

Investigation of Ca/Mg/Zn Metals Mixing Ratio for Production of Soap with High Alkali Content

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Abstract—A study about variation of calcium metal concentration in mixed Ca/Mg/Zn metal to produce of soap with high alkaline content together with oleic acid was studied. Calcium metal which is used vary from 15 (15 μ), 50 (50 μ) and 85 (85 μ) % with modified fusion as method for saponification. Variation of calcium metal into mixture of Ca/Mg/Zn metal is proved to have different effect to alkaline content value and oleic acid conversion into basic soap. Soap from variation of 85 μ had alkaline content of 44.5% weight. Inside the whole soap produced from 15 μ , 50 μ and 85 μ , hydroxyl group was detected with low intensity inside the range of wavenumber length of 3200-3570 cm^{-1} according to FT-IR spectrum. Maximum conversion of oleic acid into soap happened when varied at 50 μ is 97.9%.

Index Terms—Metal mixing, alkaline content, soap, hydroxyl group.

I. INTRODUCTION

Interest in renewable fuels has been encouraged in recent years by a number of environmental, economic and geopolitical considerations, including global warming, dwindling petroleum deposits, rising crude oil prices and a desire for energy independence [1]. Against this background, biofuels – fuels derived from biomass – have been proposed as a renewable, carbon-neutral alternative to fossil fuels.

Although fatty acid methyl esters (FAMEs) obtained from the transesterification of triglyceride with methanol have received significant attention as a renewable diesel fuel, the presence of oxygen in the molecule induces oxidative and thermal instability and lowers its heating value [2].

Today many researchers are interested in conducting research with a target to produce renewable fuels as fossil fuels alternative which has compatible characteristic. Therefore, there is increasing interest in utilizing biomass as a feedstock for production of alternative fuel. This is primarily due to the renewability and environmental

friendliness of this type of raw material [3]. A number of efforts have been made by researchers to find sources of raw materials [4] and production methods [5] that have the potential for the realization of the research targets mentioned above. One of the raw materials that has been investigated and is known to have great potential for producing biohydrocarbon type renewable fuels is metal soap (derivative of vegetable oil and fat or fatty acids). Our previous studies have shown that the magnesium basic soap derived from stearic acids can be converted into renewable fuel. An alternative path that can occur under milder condition is via that decarboxylation reaction, which can convert the basic soap into biohydrocarbon components [6]. For instances, Mg-Zn basic soap has been successfully used as a reactant to be decarboxylated into jet biofuel [7]. However, not all metal soaps are good for use as raw material for making biohydrocarbons via decarboxylation, except basic soap [8]. The prepared of basic soaps has been known to be successful with two-valent metals from the alkaline earth and transitional groups. Our previous research which used a mixture of two metals, namely Mg/Fe for soap making, has been proven to form basic soaps according to the results of analysis of pH and acid numbers [9]. However, the biohydrocarbon from the decarboxylation of the soap still contains a high fraction of olefins (> 30%) almost equal to the paraffin fraction. Further investigation related to the high fraction of olefins in biohydrocarbons from decarboxylation of Mg/Fe soap proves that this condition is caused by the hydroxide of the metal Mg in the reactants (Mg/Fe base soap) that has disappeared at a temperature of around 300 °C [10], before the decarboxylation process reaches a temperature of 375 °C. As a result, more of the reactants decomposed at temperatures > 300 °C take place with little or no hydroxide in them. Such a phenomenon will certainly produce many fractions of olefins rather than paraffins. After knowing the triggers for the formation of olefin fractions, two important things related to soap need to be studied further, namely first, determine the level of hydroxide by calculating the alkaline content. Alkaline content is the number of alkaline bases that combine as soap along with fatty acids [11]. Alkaline content analysis is intended to quantitatively determine the basic level of soap and be the initial guide to the liquid biohydrocarbons produced. If soap is produced based on oleic acid, then the maximum value of alkaline content of basic soap reaches 50% by weight. When the soap produced has a maximum alkaline content, the soap is very good to be used as a decarboxylation reactant to produce liquid biohydrocarbons with a dominant paraffin fraction. Second, mixing other metals (other than Mg) for soap making, so that

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basic soap can be obtained that does not lose its hydroxide until the decarboxylation temperature reaches 400 °C. Ono and Hattori [12] report that the hydroxide of metal Ca, will only experience rapid decomposition and loss of hydroxide at a temperature of 450 °C or a temperature above the decarboxylation point. Therefore a thought was made to reduce a number of moles of Mg and replace them with Ca for making basic soap. The expectation is to get soap with a maximum value of alkaline content which is close to or reaching 50% by weight, and not to lose hydroxide until the decarboxylation temperature reaches 400 °C. However, the suitable Ca content to replace a portion of Mg so that it has a superior performance for making basic soap still needs to be studied further. Therefore, this study aims to obtain a superior performance of Ca / Mg / Zn in basic soaps in terms of the alkali content value parameters.

II. MATERIALS AND METHOD

A. Materials

Oleic acid ($C_{17}H_{33}COOH$, 75%) was obtained from PT. Energi Sejahtera Mas. Calcium acetate $[Ca(CH_3COO)_2 \cdot xH_2O]$, Magnesium acetate $[Mg(CH_3COO)_2 \cdot 4H_2O]$ and Zinc acetate $[Zn(CH_3COO)_2 \cdot 2H_2O]$ were purchased from Merck. Sodium hydroxide (NaOH) was purchased from PT. Brataco Bandung.

B. Treatment of Metal Mixtures

The ratio of Ca metal compounds to Ca/Mg/Zn mixtures is chosen in the range of 15 to 85% by weight. Three point ratios that are determined for the effect of basic soap content, respectively are 15, 50 and 85% by weight. The three metal inclusion points were then expressed as treatments $\mu 15$, $\mu 50$ and $\mu 85$.

C. Saponification

The Ca/Mg/Zn basic soap was prepared by using the modified fusion method, using oleic acid as the oil feedstock. The procedure is as follows: the oleic acid 0.1 mol and 0.05 mol of mix-metal hydroxide were fed into blender whereas mixed. Then the mixture was heated to 40 – 45 °C, added 4 ml of water and 0.18 of formic acid 98 – 100 %. The mixing was finished at least 30 minute, then the basic soap was formed, dried at 60 °C. The saponification experiments were performed in a stainless steel heating blender operating in a batch mode.

D. Variable Analysis

The variables observed were alkali content, conversion of oleic acid to soap and Fourier Transform Infra-Red (FT-IR) analysis. The number and strength of hydroxide molecule of the basic soap were characterized by FT-IR. The FT-IR spectra were measured on a Alpha Platinum Bruker FT-IR spectrometer with Platinum Diamond sampling. FTIR spectrometer over a range of 500-4000 cm^{-1} . The pyridine use as a probe molecule. Infrared spectroscopic measurements of the adsorbed pyridine (Py-IR) were recorded on a Bruker Equinox 55 spectrometer. The self-supported wafer sample (*90 g) was placed in a gas-tight

cell with CaF_2 windows. Initially, the sample was pretreated in He flow at 773 K for 2 h. Then, it was cooled to 423 K, and a blank spectrum was taken. Saturated pyridine vapor was introduced into the cell for 2 h in order to saturate the acid sites. The excess pyridine was then purged from the cell by flowing He for 12 h. Four spectra were obtained for each sample at 423 K, both on the saturated sample, and after outgassing at increasing temperatures from 573 to 773 K.

Total alkali content (TAC) are the sum of the alkali bases combined as soap with fatty and rosin acids. Total alkali content was determined by titration method. The total alkali content is given by mass, by the formulae:

$TAC = 0.056 \times (V_o T_o - V_1 T_1) \times (100/m)$, expressed as potassium hydroxide (KOH) for potassium soap;

where: m is mass, in grams of the test portion; V_o is the volume, in milliliters of the standard volumetric acid solution used; V_1 is the volume, in milliliters, of the standard volumetric sodium/potassium hydroxide solution used; T_o is the exact normality of the standard volumetric acid solution; T_1 is the exact normality of the standard volumetric sodium/potassium hydroxide solution [13].

Fatty acid conversion was determined by equation:

$Conversion = ((initial\ acid\ value - final\ acid\ value) / initial\ acid\ value) \times 100\%$

III. RESULT AND DISCUSSION

This section presents information about hydroxide content as a guide related to the alkalinity, Fourier Transform Infra-Red (FT-IR) of the basic soap and conversion of oleic acid into the soaps.

A. Alkaline Content

Initial work focused on testing the influence of different calcium metal content on the alkaline content of Ca/Mg/Zn basic soap derived from oleic acid. Fig. 1 shows that the variation of the metal content of calcium in the metal mixture Ca/Mg/Zn to form soap with oleic acid through the saponification process, affects the alkaline content of the soap produced. Ca/Mg/Zn basic soap with calcium content are 85% (85μ) provided higher alkaline content than that achieved in the basic soap with 50μ and 25μ . It seems that more hydroxide (OH) content is formed in the basic soap when the metal mixture Ca/Mg/Zn used for making soap with oleic acid is included 85% (85μ) calcium compound (calcium acetate).

In other words, the inclusion of 85μ of calcium acetate compounds in a mixture of metal Ca / Mg / Zn creates a greater opportunity to form basic soap with oleic acid. The opportunity was evidenced by the higher alkaline content produced by the soap from the 85μ treatment, which is about 44.5% by weight compared to the treatment of 50μ (38.4% by weight) and 15μ (39.7% by weight).

The data in Fig. 1 show that the 85μ calcium acetate is more effective for saponification reaction to result the Ca/Mg/Zn basic soap derived oleic acid. Interestingly, the alkaline content of basic soap with 35% (35μ) calcium acetate was 39.7% by weight or higher around 1.3% by weight than 38.4% by weight for 50μ . Indeed, this difference

is considered small and not significant so it can be ignored.

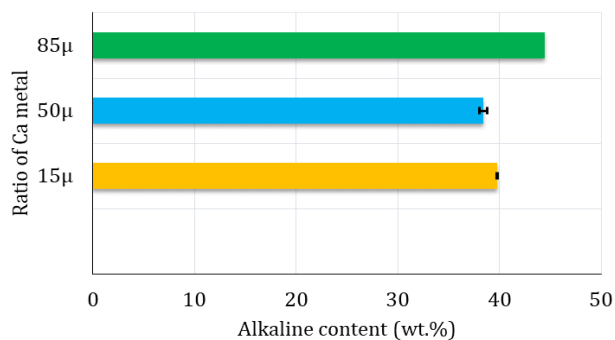


Fig. 1. Effect Ca metal ratio on alkali content.

B. Fourier Transform Infra-Red (FT-IR)

To ensure that a mixture of Ca/Mg/Zn metal has formed basic soap along with oleic acid through saponification reaction, FT-IR analysis needs to be done. FT-IR spectrum was measured to analyze the change of hydroxide contents in basic soap. The peak intensity of the hydroxyl group (-OH) usually appears in the range of wavenumber regions between 3200-3570 cm^{-1} [14].

In FT-IR spectra of Fig. 2 the peak intensity of hydroxyl group (-OH) tends to be uniform although Ca content was increased from 35μ to 85μ. It shows that at a treatment of 15μ, 50μ and 85μ detected have a hydroxyl (-OH) group with a weak intensity in a very wide peak (in the form of a valley) in the range of wavenumber areas between 3200 and 3570 cm^{-1} . The detection of the -OH group is a measure of the progress of the saponification reaction with a mixture of Ca/Mg/Zn metals and the exchangeable proton of carboxylic acid group. This phenomenon implies that the soap produced by the three treatments is basic soap.

In the FT-IR spectrum shown by Fig. 2 also appears that the peak intensity in the range 3200-3570 cm^{-1} decreases when the Calcium content included increases. Especially, -OH group almost disappears if Ca content is 85μ. Although the intensity of the FT-IR spectrum pointing to the -OH group appears to be weak, it is sufficient to suggest that basic soap has been formed during the saponification reaction. Indeed, the formation of basic soap $[M(RCOO)(OH)]$ has been confirmed, however, a number of stoichiometric soap $[M(RCOO)_2]$ is estimated to still be formed as well. This phenomenon can be shown by the alkaline content of the three treatments not reaching a maximum value which is 50% weight [15].

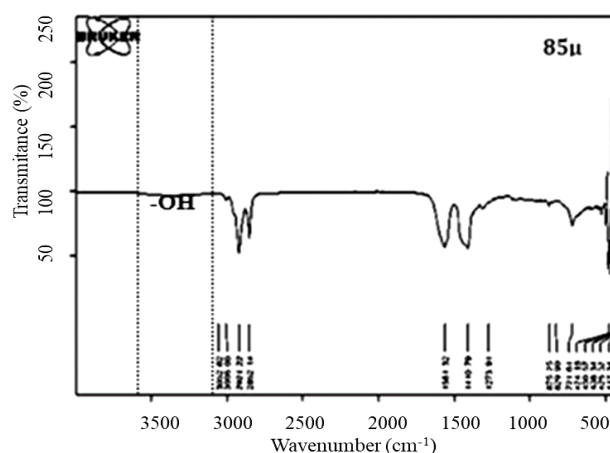
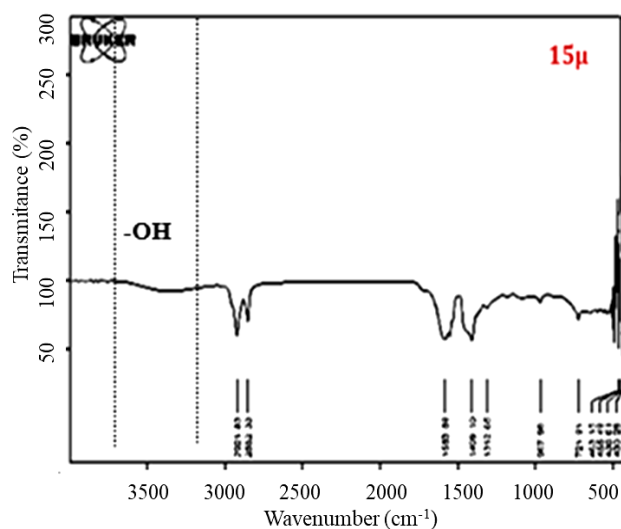
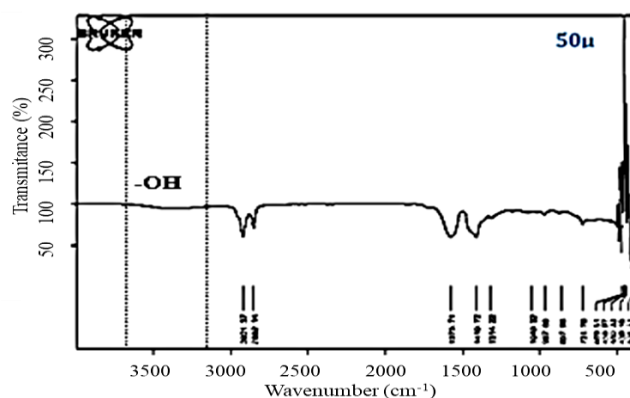


Fig. 2. FT-IR spectra of the basic soaps based on 15μ, 50μ and 85μ.

Previously there was an expectation that there would be an increase in the peak intensity of the transmittance of the -OH group with the increase in the value of the alkaline content. However, the results of FT-IR analysis show that there is no effect of the alkaline content on the peak intensity of the -OH transmittance intensity as well as the width shift of wavenumber. This fact gives a signal that, the concentration difference of Ca metal inclusion for a mixture of Ca/Mg/Zn only affects the alkali content and not at the peak transmittance intensity of the FT-IR spectrum.

C. Conversion

The conversion of oleic acid into Ca/Mg/Zn basic soap is shown in Fig. 3. And Fig. 3 shows that variations in the concentration of metal Ca in a mixture of Ca/Mg/Zn metal in the range of 15 - 85% effectively converts oleic acid into soap with conversion rates exceeding 90%.

Inclusion of 50% (or 50μ) of calcium acetate in the Ca/Mg/Zn metal mixture has converted around 97.9% by weight of oleic acid into soap, 2.5% higher than 15μ and 3.5% compared to 85μ. This means that the performance of the Ca/Mg/Zn metal mixture for converting oleic acid becomes better, when the inclusion of calcium acetate in the metal mixture is 50μ.

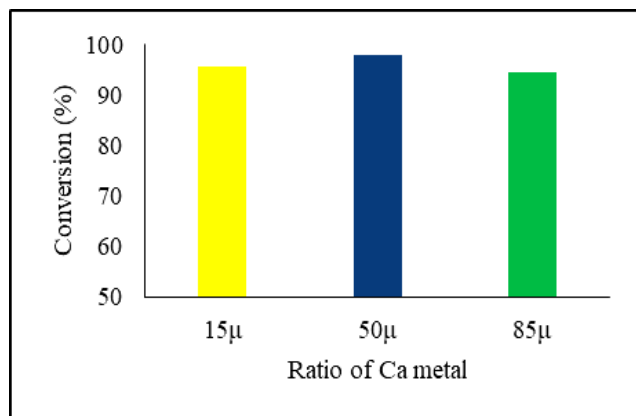


Fig. 3. Conversion of oleic acid to soap.

The conversion activity was very high at 50μ and under these conditions, converting almost reaches 100% of the feed. Lower conversions can be observed at 85μ, but it is almost similar to 35μ. Although the 50μ treatment seems more effective in converting oleic acid to soap, however, the soap produced is not entirely basic soap $[M(RCOO)(OH)]$. It can be seen from the alkali content of the content at 50μ much smaller than 85μ. Thus a number of stoichiometric soap $[M(RCOO)_2]$ are guessed to have formed in experiments with a calcium concentration of 50μ.

IV. CONCLUSION

The variation of calcium content in the metal mixture Ca/Mg/Zn for making basic soap affects the alkaline content of the soap and the conversion of oleic acid to soap. The highest alkaline content value is 44.5% by weight produced by the 85μ treatment. Oleic acid conversion into soap by 97.9% was produced by treatment 50μ, higher than 15μ and 85μ. Soap from a mixture of Ca/Mg/Zn metal with calcium metal inclusion in the range of 15-85μ with oleic acid was detected with weak intensity, as basic soap containing the -OH group in the wavenumber width range 3200-3570 cm^{-1} according to the FT-IR spectrum.

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