temperatures of reaction mixture made with initial mixing temperature of 60, 70, 80, and 90 °C differed with the range between 90-100 °C, which were different from the experiment conducted by Scott [14]. The author found that the modified fusion reaction initiated at 90-100°C and reached the peak temperature of 100-200 °C. This may be caused by the different operating conditions such as mixing equipment. Just like the experiment by Scott, the experiment in this research also showed that the reaction can be said to end when the mixture reached its peak temperature.

Both figures, Figure 1 and 2, show the increasing temperature during the experiment. To more easily understand the stages in the reaction of calcium soap production, the reaction itself can be divided into four stages. The stages are depicted in form of zones in Figure 3. The reaction stages that represent the four zones are shown in Figure 4.

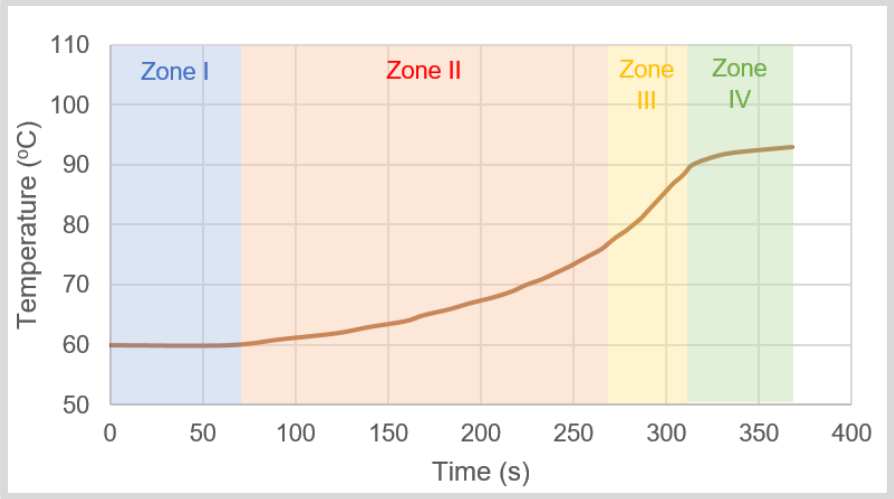

Figure 3. Reaction temperature profile as a function of reaction time at 60 °C mixing temperature and mole ratio of calcium source to PFAD = 1.15

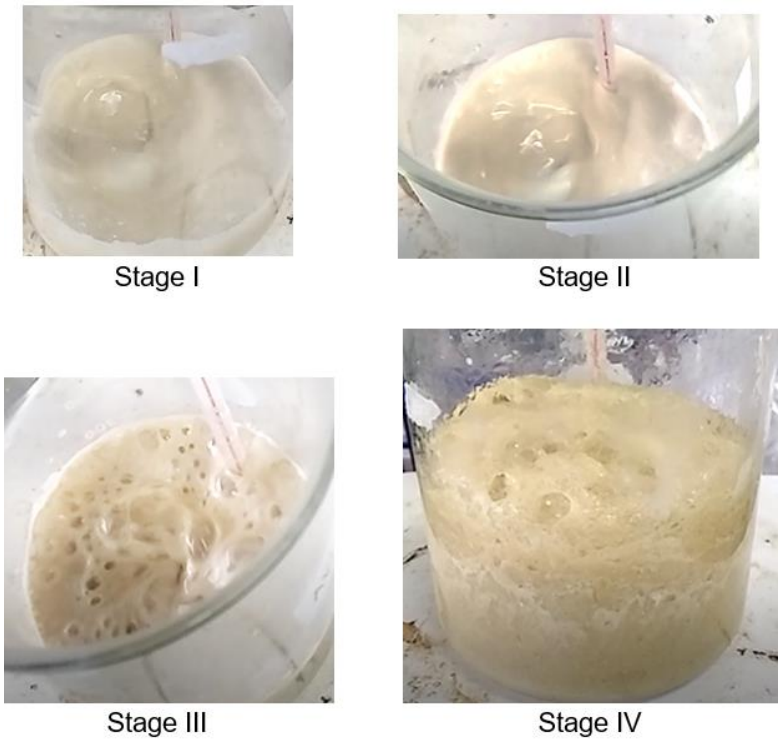

Figure 4. Images of PFAD saponification reaction stages

Zone I (highlighted blue) shows that at the beginning of the reaction, the mixture underwent temperature adjustment after all raw materials were mixed. It can be observed for the samples which were made with various initial mixing temperature above 60 ^{o}C that the temperature of the mixture fell slightly and then rose to the specified mixture temperature. Meanwhile, with the initial mixing temperature of 60 ^{o}C, the mixture temperature remained the same. Zone II (highlighted red) shows that the mixture temperature starts to rise. This was due to an exothermic reaction from dissolving calcium source with water. At the time the mixture reached the optimal temperature for saponification reaction, which is shown by zone III (highlighted yellow), the reaction took place while continuing to raise the mixture temperature more rapidly than that of in zone II. Zone IV (highlighted green) shows the reaction temperature as it reached its peak. It can be seen that the higher the initial mixing temperature, the higher the peak temperature values reached by the reaction mixture.

Stage I shows that at the beginning of the reaction there were no changes in the appearance of the mixed raw materials, the changes that occur only changes in temperature which depended on the initial mixing temperature used. There were no changes in appearance in stage II as well, however as mentioned in the prior paragraph, the mixture temperature increased slowly during the dissolution of calcium source and water. Stage III shows the beginning of the saponification reaction. At the beginning of stage III, the mixture started to expand while forming a more viscous mixture. As the mixture expands, the temperature also kept increasing until it reached its peak in stage IV. After the peak temperature was reached, the mixture will stop expanding as the temperature dropped. At the end of the reaction, the mixture could expand to four times the initial volume.

Other than peak temperatures, the reaction times are also shown in Figure 1 and 2. Both Figure 1 and 2 show that higher initial mixing temperature boosted the reaction time needed to reach the peak temperature significantly. This is shown by the higher the initial mixing temperature the greater the slope of the graph. This means that the temperature of the reaction mixture increases faster. However, it was found in the experiment that the reaction time did not ensure the same reaction conversion. The faster the reaction time meant the less time for the mixing, meanwhile mixing was important in this experiment. To ensure a high reaction conversion in the process, the raw materials had to be well mixed during the reaction. Just as Burgos and Bailey [16] proposed, a disadvantage with known methods of preparing such ruminant feedstuff is that they may not provide adequate mixing of the fatty acids,

calcium oxide, and water, resulting in pockets of unreacted chemicals. Such unreacted chemicals make the mixture unstable. If such unreacted chemicals later come in contact with water, they will cause an exothermal reaction that releases a lot of heat.

The products were then analyzed by determining the acid value. Products with lower acid value were known to achieve higher reaction conversion. All samples produced with different initial mixing temperatures and reactants mole ratios gave similar trends of acid value. Therefore, only two sets of data samples were selected to be presented. The acid values for the variation of the mole ratio of calcium source and PFAD 1 and 1.15 using all the initial mixing temperature are shown in Figure 5.

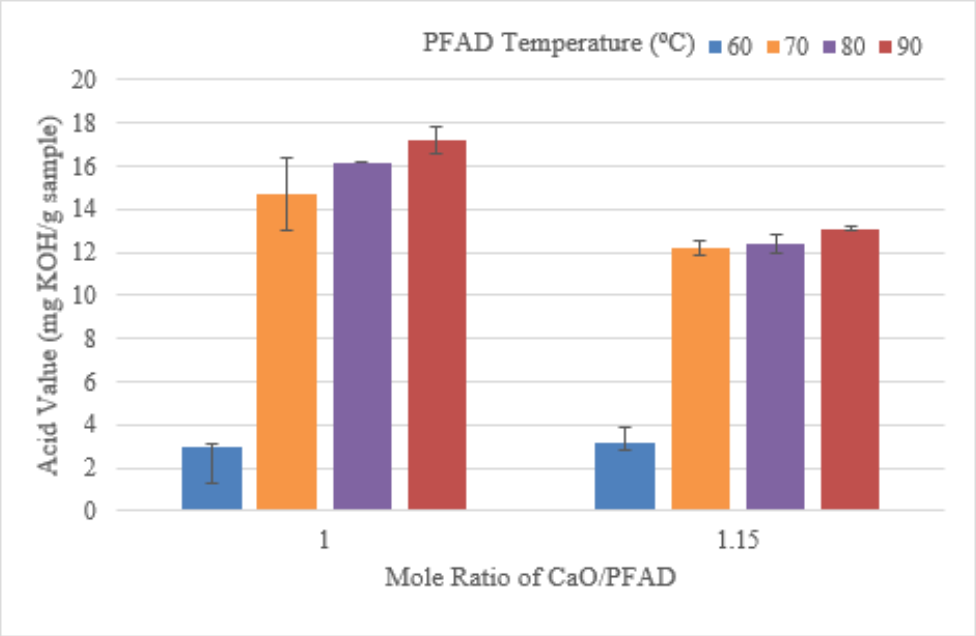

Figure 5. The acid value of the products as a function of CaO to PFAD mole ratio and initial mixing temperature

The low acid value indicates high reaction conversion because the amount of free fatty acids remaining in the calcium soap are lower. Based on the results, the higher the mole ratio of the reactant, the lower the acid value of the product or the higher the reaction conversion. The larger mole of the reactant meant more amount of calcium source was added to a certain amount of PFAD. The use of excess amounts of calcium source could ensure that almost all free fatty acids reacted with calcium source to form calcium soaps. However, a lower ratio was preferred to reduce excess amount of calcium in the product, which may result in the inhibition of the absorption of other minerals such as zinc and phosphorus in dairy cow digestion [17]. The obtained profile was consistent with the previous statement by Handojo et al. [18].

In contrast to the reactant mole ratio, lower product acid values were obtained at lower initial mixing temperatures. This trend also appeared on every data sets of the same reactant mole ratio in this research, which may be because of the shift equilibrium reaction. Furthermore, it is depicted in Figure 5 that generally, the reaction conversion was not significantly influenced by adjusting the temperature at 70, 80, and 90 ^{o}C. On the other hand, the increase in acid value was seemingly drastic at the temperature from 60 to 70 ^{o}C. The high temperature of the mixture may hinder the reaction process since the reaction itself is exothermic. Another possibility was that the higher the temperature of the mixture, the easier the water evaporates. This may cause a problem to the reaction since an amount of water (as a catalyst) is needed to dissolve the calcium source to facilitate the reaction in the liquid phase. Thus, it can be concluded that for this process, the lowest possible initial mixing temperature is preferred, which is 60 ^{o}C (PFAD has melted completely).

4. Conclusion

The best operating condition for producing calcium soap is required to achieve the highest reaction conversion (lowest acid value). The initial mixing temperature is one of the variables that affect the saponification reaction of calcium soap. This study found that the higher the initial mixing temperature, the higher the peak temperature values reached and also the less time needed to complete the reaction. However, the lowest possible initial mixing temperature is recommended to achieve a higher reaction conversion (the lower acid value), which was found to be 60 ^{o}C.

Acknowledgement

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