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Calcium soap from palm fatty acid distillate for ruminant feed: The influence of water temperature

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Abstract. As the largest palm oil producing country in the world, Indonesia also produces abundant amount of Palm Fatty Acid Distillate (PFAD), a by-product of Crude Palm Oil (CPO) refining process. PFAD can be utilized as the raw material for calcium soap, ruminant feed that is widely used to increase milk yield, as well as to increase the ruminant's fertility. However, the practice of feeding ruminants with calcium soap has not been practiced in Indonesia, which makes it imperative to develop calcium soap production process from PFAD within the country. This research aimed to study the effect of operating conditions of the saponification reaction using PFAD and CaO as reactants on the quality of the calcium soap obtained. The saponification reaction was carried out by modified fusion method. A range of stoichiometric mole ratios of CaO to PFAD (1.0 to 1.6) and the temperature of water (60-90°C) were studied in this research. An increase in the stoichiometric mole ratio of CaO/PFAD was observed to cause a decrease in the acid value, which indicates an increase in the reaction conversion. In contrast, the temperature of water was found to have little impact on the acid value of the product.

1. Introduction

Indonesia is the largest producer of palm oil in the world. In 2016, it contributed to approximately 54% of the world total palm oil production, with annual palm oil production of 32.5 million metric ton per year [1,2]. The crude palm oil (CPO) is refined to obtain Refined, Bleached, and Deodorized (RBD) palm oil that takes 95% of the initial mass of the CPO. The 5% remaining fraction is the by-product, which is known as palm fatty acid distillate (PFAD) [3]. Most of the produced PFAD in Indonesia is exported directly without further processing. According to Central Bureau of Statistics, approximately 94-99 thousand metric tons PFAD was exported each month in the second quarter of 2017 [4]. In fact, fat content in PFAD can reach 81.7% and has a lot of potentials to be used as raw materials for oleochemical, biofuel, and ruminant feed production [4]. Among these three alternatives, the utilisation of PFAD for ruminant (animals with four stomachs) feed has not been explored in Indonesia, which makes it necessary as well as promising to develop the production process of this product.

Calcium soap is widely used in countries other than Indonesia as supplement for ruminants, as feeding ruminants with calcium soap can increase the yield of milk up to 5-8% and fat content in the milk up to 0.2-0.3%. Ruminants need high energy diets for producing milk, which is ideally supplied by fat. However, their rumen cannot tolerate the presence of free fatty acids as they disturb fiber digestive process in the rumen. Unlike free fatty acids, calcium soap is inert in the rumen of ruminants



due to its 'protected fat' form, enabling it to be transported to the later part of the digestive system. Later in abomasum, PFAD will be broken into fatty acids that can be absorbed and used for milk production or as an energy source. Hence, feeding ruminants with calcium soap is expected to increase the absorption of fat and calcium in ruminant's digestion system. [6]. Moreover, it has been proven to increase the ruminant's fertility by 20% [7].

From commercial point of view, the benefits of calcium soap for ruminants will be the answer for the challenges faced by Indonesian dairy farmers. In 2014, milk productivity in Indonesia was only 1.6 tonnes of milk per cow per year; making Indonesia is left behind China, Thailand, and Australia (2.9, 4.6 and 5.7 tonnes per cow per year, respectively) in terms of its local dairy production [8]. Since this low productivity can be attributed to the absence of calcium soap in the diets of Indonesian milk cows, the introduction of calcium soap for ruminant feed in Indonesia is potential to increase the milk productivity, as well as give added values to non-exported PFAD.

Calcium soap is a product of saponification reaction that can be produced through several saponification method alternatives. Modified fusion reaction is a popular method for saponification, which is carried out by reacting fatty acids with alkaline or alkaline earth ions source, which can be in the form of hydroxide, oxide, or salt [9]. Particularly for calcium soap production, Ca(OH)_2 and CaO are the most common calcium source. With Ca(OH)_2 , the highest conversion obtained is 98% at stoichiometric mole ratio $\text{Ca(OH)}_2/\text{PFAD}$ of 3 [10]. Meanwhile, CaO was shown to give better result than Ca(OH)_2 in terms of reaction time, yield, and energy consumption. In PFAD saponification reaction, water is also added as the catalyst to initiate the reaction [11].

This study aims to evaluate the production of calcium soap from PFAD and CaO for ruminant feed. Specifically, this research looks into the influence of water temperature on the saponification reaction of PFAD to produce calcium soap. Reaction conversion is selected as the quantitative parameter to be observed, which is expressed by the acid value of the calcium soap. Additionally, the effect of water temperature on the saponification reaction time required was also studied.

2. Materials and Methods

2.1 Materials

Materials used in this research were technical grade CaO 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

The calcium soap was prepared using modified fusion method. 50 g PFAD was preheated to 60°C until completely melted, then CaO powder ($d \leq 100$ mesh) with a mole ratio of CaO/PFAD that ranged from 1 to 1.6 was added. Immediately after homogeneous mixing was achieved, water at various temperature within the range of $60\text{--}90^\circ\text{C}$ was added to the mixture.

2.3 Acid value determination

For all experiments, the analysis of the extent of reaction 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 indicator. The acid value in the product was calculated with the following equation:

$$\text{Acid value} = \frac{(56.1 \times c \times V)}{m} \quad (1)$$

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 Discussions

3.1 The effect of water temperature on reaction time

Water was added to the PFAD/CaO mixture at four different initial water temperatures: 60, 70, 80, and 90°C. Stoichiometric mole ratio of CaO/PFAD was fixed at 1.4, and water:PFAD (w/w) ratio was fixed at 1:5. The change of reaction temperature with respect to reaction time was plotted for each water temperature, as depicted in figure 1. The plot was terminated as the temperature reached its peak.

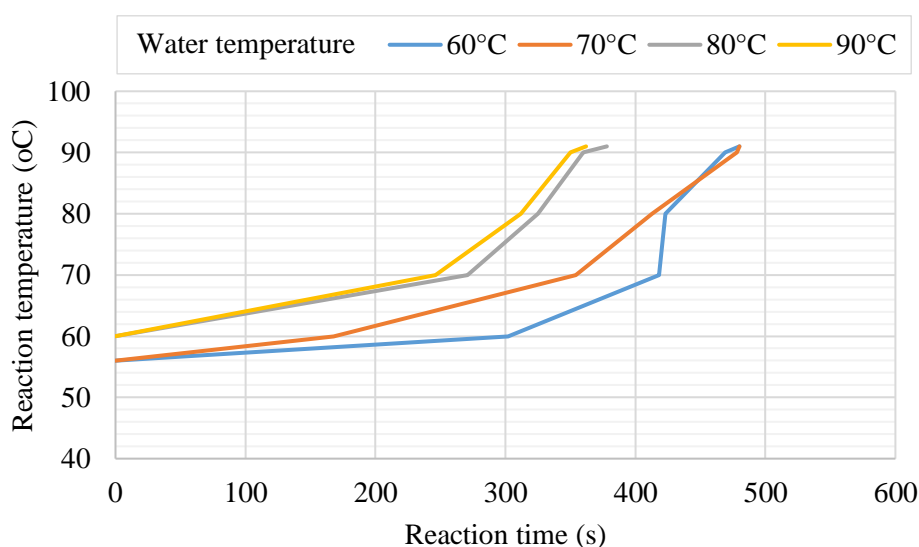


Figure 1. Reaction temperature vs reaction time at various initial water temperature

Generally, saponification reaction requires high temperature of about 150-200°C. However, in modified fusion reaction this high temperature can be reduced up to 90-100°C by the addition of small amount of water. The exothermic reaction of CaO and water produces heat which helps the reaction reach the saponification temperature. As a result, the modified fusion reaction that initiates at 90-100°C and reaches the peak temperature of 100-200°C. Hence, the energy to heat up the reaction mixture can be lowered [12].

From figure 1, the effect of various initial water temperature on the time needed for the system to reach the peak temperature can be observed. The peak temperatures of reaction mixture made with water temperature of 60, 70, 80, and 90°C are relatively similar (approximately 91°C), which are different from the statement made by Scott [12]. Additionally, there was no significant effect of initial water temperature on the peak temperature values reached by the reaction mixture. This phenomenon is mainly caused by the different initial temperature condition. In this research, the initial temperature is 60°C for the molten PFAD and 60-90°C for the water, while the initial temperature described by Scott is in the range of 90-100°C [12].

Figure 1 shows that higher water temperature will boost the reaction time needed to reach the peak temperature significantly. However, the use of water at higher temperature will consume more energy, as longer time is required to heat the water. Therefore, economic analysis and the heat balance of the reaction need to be researched further for making the most economical process.

3.2 The effect of water temperature on acid value

Water temperatures that are used on experiments are 60, 70, 80, and 90°C. The acid value of the product with various water temperature and stoichiometric mole of CaO/PFAD are shown in figure 2.

At same CaO/PFAD stoichiometric mole ratio, it was observed that an increase in water temperature from 60-90°C decreased the acid value of calcium soap produced. The acid value of the product decreased as the stoichiometric mole ratio of CaO/PFAD increased from 1.2 to 1.6. Various stoichiometric mole ratio have greater effect than water temperature on the acid value of the product as water temperature was found to have negligible effect on the acid value of the product.

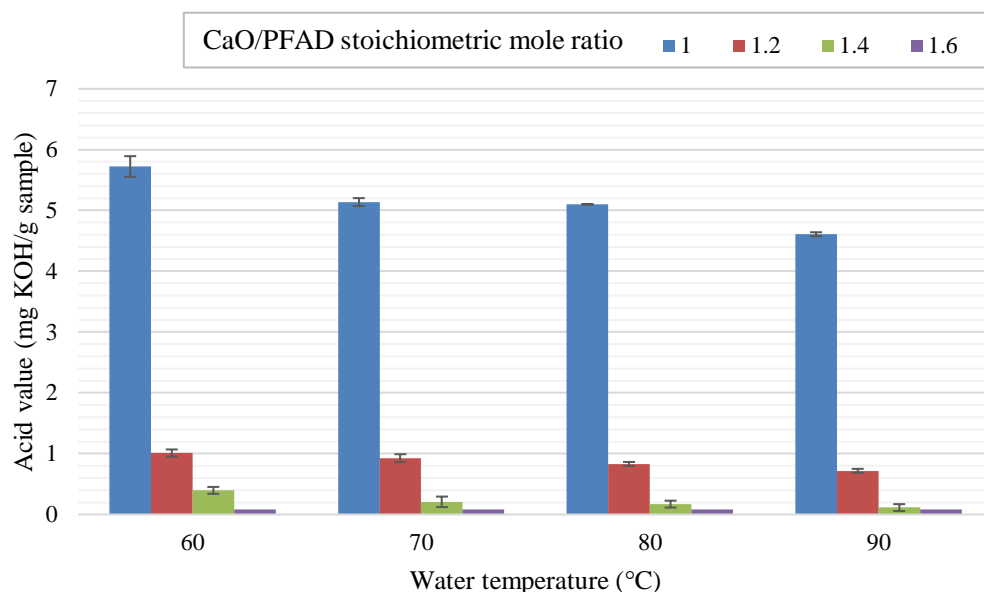


Figure 2. The effect of water temperature on acid the acid value of the product at various stoichiometric mole ratio

4. Conclusions

Increasing water temperature shortens the time needed to reach peak temperature significantly, but has little influence on the acid value of the product. Meanwhile, the acid value changes significantly with the variation of CaO/PFAD stoichiometric mole ratio. Taking into account the energy requirement for the production of calcium soap from PFAD, it is then better to go for the combination of water temperature and reaction time that gives the most optimum energy requirement, which can be done through economic analysis based on energy consumption.

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