PRODUCTION AND CHARACTERIZATION OF THE BASIC SOAPS OBTAINED BY DOUBLE DECOMPOSITION AND DIRECT PROCESS OF PALM STEARIN OILS

Godlief F Neonufa2*, Meiti Pratiwi1, Ronny Purwadi1, Tirto Prakoso1, Tatang H Soerawidjaja1, Lidya Elizabeth1

1 Chemical Engineering, Institut Teknologi Bandung, Ganesha Street No 10, Bandung City, West Java, 40132, Indonesia
2 Department of Agricultural Product Technology, Universitas Kristen Artha Wacana, Adi Sucipto Street No 147, Oesapa, Kupang, NTT, 85000, Indonesia

(Received: Month Year / Revised: Month Year / Accepted: Month Year)

ABSTRACT

The direct and double decomposition process of palm stearin oil were evaluated for the production of basic soaps as a decarboxylation feedstock to drop-in fuel produce. The metals proposed for the saponification reaction was magnesium which has a high-basicity and is a low-cost metal. The Fourier transform infrared spectroscopy profile of the Mg(OH)-stearin basic soaps obtained by both direct and double decomposition processes showed hydrocarbon groups such as alkanes and alkene, without the oxygenate groups. The basic soap products generated by the double decomposition process showed better basicity level which was determined based on the IR spectrum intensity, especially of the –OH group. The type of saponification process used in the resulted basic soaps can provide a different effect on the generated basic soaps characteristic.

Keywords: Basic Soap; Decarboxylation; Drop-in fuel; Palm Stearin; Saponification

1. INTRODUCTION

Since the past few decades, excessive use of fossil resources (mainly liquid fuel) as mono-energy in transportation and industries has been leading to both energy crisis and many environmental concern (Sinthupinyo et al., 2009). To solve this problem, the renewable liquid fuel from vegetable oils has been promoted as the alternative approach to replace fossil fuel. Biofuels have been seen as the nearest-term answer to the need for alternatives to petroleum fuels in the transportation sector (Demirbas, 2008). Biodiesel is one type of biofuel that has been established as a renewable fuel. However, biodiesel is a type of oxygenated fuel (Kubickova et al., 2005), therefore, its utilization is very limited (approximately 15-20 volume%) as a blended agent for petroleum fuel. Green diesel refers to liquid hydrocarbons fuel that do not contain oxygen in their molecular structure. Therefore, green diesel’s properties are similar to petroleum fuel that can be used in greater quantities, even up to 100 volume% (Neonufa, 2018). As raw materials, vegetable oils have the capacity to storage large amounts of energy. It is directly related to their chemical structure that contains similar carbon chains to the common fuels such as gasoline and diesel (Romero et al., 2018). The main component of vegetable oil and fat is triglyceride, i.e. an ester of glycerol and three fatty acids.

*Corresponding author’s email: godliefneonufa@gmail.com, Tel. +62-85-339111888, Fax. +00-00-000000
Permalink/DOI: https://doi.org/10.14716/ijtech.vxix.xxxx
The fatty acids are carboxylic acid with long aliphatic chain. It can be considered as carboxylic acids contaminated by carbon dioxide (RCOOH). Fatty acids are essential components of lipid fraction of living organisms and are common constituents of ancient and recent sediments (Kallai et al., 1984). The basic idea of hydrodeoxygenation or decarboxylation is to produce liquid hydrocarbon fuel by removing carbon dioxide from the molecule chain of fatty acids. Both hydrodeoxygenation and decarboxylation processes can be applied directly to oils and fats or fatty acids. The disadvantage of the direct application of both methods mentioned above to remove the oxygen in the molecular chains of oils and fats or fatty acids is that it required a lot of hydrogen and noble metal catalysts such as Pd and Pt (Fu et al., 2010). In addition, biohydrocarbon products still contain many unexpected free fatty acids in the fuel (Fu et al., 2011). Metal basic soaps are derivatives of the oils and fats of vegetable which have been proven to be excellent feedstock for decarboxylation process to produce green diesel (Neonufa et al., 2017a). In 1947, Chang and Wan have reported that decarboxylation of metal soaps from Tung oil can produced liquid hydrocarbon fuel. According to Neonufa et al., (2017b) the green diesel product resulting from metal basic soaps decarboxylation contains no more free fatty acids. There are three main processes applied to the metal basic soaps manufacture which are double decomposition, fusion, and metal-acid reaction. The first process involves two reactions; first, aqueous caustic and fatty acids are mixed to form a sodium soap, subsequently, the sodium soap and an inorganic metal (or mix metals) salt are reacted to form the metal basic soap. The second process involves the fatty acid and metal oxide reaction. The third process involves the fatty acid and free metal powders to form polyvalent metal soap (Elliot, 1946). The first process or double decomposition process is the most widely used in commercial scale. In the fusion process, the main concern is that the feedstock (fatty acids) must be pure grade. The metal-acid reaction process is the least used of the three commercial processes (Pratiwi et al., 2016). Another method to prepare the metal basis soaps has been introduced by Blachford (1982), it was the direct method. Through this method, the metal basic soaps were produced directly by reacting palm stearin and magnesium hydroxide. Each method produces metal basic soaps with different characters that tend to produce liquid products with different quality profiles as well (Akani et al., 1992). The purpose of this study is to investigate the production and characterization of magnesium basic soaps manufactured by direct and double decomposition (metathesis) methods. In addition, it is also geared to find the best production process of metal soaps most effectively used as basic soaps feed of decarboxylation processes to generate biohydrocarbon fuel.

2. METHODS

Palm stearin used in this research was supplied by local oil refinery in West Java, Indonesia. The saponification and acid value of palm stearin are 190.7 mg KOH/g and 0.6 mg KOH/g, respectively. The composition of palm stearin were mainly of 68.24 mole% of palmitic acid (C16:0), 5 mole% of stearic acid (C18:0), and 20.63 mole% of oleic acid (C18:1). Commercial-grade magnesium hydroxide and zinc hydroxide were supplied by Sigma-Aldrich Corporation of Merck KGaA in Singapore. Magnesium-zinc (mixture) stearin has been obtained from direct reaction of palm stearin and magnesium hydroxide (Blachford, 1982).

2.1. The preparation of Magnesium basic soaps

Direct (Blachford) method: Magnesium basic soaps are produced from a reaction mixture which initially comprises of Mg-hydroxide, water and a palm stearin (modified of Blachford, 1982). First, the reaction mixture is agitated; next, the reactants are poured into the agitated mixture to produce a metallic soap and glycerol. The saponification reaction was carried out at 140 to 180 °C and around 10 bars pressure for 3 hours in a mini-stainless steel autoclave in the presence of excess water to dissolve the glycerol formed in the reaction mixture; as a result, reactions between by-product glycerol and the product of magnesium basic soap is substantially hindered. The amount of palm stearin (triglyceride) and Mg(OH)₂ were approximately the same
with their stoichiometric reaction (see reaction 1 and 2). Two types of metal soaps were produced by this method, Mg-stearin (Mg(RCOO)$_2$) and Mg-stearin basic soaps (Mg(RCOO)(OH)). The chemistry of saponification reaction by direct method may be expressed briefly as follows:

$$2\text{H}_2\text{C(OOCR)}\text{CH(OOCR)}\text{CH}_2\text{(OOCR)} + 3\text{Mg(OH)}_2 \rightarrow 2\text{CH}_2\text{OH.CH(OH)}\text{.CH}_2\text{OH} + 3\text{Mg(RCOO)}_2$$  \hspace{1cm} (1)$$

the saponification reaction to produce Mg-basic soaps is as follows:

$$\text{H}_2\text{C(OOCR)}\text{CH(OOCR)}\text{CH}_2\text{(OOCR)} + 3\text{Mg(OH)}_2 \rightarrow \text{CH}_2\text{OH.CH(OH)}\text{.CH}_2\text{OH} + 3\text{Mg(RCOO)(OH)}$$  \hspace{1cm} (2)$$

The reaction mixture is allowed to separate into an aqueous layer and a molten layer of product magnesium basic soap. Under a pressure like that, the aqueous layer is essentially quiescent and the molten metallic soap layer is dissociated from the aqueous layer. The molten layer was removed from the reactor, and then washed with hot water and filtered with Buchner filter. The obtained slurry was dried overnight at 60 °C in the oven, and crushed into Mg basic soaps powder.

Double decomposition (metathesis) method: Metallic basic soaps are commonly prepared by a double decomposition process. According to Rogers et al. (1959) double decomposition process involves two basic reaction: the first, reaction of aqueous caustic (in excess) and the fatty acid (stearin) to form a sodium soap dissolve in an aqueous phase, and the second, reaction of the sodium soap with an inorganic metal salt (Mg salt) to form the metal basic soap (see reaction 3 and 4). The chemistry of its process may be expressed briefly as follows:

$$\text{NaOH (excess)} + \text{RCOOH} \rightarrow \text{RCOONa} + \text{H}_2\text{O}$$  \hspace{1cm} (3)$$

$$\text{RCOONa} + \text{Mg(OH)(NO}_3\text{)} \rightarrow (\text{RCOO})\text{Mg(OH)} + \text{Na(NO}_3\text{)}$$  \hspace{1cm} (4)$$

The metal basic soap ((RCOO)Mg(OH)) has been used as feedstock to decarboxylation process to produce renewable fuels.

2.2. Magnesium basic soap characterization

The conversion of metallic basic soaps was determined by weighing the wash water before and after the purification of the soaps. The structure of the soaps solid phase was obtained by X-ray diffraction techniques. The X-ray diffraction patterns were recorded with a Rigaku Geigerflex RBRU 200. The CuKα radiations were used over the diffraction angle range $2\theta = 3°-65°$. The topography surface of the metallic basic soaps were obtained with Scanning Electron Microscope (SEM). Fourier Transform Infrared (FTIR) were used to determine the metallic basic soaps which was based on the hydroxide ion content in the basic soaps. The infrared spectra were recorded at room temperature with a PerkinElmer FTIR Spectrometer, Model 1750 (PerkinElmer Corporation, Norwalk, CT), equipped with a deuterated triglycine sulfate detector and controlled by a PerkinElmer 7300 PC. The software used for FTIR data collection was the Infrared Data Management system. The instruments were maintained at constant humidity to minimize water vapor interference.

3. RESULTS AND DISCUSSION

3.1. Fourier Transform Infrared Analysis of soap
Results should be clear and concise. Fourier Transform Infrared (FT-IR) spectra of Mg(OH)-stearin basic soap powders produced in the direct process and double decomposition process are shown in Figure 1a and 1b, respectively.

The IR spectrum of the Mg(OH)-stearin basic soap sample shown in Figure 1a and 1b possessed an intense broadband between approximately 3700 and 500 cm\(^{-1}\) which may be represented as a superimposition of deformational vibrations of physically adsorbed water (Allegra & Ronca, 1978), vibration of structural OH- groups (Roy et al., 1953), and of characteristic stretching vibration of the Mg\(^{2+}\)-OH\(^{-}\) bond in Mg, Al-hydroxy carbonate (Allegra & Ronca, 1978). The wavenumbers of important absorption in the IR spectra of Mg(OH)-stearin basic soap were compared with those of corresponding fatty acids, i.e. myristic (14:0) palmitic (16:0) and stearic (18:0). Infra-red analysis showed that both saponification methods had similar wavenumber characteristic. The absorption maxima near 3460-3475 cm\(^{-1}\) in the spectra of fatty acid indicates the presence of a hydroxyl group. Magnesium basic soaps based on double decomposition method had higher hydroxyl group intensity compared to the direct method. Possibly, it is due to the fact that manufacture of basic soap by double decomposition reaction is more complete than the direct method. The absorption bands were observed near 2922.54 -2855.27 cm\(^{-1}\) according to C-H stretching in the fatty acid spectrum. The intensity of C-H stretching was observed to be higher in the spectrum of Mg-stearin basic soaps based on double decomposition method than direct method. Similarly, the absorption band observed near 1570.43-1450.31 cm\(^{-1}\) was corresponding to the carboxyl group of the fatty acid. The spectrum with wavenumbers as mentioned above were observed in the basic soap that has been manufactured by direct method and double decomposition method. Even so, the spectrum intensity observed from basic soaps based on double decomposition methods was still higher than direct method. Therefore, in the case of the strength of the hydroxyl group spectrum intensity that reflects the basicity levels of magnesium basic soap, the double decomposition method is the best to be applied to produce the metallic basic soap. However, it should be noted that the drawback of the soaps manufacture by the double decomposition method is the requirement of higher material cost and the production of a lot of unexpected waste (Pratiwi et al., 2016).

3.2. X-Ray Diffraction Analysis

The thermal decomposition of Mg(OH)-stearin basic soap was studied by X-ray diffraction. Diffractogram recorders for the Mg(OH)-stearin basic soaps resulted from both direct and double decomposition process were calcined at 900 °C for 12 hours. X-ray diffraction pattern of Mg(OH)-stearin basic soap, given in Figure 2 for direct and double decomposition process indicate that these basic soaps were sharp and had symmetrical peaks which gave clear indication that both sample were well crystallised and the peaks corresponding to 20 values
near 12°, 23° and 39° were the characteristic of magnesium soaps structures (Jablonska et al., 2013).

Figure 2 XRD patterns of dried Mg(OH) basic soaps based on direct (●) and double decomposition (●) methods

The diffractogram in Figure 2 showed that the basicity of Mg(OH)-stearin resulted by direct method more stable than double decomposition method at 900 °C. This can be seen from the sharp diffraction lines with low intensity displayed by diffractogram of Mg(OH)-stearin basic soaps based on double decomposition method. XRD pattern shows that all peaks at a certain 2θ for Mg(OH)-stearin basic soap based on double decomposition was lower than the direct method. It also showed that Mg(OH)-stearin basic soap resulted by direct method stabilized at 900 °C during 12 hours was more crystalline than that obtained by double decomposition.

3.3 Scanning Electron Microscope (SEM) Analysis

The particle morphology of Mg(OH)-stearin basic soaps powder produced by the direct process and double decomposition process is given as SEM microphotograph in Figure 3a and 3b, respectively.

Figure 3 SEM micrograph of Mg(OH)-stearin basic soaps based on direct method (a) and double decomposition method (b)

From the micrographs of Scanning Electron Microscopy (SEM), it was seen that Mg(OH)-stearin powder of both direct and double decomposition process had amorphous particle morphology structure and the average particle size was 500 μm. There appears to be no significant morphological particle difference between Mg (OH) -steain basic soap manufactured by the
direct process and the double decomposition process. Accordingly, differences in the method of manufacturing soap with magnesium metal did not have a significant effect on the morphological particle of the magnesium basic soap produced.

3.4 Fourier Transform Infrared (FT-IR) Analysis of Fuel

FTIR spectra of liquid bio-hydrocarbon fuel generated by decarboxylation of Mg(OH)-stearin basic soaps based on direct process and double decomposition process are shown in Figure 4.

![Figure 4 IR spectrum of bio-hydrocarbon fuels generated by decarboxylation of Mg(OH)-stearin basic soaps](image)

Figure 4 shows that liquid biohydrocarbons produced by decarboxylation of Mg(OH)-stearin basic soaps, were identified to only had C-C, C-H and C = C groups without oxygenate groups. It shows that the methods of manufacturing basic soaps based on direct and double decomposition process have resulted in good basic soaps as expected for decarboxylation feedstock to produce bio-hydrocarbon fuel.

4. CONCLUSION

The direct method and the double decomposition method are both applicable for the manufacture of Mg(OH)-stearin basic soap. The double decomposition method resulted in Mg(OH)-stearin basic soap that has a better basicity level which is determined based on the IR spectrum intensity, especially of the –OH group. Mg(OH)-stearin basic soap resulted by direct method is more stabilized at 900 °C during 12 hours and is more crystalline than that obtained by double decomposition. There are no significant morphological particle difference between the Mg (OH)-stearin basic soap manufactured by the direct process and the double decomposition process. Liquid bio-hydrocarbons produced from the Mg(OH)-stearin soap decarboxylation process do not contain oxygen functional groups.

5. ACKNOWLEDGEMENT

This work was supported by Indonesian Oil Palm Estate Fund Agency (BPDPKS) under GRS-16 Grant.

6. REFERENCES


