

The Effect of Adding Mg-Zn/Al Hydrotalcite on the Decarboxylation Product of Hydroxy Pelargonate Soap

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ARTICLE INFORMATION	ABSTRACT
Received 30 September 2022 Accepted 5 Mei 2023 doi.org/10.35313/fluida.v16i1.4502	<p><i>Pelargonic acid is a by-product of the ozonolysis reaction of oleic acid to azelic acid. Pelargonic acid decarboxylation is the process of removing a carboxyl group (-COO-) from pelargonic acid (C₉H₁₈O₂) to produce n-octane (C₈H₁₈) hydrocarbons, which are the main group of hydrocarbons that make up gasoline. The main parameter in gasoline is the octane number. The octane number of n-octane (C₈H₁₈) is 15, which is considered low, while good gasoline is desired to have a high-octane number. To convert straight-chain alkanes and alkenes into branched alkanes and alkenes, an isomerization process can be carried out on vapor-cracking products using a solid catalyst. Transition metals and their compounds can be used as catalysts. Transition metals are able to change the oxidation state, create complex compounds, absorb other substances on the metal surface, and activate these substances. The transition metals used in this study are Zn and Al. The stages of the research process were the preparation of Mg-Zn/Al hydrotalcite base, the manufacturing of hydroxy pelargonate soap, and the decarboxylation of hydroxy pelargonate soap. The results of this study found that the highest product gain, namely 64.76%, occurred when Mg-Zn/Al = 5:5:2 hydrotalcite was in 300% excess. The highest product selectivity to 2.16% n-octane occurred in the use of a 300% excess of Mg-Zn/Al = 3:3:2 hydrotalcite. A low Al/Mg/Zn ratio of 2:10 can increase product yield; a high Al/Mg/Zn ratio of 2:6 can increase product selectivity and lower the freezing point.</i></p>
<p><i>Keywords:</i> Pelargonic acid Decarboxylation Isomerization Mg-Zn/Al</p>	

INTRODUCTION

The increase in domestic fuel production in 2021 relative to 2020 is not proportional to the rise in fuel imports' value. Domestic fuel production increased from 251.47 million barrels in 2020 to 256.05 million barrels in 2021. On the other hand, fuel imports increased from 131.29 million barrels in 2020 to 183.61 million barrels in 2021 [1]. The import value of Indonesian petroleum products or fuel oil (BBM) increased by 74% from US\$ 8.28 billion in 2020 to US\$ 14.39 billion, or approximately 205.7 trillion rupiah, in 2021. The increase in petroleum imports in 2021 is due to the rise in global crude oil prices [2]. Research on biofuels must be encouraged to attain energy independence by reducing the country's reliance on imported fuels.

In the laboratory, oleic acid is oxidized with a KMnO₄ solution to produce pelargonic acid [3]. On an industrial scale, pelargonic acid is a byproduct of the industrial ozonolysis of oleic acid into azelic acid. **Table 1** shows some oleic acid sources with different contents (%w/w).

Saponification is the hydrolysis of an ester under alkaline conditions that yields the carboxylic acid's salt and alcohol. Saponification is the reaction between an alkali metal (base) and oil or lipid, resulting in soap formation. The saponification reaction aims to produce soaps (fatty salts) that can be fed to decarboxylation reactions [5].

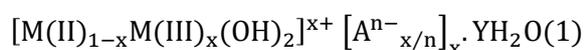
Table 1. Source of oleic acid

Source	Content (%w/w)
Coconut	6-8
Palm kernel	9-16
Nutmeg	≈10
Palm	38-44
<i>Pongamia pinnata</i>	44-72
<i>Chalophyllum inophyllum</i>	48-53
<i>Jatropha curcas</i>	37-63
Canola	52-66
Cotton seed	9-32
Kapok seeds	21-22
Cloudy seeds	8-9
Soya bean	20-30
Rubber seeds	17-30
Candlenut	10.5
<i>Reutealis trisperma</i>	11,6
Tung	4-9

Decarboxylation removes the carboxyl group (-COOH) from a chemical compound to produce carbon dioxide (CO₂). Decarboxylation can be accomplished thermally, photochemically, or catalytically using a catalyst. With the aid of metal catalysts, decarboxylation reactions can be carried out. Using a Pd/C catalyst, Snare et al. decarboxylated stearic acid to obtain C₁₇ hydrocarbons [6]. Setiadi and Suranto conducted a saponification reaction to produce heavy ions (soap) from jatropha oil and a strong base Ca(OH)₂. The fatty salts conducted a decarboxylation reaction with excess Ca(OH)₂. This decarboxylation reaction yields straight-chain hydrocarbons with C atom lengths between C₁₃ and C₂₈, also known as diesel [5].

From the pyrolysis of calcium soap, Chang and Wan discovered hydrocarbons similar to crude oil [7]. The by-product of decarboxylation with calcium soap is calcium carbonate. Calcium carbonate requires a decomposition temperature of 973 K [8], so it is necessary to investigate different transition metals that produce carbonate compounds that decompose at lower temperatures.

Hydrotalcite is a hydroxide compound with two layers that contain transition metal ions [9]. In its natural state, hydrotalcite is a magnesium and aluminium hydroxycarbonate with the formula [Mg₆Al₂(OH)₁₆]²⁺CO₃²⁻·4H₂O. The general equation for hydrotalcite is given below:



with M(II) are examples of divalent metal

cations, like Mg²⁺, Zn²⁺, Ni²⁺, Cu²⁺, Mn²⁺, and Co²⁺; on the other hand, Al³⁺, Cr³⁺, and Fe³⁺ are trivalent metal cations. Hydrotalcite is similar to brucite Mg(OH)₂, with Mg²⁺ ions encircled by six OH⁻ ions in an octahedral [10]. The Mg²⁺ anion in hydrotalcite is substituted by the cation aluminium [11].

The metal magnesium is environmentally beneficial. Magnesium carbonate's melting point (decomposition) is 350°C [12]. According to equilibrium calculations, magnesium carbonate (MgCO₃) readily decomposes into CO₂ and MgO under operating conditions [8].

Decarboxylation of pelargonic acid is the elimination of the carboxyl group (-COO-) from pelargonic acid (C₉H₁₈O₂) in order to generate n-octane hydrocarbons (C₈H₁₈). C₈ hydrocarbons are the predominant type of hydrocarbon found in gasoline. The primary characteristic of gasoline is its octane number. The octane number of n-octane (C₈H₁₈) is -15; on the other hand, the desired gasoline has a high octane number. **Table 2** displays that the isomeric compounds of n-octane (C₈H₁₈) have high octane numbers.

Table 2. Research octane numbers of n-octane isomers

No	Compound	Research Octane Number
1	n-Octane	-15
2	2-Methylheptane	21
3	3-Methylheptane	27
4	4-Methylheptane	26
5	2,2-Dimethylhexane	72
6	2,3-Dimethylhexane	71
7	2,4-Dimethylhexane	65
8	2,5-Dimethylhexane	55
9	3,3-Dimethylhexane	74
10	3,4-Dimethylhexane	75
11	2,2,3-Trimethylpentane	110
12	2,2,4-Trimethylpentane	100
13	2,3,3-Trimethylpentane	106
14	2,3,4-Trimethylpentane	103
15	3-Ethylhexane	34
16	3-Ethyl-2-methylpentane	87
17	3-Ethyl-3-methylpentane	81

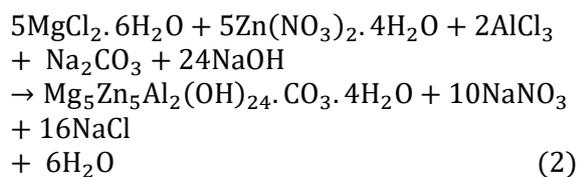
Solid catalysts can isomerise and/or hydroisomerise the cracking product vapors to convert straight-chain alkanes and alkenes into branched alkanes and alkenes, such as converting n-octane into isooctane (2,2,4-trimethylpentane). If the catalyst used in the decarboxylation reaction can

branch the product, the resulting product will have a high octane number.

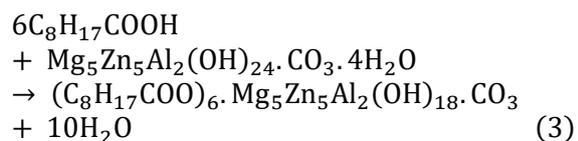
High activation energy is required for isomerization reactions; therefore, a catalyst is required. Pt, Pd, and Ag have been extensively used as catalysts in the isomerization of hydrocarbons into branched hydrocarbons (high octane numbers). Green diesel is produced by the decarboxylation reaction of free fatty acids with a 5% w/w Pd/Si-C-4 catalyst at 300 °C and 15 bar pressure [13]. The price of Pt, Pd, and Ag catalysts is high, so it is necessary to research ZnMg(OH)₂ catalysts, which are less expensive transition metals, to form a branch during the saponification reaction.

Since they can alter oxidation levels, form complex compounds, incorporate other substances on metal surfaces, and activate them, transition metals and their compounds can be used as catalysts. Lange et al, found the effectiveness of transition metal promoters on n-butane isomerization with a temperature of 373 K to be Mn > Fe > Co > Zn, which means the more to the left of the location of an element in the periodic table, the greater its effectiveness [14], in contrast to Vera et al., who found the activity of transition metal promoters on the isomerization of n-butane with a temperature of 473 K from left to right in the periodic table to be Cr Fe Co Ni [15].

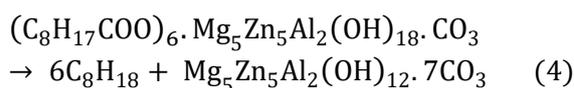
The following reaction occurs when producing Mg-Zn/Al hydrotalcite base:



The reaction of Mg-Zn/Al hydrotalcite with hydroxy pelargonate detergent base is as follows:



The following describes the decarboxylation reaction of hydroxy pelargonate soap with a Mg-Zn/Al hydrotalcite base:



This study aimed to ascertain the effect of adding Mg-Zn/Al hydrotalcite on the decarboxylation product of hydroxy pelargonate soap.

METHODS

The materials used in this research are pelargonic acid, NaOH, KOH, MgCl₂·6H₂O, Zn(NO₃)₂·4H₂O, AlCl₃, Na₂CO₃, NH₄OH, NH₄Cl, NaHCO₃, 96% ethanol, concentrated H₂SO₄, 2,4-dinitrophenylhydrazine, concentrated HCl, N₂ gas, and deionized water. Mg-Zn/Al hydrotalcite was produced by precipitating solutions of MgCl₂·6H₂O, Zn(NO₃)₂·4H₂O, AlCl₃, and NaHCO₃ under high tension.

In order to produce hydroxy-pelargonic soap, pelargonic acid was dissolved in ethanol, reacted with Mg-Zn/Al hydrotalcite, and then refluxed for 2 hours at 78 °C to complete the reaction. Three hours were spent decarboxylating hydroxy-pelargonic soap at 360 °C and atmospheric pressure.

Pelargonate hydroxy soap is made with 300% excess Mg-Zn/Al = 5:5:2 hydrotalcite variation and excess 300% Mg-Zn/Al = 3:3:2%. Using an excess of Mg-Zn/Al hydrotalcite to cause a saponification reaction between pelargonic acid (C₈H₁₇COOH) and Mg₅Zn₅Al₂(OH)₂₄·CO₃·4H₂O hydrotalcite base forms fatty salts, followed by a decarboxylation reaction.

A test for freezing point and trace ketones determined the findings of this study. The compounds in the decarboxylation product were analyzed using GC-MS, and the yield of the product was calculated using the following equation:

$$\% \text{yield} = \frac{\text{Total product amount}}{\text{Theoretical product quantity}} \quad (5)$$

RESULT AND DISCUSSION

Table 3 displays the decarboxylation results of hydroxy pelargonate soap with a Mg-Zn/Al hydrotalcite base. The findings of the freezing point and trace ketone tests for decarboxylation products are shown in **Table 4**.

Table 3. Results of decarboxylation

No	Variation	Feed (g)	Research results		Yields (%)
			Product (g)	Residue (g)	
1	Mg-Zn/Al=5:5:2 excess 300%	20	4.975	10.905	65.76%
2	Mg-Zn/Al=3:3:2 excess 300%	20	4.618	9.982	61.45%

Table 4. Freezing point test and trace ketone test results for decarboxylation products

No	Variation	Freezing point	Traces of ketones
1	Mg-Zn/Al=5:5:2 excess 300%	33	enough lots of compound ketones
2	Mg-Zn/Al=3:3:2 excess 300%	25	treads compound ketones

Table 3 shows that hydroxy pelargonate soap has an excess of 300% of Mg-Zn/Al in a 5:5:2 hydrotalcite base, resulting in a product yield of 65.76% and a freezing point of 33°C. Numerous ketone compounds were detected in the decarboxylation product, as determined by a test for trace ketone levels.

The product yield of hydroxy pelargonate soap with an hydrotalcite base Mg-Zn/Al = 3:3:2 excess 300% was 61.45%, and the freezing point was 25°C. The results of the ketone trace test indicated that the decarboxylation product contained traces of ketone compounds.

According to the results, using hydrotalcite Mg-Zn/Al = 5:5:2 excess 300% yielded a solid phase product, and using hydrotalcite Mg-Zn/Al = 3:3:2 excess 300% yielded a liquid phase product with a lower product yield and freezing point than hydrotalcite Mg-Zn/Al = 5:5:2 excess 300%. In line with the findings of Neonufa et al., who investigated the effect of metal combinations on the decarboxylation reaction of stearin soap, the Mg-Zn metal combination produced the highest liquid hydrocarbon product yield of 47.46% w/w compared to the Mg-Al, Mg-Cu, Mg-Fe, and Mg metal combinations. This suggests that the Mg-Zn metal combination catalyzes essential soaps into biohydrocarbons with the most excellent vigor [16].

The trace ketone test results are displayed in **Table 4**. The trace ketone test aims to determine if a product contains oxygen. The results of the trace ketone test indicate that the use of hydrotalcite (Mg-Zn/Al = 5:5:2 in excess of 300%) contains a significant amount of ketone compounds. In contrast, using hydrotalcite, Mg-Zn/Al = 3:3:2, excess 300% contains traces of ketone compounds. This indicates more

oxygen elements in hydrotalcite (Mg-Zn/Al = 5:5:2 excess 300%). This demonstrates that more Zn produces more ketone compounds, even though Indonesian premium, pertalite, and pertamax turbo contain a maximum of 2.7% m/m oxygen [17]. Table 5 displays the results of the GC-MS analysis of the decarboxylation products of hydroxy pelargonate soap with hydrotalcite bases: Mg-Zn/Al = 5:5:2 excess 300% and Mg-Zn/Al = 3:3:2 excess 300%.

Table 5. Results of analysis of decarboxylation products of hydroxy pelargonic soap with hydrotalcite bases

Mg-Zn/Al = 5:5:2 300% excess	
9- Heptadecanone	50.30%
2- Decanone	10.30%
3- Heptadecenes	7.54%
n- Pentadecanol	3.85%
5- Heptadecenes	3.02%
1- Heptene	2.51%
3- Undecanone	1.83%
1- Octene	1.77%
n- Octane	1.52%
Mg-Zn/Al = 3:3:2 300% excess	
9- Heptadecanone	41.52%
2- Decanone	16.00%
n- Nonadecanol -1	6.96%
1- Heptene	3.30%
5- Heptadecenes	2.89%
n- Pentadecanol	2.89%
1- Octene	2.65%
n- Octane	2.16%

According to test results, The decarboxylation product of hydroxy pelargonate soap with hydrotalcite base Mg-Zn/Al = 5:5:2 excess 300% comprised 50.30% 9-Heptadecanone, 10.30% 2-Decanone, and 1.52% n-Octane. However, the decarboxylation product of hydroxy pelargonate soap with hydrotalcite base Mg-Zn/Al = 3:3:2 excess (300%) contains 41.52% 9-Heptadecanone, 16.00% 2-Decanone, and 2.16% n-Octane.

According to the results, using hydrotalcite Mg-Zn/Al = 3:3:2 excess 300% yields liquid phase decarboxylation products with the highest selectivity on the desired product, namely n-octane, at 2.16%. However, it produces the least amount of 9-Heptadecanone at 16.00% and products with the lowest freezing point at 25°C. The decarboxylation product has many ketone compounds, even though 61.45% of the

starting material is converted into the final product.

The maximum product yield was achieved with Mg-Zn/Al = 5:5:2 excess 300%, which was 65.76%. Using Mg-Zn/Al = 3:3:2 in excess of 300% resulted in the highest product selectivity for n-octane, 2.16 %. **Figure 1** compares the Zn ratio's effect on product yield and selectivity to the desired product, n-octane.

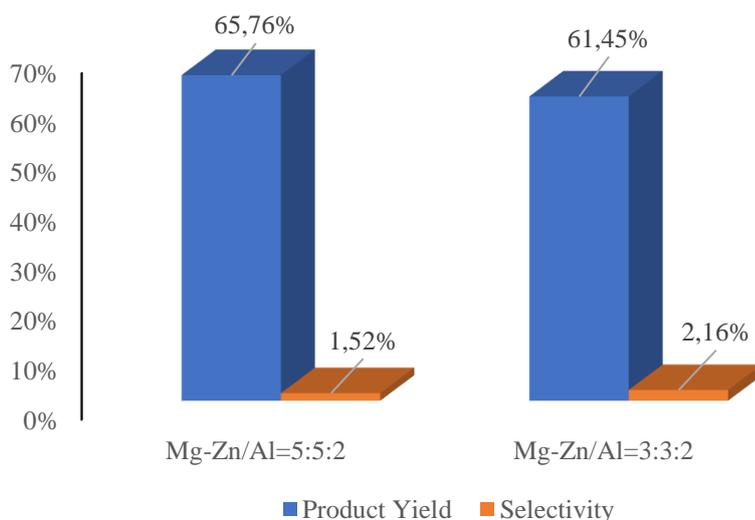


Figure 1. Zn ratio's effect on product yield and selectivity to the desired product, n-octane

Based on **Figure 1**, at Mg-Zn/Al = 5:5:2, the ratio of Al in Mg-Zn can be interpreted as being smaller than at Mg-Zn/Al = 3:3:2. A lower Al/Mg/Zn ratio can result in a greater product yield. At Mg-Zn/Al = 3:3:2, the ratio of Al in Mg-Zn can be interpreted as being more significant than at Mg-Zn/Al = 5:5:2. The increased Al/Mg/Zn ratio reduces the product selectivity of 9-Heptadecanone while increasing the product selectivity of the desired product, n-octane, and lowering the freezing point. According to the findings of Neonufa et al.'s study on the influence of metal combinations on the decarboxylation reaction of stearin soap, Al metal stimulates the synthesis of isoalkanes more than Mg metal alone. The inclusion of Al metal in Mg and Zn metal in Mg stimulates the production of isoalkanes almost similarly. [16].

CONCLUSION

This study found that employing Mg-Zn/Al = 5:5:2 excess (300%) hydrotalcite produced the maximum product yield of 64.76%. The highest product selectivity to n-octane, 2.16 %, was achieved with Mg-Zn/Al = 3:2:2 excess (300%) hydrotalcite. A low Al/Mg/Zn ratio of 2:10 can increase product yield, whereas a high Al/Mg/Zn ratio of 2:6 can increase product selectivity and reduce the freezing point.

ACKNOWLEDGEMENT

Thank you to LPDP for providing the funding for this research.

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