Magnesium stearine production via direct reaction of palm stearine and magnesium hydroxide

M Pratiwi¹, P Ylitervo², A Pettersson², T Prakoso¹ and T H Soerawidjaja¹

¹Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132, West Java, Indonesia
²Swedish Centre for Resource Recovery, University of Borås, 50332 Borås, Sweden

Email: meiti.pratiwi@itb.ac.id

Abstract. The fossil oil production could not compensate with the increase of its consumption, because of this reason the renewable alternative energy source is needed to meet this requirement of this fuel. One of the methods to produce hydrocarbon is by decarboxylation of fatty acids. Vegetable oil and fats are the greatest source of fatty acids, so these can be used as raw material for biohydrocarbon production. From other researchers on their past researchs, by heating base soap from divalent metal, those metal salts will decarboxylate and produce hydrocarbon. This study investigate the process and characterization of magnesium soaps from palm stearine by Blachford method. The metal soaps are synthesized by direct reaction of palm stearine and magnesium hydroxide to produce magnesium stearine and magnesium stearine base soaps at 140-180 °C and 6-10 bar for 3-6 hours. The operation process which succeed to gain metal soaps is 180 °C, 10 bar, for 3-6 hours. These metal soaps are then compared with commercial magnesium stearate. Based on Thermogravimetry Analysis (TGA) results, the decomposition temperature of all the metal soaps were 250 °C. Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX) analysis have shown the traces of sodium sulphate for magnesium stearate commercial and magnesium hydroxide for both type of magnesium stearine soaps. The analysis results from Microwave Plasma-Atomic Emission Spectrometry (MP-AES) have shown that the magnesium content of magnesium stearine approximate with magnesium stearate commercial and lower compare with magnesium stearine base soaps. These experiments suggest that the presented saponification process method could produced metal soaps comparable with the commercial metal soaps.

1. Introduction

Vegetable oil or fat become one of important renewable resource (Güner et al, 2006). Those were extracted from plants, such as coconut, palm oil, sunflower, rapeseed, rubber, jatropha, etc. The main component of oil/fat is triglyceride, an ester of glycerol and three fatty acids. Fatty acids are carboxylic acid with long aliphatic chain. In addition, fatty acids can recognized as carboxylic acids contained by carbon dioxide (RCOOH). The basic idea of this study is to produce hydrocarbon by removing carbon dioxide from fatty acid chain.

In 1947, Chang and Wan [2] reported that by decarboxylation of metal soaps from Tung oil, it can produced of hydrocarbon. The divalent and higher valent metal soaps are water insoluble, but those metal soaps are soluble in various organics solvents [3]. Metal soaps have many application areas such
as driers in paints or inks; lubricants; stabilizers for plastics; fungicides; as catalysts for polymerization, condensation, and hydrogenation; as coatings for ceramic glazes; wire drawing; and waterproofing agents [3,4,5].

Three common processes used in the metal soap manufacture are double decomposition, fusion, and metal-acid reaction processes [6,7]. The first process involves two reactions: aqueous caustic and fatty acids reaction to form a sodium soap, and the sodium and an inorganic metal salt reaction to form the metal 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. 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 raw materials must be pure grade. The metal-acid reaction process is the least used of the three commercial processes [7].

The synthesis of metal soap was carried out with dipolar aprotic solvent, such as acetone, as liquid reaction medium, as described in [8,9]. [10] reported the production of zinc salt by stirring a mixture comprising of zinc oxide, water, molten fatty acids, and citric acids or phosphoric acids as catalyst.

The raw materials in above mentioned processes are fatty acids. This experiment synthesized the metal soaps using triglyceride as the feed for saponification reaction. The abundance and low cost of triglyceride compared to the fatty acids are the main interests of this research. Most of the previous researches were using the metathesis method to produce metal soaps from vegetable oil/fat or triglyceride [11, 12, 13, 14, 15].

[16] reported that by heating divalent metal base soap, such as calcium and magnesium, without air at atmospheric pressure and higher temperature (200-400 °C), the decarboxylation reaction occurred to produced hydrocarbon.

This report will present the production of metal soaps via direct reaction of palm stearine and magnesium hydroxide by the Blachford [17] method. The aim of this research is to investigate the characteristics of the metal soaps produced by direct reaction of palm stearine and magnesium hydroxide by Blachford method and the produced metal soaps is compared with the commercial magnesium stearate.

2. Experimental

Palm stearine used in this research was taken from local oil refinery. The saponification and acid value of palm stearine is 190.7 mg KOH/g and 0.6 mg KOH/g. The composition of palm stearine were mainly of 68.24%-mol palmitic acid, 5%-mol stearic acid, and 20.63%-mol oleic acid. The magnesium hydroxide was prepared by co-precipitation of MgCl₂·6H₂O with sodium hydroxide (modified from [18,19]). Magnesium stearine obtained from direct reaction of palm stearine and magnesium hydroxide [17]. Magnesium stearic, technical grade, was used to compare with the metal soaps products.

2.1. Preparation of magnesium hydroxide
The magnesium hydroxide was prepared by using two burrettes, the first burrette filled with 100 ml of 0.5 M MgCl₂·6H₂O (A) and the second burrette with 500 ml of 0.6 M NaOH (B). The co-precipitation process controlled by the drop rate of burrette B, which was 5 times higher than the drop rate of burrette A. The co-precipitation was conducted under vigorous stirring at room temperature. The pH of the solutions was maintained at 8.5 with Triz buffer. When the co-precipitation process was finished, the suspensions were kept stirred for 30 minutes, then the suspensions was filtered with Buchner filter and washed with hot water (60 °C). Afterwards, the slurry was dried at room temperature, and then dried at 105°C for 12 hours. The dry slurry was ground, formed Mg(OH)₂ white powder.

2.2. The preparation of magnesium stearine soaps via direct reaction
The magnesium hydroxide was prepared by using two burrettes, the first burrette filled with 100 ml of 0.5 M MgCl₂·6H₂O (A) and the second burrette with 500 ml of 0.6 M NaOH (B). The co-precipitation
process controlled by the drop rate of burette B, which was 5 times higher than the drop rate of burette A. The co-precipitation was conducted under vigorous stirring at room temperature. The pH of the solutions was maintained at 8.5 with Triz buffer. When the co-precipitation process was finished, the suspensions were kept stirred for 30 minutes, then the suspensions was filtered with Buchner filter and washed with hot water (60 °C). Afterwards, the slurry was dried at room temperature, and then dried at 105°C for 12 hours. The dry slurry was ground, formed Mg(OH)_2 white powder.

The saponification reaction was carried out at 140 and 180 °C using Blachford method [17] by reacting palm stearine, magnesium hydroxide, and water. The amount of triglyceride and magnesium hydroxide were approximately same with their stoichiometric reaction (see Reaction 1 and 2). Two types of metal soaps were produced by this method, magnesium stearine (Mg(RCOO)_2) and magnesium stearine base soaps (Mg(RCOO)(OH)). The time of reaction were 3 and 6 hr for the magnesium base soaps, and 3 hr for magnesium stearine.

The saponification reaction produce magnesium stearine as follows:
\[
2 \text{H}_2\text{C(OOCR)}\text{CH(OOCR)CH}_2\text{(OOCR)} + 3 \text{Mg(OH)}_2 \rightarrow 2 \text{CH}_2\text{OH.CH(OH) \cdot CH}_2\text{OH} + 3 \text{Mg(RCOO)}_2
\]  
(reaction 1)

and the saponification reaction for magnesium base soap:
\[
\text{H}_2\text{C(OOCR)}\text{CH(OOCR)CH}_2\text{(OOCR)} + 3 \text{Mg(OH)}_2 \rightarrow \text{CH}_2\text{OH.CH(OH) \cdot CH}_2\text{OH} + 3 \text{Mg(RCOO)(OH)}
\]  
(reactio

The reaction was performed at 100 ml mini-stainless steel autoclave. The reaction pressure was 6 bar at 140 °C and 10 bar at 180 °C. 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, then ground it into magnesium soap powder.

2.3. Magnesium soaps characterization
The conversion of metal soaps was determined by weighing the wash water before and after the purification of the metal soaps. The thermal behaviour of metal soaps were obtained with TGA instrument (TGA/DSC 3* Star* System Mettler Toledo). The samples were heated from 25 to 700 °C at a constant heat rate of 5 K/min under 80 ml/min nitrogen gas flow. The MP-AES instrument (Agilent Technologies) was conducted to measure the magnesium contents of the metal soaps, by using standard solutions with 1-10 ppm of magnesium. The metal soap samples were digested in nitric acid solution 65% using Microwave Ethos Up (program: 12 °C/min to reach 200 °C and hold for 10 min). SEM instrumen were used to investigate the topography surface of the metal soaps and magnesium content in the metal soaps surface, with secondary electrons (LFD), backscattered electrons (SSD), and EDX.

3. Results and discussion

3.1. Saponification reaction
The saponification reaction was unsuccessfully conducted at 140 °C. The appearance of the metal soaps that produced at this operation condition were like slurry at room temperature. The preparation of metal soaps at 180 °C produced magnesium stearine and magnesium stearine base soap. However, the texture of the produced metal soaps were different to the commercial magnesium stearate. The metal soaps produced has rougher texture compared with commercial magnesium stearate, which is very powdery and fluffy. The purification was performed by washed the metal soaps with hot water. The metal soaps were insoluble in water, but the glycerol was soluble and the triglyceride slightly soluble in hot water. The purification was aimed to remove the produced glycerol and, slightly, remained triglyceride in saponification products. The reaction conversion was determined by the weight of the wash water before and after the washing step, in addition to the visual look of the wash water. There were no significant difference in weight of the washing water and no triglycerides were observed in the water after wash, indicating that the reaction conversion was nearly 100%.
following analysis (TGA, SEM-EDX, and MP-AES) were performed on magnesium stearate, magnesium stearine, magnesium base stearine (3 hr reaction), and magnesium base stearine (3 and 6 hr reaction).

3.2. TGA
The TGA result of four types of magnesium soaps, comprised of magnesium stearate, magnesium stearine, magnesium stearine base soap with either 3 (Mg(stearine)$_2$) and 3-Mg(stearine)(OH)) or 6 (6-Mg(stearine)(OH)) hr saponification reaction at 180 °C, are given in Fig.1. The thermal decomposition of magnesium soaps can be expressed as: Mg(RCOO)$_2$ $\rightarrow$ RCO$^-$ + CO$_2$ + MgO (reaction 3)

The final residues weight for magnesium stearate and magnesium stearine were similar compared with the molecular formula of magnesium oxide. The final residue of magnesium base soaps were higher than magnesium stearate and magnesium stearine, because the amount of magnesium hydroxide as reactant in the Reaction 2 is twice from Reaction 1.

![TGA curves of magnesium soaps](image)

**Figure 1.** TGA curves of magnesium soaps

The thermogravimetric analysis (Figure 1) shows that these soaps lose their moisture up to 110 °C, then the weight was stable at 110 °C until 300°C. Between 300 and 500 °C the samples decomposed very rapidly. And finally show small weight change during further increased temperature.

Both of magnesium base stearine have similar thermal behaviour. The magnesium stearine decomposed more rapidly compared with the magnesium stearate. It may because of the difference of the fatty acids content in the metal soaps. The magnesium stearine comprise unsaturated fatty acids, oleic acids, the double bond is easier to decompose compared to the saturated bond. Typical fatty acids composition in commercial magnesium stearate is saturated fatty acids, e.g. palmitic and stearic acid.

3.3. SEM-EDX
The SEM-EDX analysis was used to determine the topography surface and magnesium content at the metal soap’s surface. Figure 2 shows the elements positioning in the magnesium stearate surface, there are interactions between sodium and sulphur, marked with the red ellips, it may be the remaining of sodium sulphate, byproduct of precipitation method. The commercial magnesium stearate was manufactured by precipitation or double decomposition reaction as follow

RCOOH (l) + NaOH (s) $\rightarrow$ RCOONa (aq) + H$_2$O (l) (reaction 4)

RCOONa (aq) + MgSO$_4$.7H$_2$O (aq) $\rightarrow$ Mg(RCOO)$_2$ (s) + Na$_2$SO$_4$ (aq) + 7H$_2$O (l) (reaction 5)
Figure 2. SEM element image of Mg(stearate)$_2$

Figure 3. SEM element image 3Mg(stearine)$_2$

Figure 4. SEM element image of 3Mg(Stearine)(OH)
Figures 3 and 4 show that there was interaction between magnesium and oxygen in the magnesium stearine and magnesium based stearine soaps. This indicate that there were remained magnesium hydroxide in the soaps (see Reaction 1 and 2), especially in the magnesium based stearine with excess of Mg(OH)$_2$.

Figure 5 a-c show the topography surface of the magnesium soaps. Magnesium stearate (5a) have the most homogenous topography surface compared with others soaps. The magnesium based stearine has more similar morphology to magnesium stearate, compared with magnesium stearine. From Figure 5b, magnesium stearine has morphology appearance like a molten soap. To get a topography surface similar to commercial magnesium soaps, the amount of magnesium hydroxide as reactant usually higher than the stoichiometry in Reaction 1 [12,13].

3.4. Magnesium content
The MP-AES analysis was carried out to quantify the magnesium content in the metal soaps. Before the MP-AES analysis, Mg$^{2+}$ ions were recovered from magnesium samples by digestion with nitric acid 65%. The weight percent of Mg$^{2+}$ ions for the metal soap samples was determined as shown in Table 1. The final residue of magnesium stearine base soaps were higher than magnesium stearine (Figure 1) due to the magnesium content in the soaps. The EDX analysis only give an indication of the ion content in the metal soaps since it measured the ion content based on the area observed. For the EDX analysis, the samples has to be homogenous in order to get reliable results.
Table 1. The magnesium content in metal soaps

| Samples                | %-% | a          | b          | c          |
|------------------------|-----|------------|------------|------------|
| Mg(stearate)₂          | 4.45 ± 0.59 | 5.91 b     | 4.84 a     |
| 3-Mg(stearine)₂        | 4.19 ± 0.22 | 4.35 b     | 5.00 a     |
| 3-Mg(stearine)(OH)     | 6.76 ± 0.60 | 6.71 b     | 9.04 c     |
| 6-Mg(stearine)(OH)     | 6.70 ± 0.61 | n.a.       | 9.04 c     |

The MP-AES measurements were carried out three times and the average values from the analysis results are reported in Table 1. The magnesium content in Mg(stearine)₂ and Mg(stearate)₂ was similar. Despite the lower weight percent from analysis compared with theoretical, these results showed that the direct reaction of magnesium hydroxide and palm stearine could be an alternative process to produce magnesium soaps.

4. Conclusion
The direct reaction of magnesium hydroxide and palm stearine produced magnesium soap at 180 °C and reaction time from 3 hours. It was not suitable to perform the direct reaction method at 140 °C, even when the reaction time already pro-longed to 6 hours, to yield magnesium soaps. Regarding thermal behaviour, the magnesium stearine produced with this method was quite comparable with the commercial magnesium stearate. This method is still needed to be improved, such as controlling the stirring rate of reaction, grinding apparatus to get homogenous size of metal hydroxide etc.

Acknowledgement
We acknowledge the support from Linnaeus Palme Program, Sweden.

References
[1] Dandik L, Aksoy H A and Erdem-Senatalar A 1998 Energy & Fuels 12 pp 1148-52
[2] Chang C and Wan S 1947 Industrial and engineering chemistri 39 pp1543-48
[3] Akanni M S, Okoh E K, Burrows H D and Ellis H A 1992 Thermochimica Acta 208 pp 1-41.
[4] Elliott S B 1946 The alkaline-earth and heavy metal soaps : American Chemical Society Monograph Series (New York : Reinhold Publishing Corporation) pp 111-43
[5] Rogers R H, Park P and Opem J D 1962 U.S.Patent No.23,047,496.
[6] Rogers R H Jr and Blew W R Jr 1959 U.S.Patent No.2,890,232.
[7] Gönen M, Balköse D, İnal F and Ülkü S 2005 Ind. Eng. Chem. Res 6 pp1627-33
[8] Akkers J B, Littler J A and Peters D C 1982 U.S. Patent No 4,337,209
[9] Akkers J B, Littler J A and Peters D C 1984 U.S. Patent No 4,427,572
[10] Chen B 2004 U.S. Patent No 6,689,894.
[11] Balköse D, Egbuchunam T O and Okieimen F E 2010 J.Therm. Anal. Calorim
[12] Folarin O and Enikanoselu O 2010 J. Appl. Sci. Environ. Manage 14 pp 69-73
[13] Folarin O M, Siyanbola S Y and Shittu A T 2011 EJEAFChe 10 pp 2623-28
[14] Isaac I O 2014 LJARCS 1 pp 14-22
[15] Ossai E 2014 J. Appl. Sci. Environ. Manage 18 pp 359-63
[16] Markley K S (editor) 1961 Fatty acids : their chemistry, properties, production, and uses part 2 (New York : Interscience publishers Inc)
[17] Blachford J 1982 U.S. Patent No 4,316,852.
[18] Matter P H and Ozkan U S 2005 J. Catal. 234 pp 463-75.
[19] Matter P H, Braden D J and Ozkan U S 2004 J. Catal. 223 pp 340-51.