Catalytic conversion of beef tallow with MgO derived from MgCO₃ for biofuels production

A Riyadhi¹,², Y Yulizar¹ and B H Susanto³

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok 16424, Indonesia
²Department of Chemistry, Faculty of Science and Technology, Universitas Islam Negeri Syarif Hidayatullah, Tangerang Selatan 15412, Indonesia
³Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok 16424, Indonesia

Corresponding author’s email: yokiy@sci.ui.ac.id

Abstract. Fuels from biological sources, such as oils and fats, receive much attention. Beef tallow is a cheap and abundant feedstock that can be converted into renewable fuels. Catalytic conversion of beef tallow was accomplished with the MgO catalyst derived from MgCO₃. Magnesium oxide catalyst was prepared by calcination of MgCO₃ at temperature 700 °C. The catalyst was tested for its performance in a fixed bed reactor at temperature 300 °C for 60 min. Conversion of beef tallow to hydrocarbons biofuels was studied. The MgO catalyst was characterized by nitrogen adsorption isotherms (BET), powder X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM). The assay activity of MgO shows all fatty acids derived from beef tallow have converted into liquid and gas fraction with a black paste residue that has a boiling point of more than 300 °C. The results of the liquid fraction composition depend on the ratio of the given MgO catalyst. At the ratio of MgO catalysts and feeds 2 wt.%, the results of liquid fraction contain the alkanes (45.61%), alkenes (4.12%), alcohols (3.96%), ketones (8.55 %), esters (23.42 %), and cyclic compounds (14.34 %), while at the ratio of 4 wt.%, the liquid fraction contains the alkanes (55.56 %), alkenes (8.94 %), alcohols (5.27 %), ketones (13.73 %) and cyclic compounds (16.50 %).

Keywords: Catalytic conversion, biofuel, beef tallow, MgO and MgCO₃

1. Introduction

Renewable fuels such as biogasoline and biodiesel can be generated from a wide range of biomass namely animal fats, cooking oil waste, and vegetable oils [1]. Fuels derived from biological sources, among them are lipid materials such as oils and fats, have received much attention. The first-generation biodiesel or fatty acid esters are generated by the transesterification reaction of animal fat or vegetable oils with alcohols and glycerol as co-product. However, the reduced flow property at low temperature of the obtained biodiesel limits its application in engine[1, 2].

Second-generation biodiesel, also called as renewable diesel by using hydrodeoxygenation, decarboxylation, and cracking technology has become a trend. Compared to the renewable diesel in the first-generation biodiesel, the quality of the second-generation renewable diesel has a lot better
performance. The second-generation renewable diesel has better fuel properties because of its higher cetane number, high energy density and lowers oxygen content [3].

The second-generation renewable diesel has high quality and environmental protection performances in the energy field [3]. The second-generation renewable diesel has chemical content equal to petrodiesel, consisting of hydrocarbon compounds such as octadecane, heptadecane, hexadecane, and pentadecane. Therefore, the renewable diesel can be used directly as fuel [3, 4].

The process of decarboxylation can convert fatty acids into linear, paraffinic hydrocarbons [5, 6]. The method of decarboxylation does not require hydrogen. It is easy to apply compared to the hydrodeoxygenation process that involves hydrogen. The process of decarboxylation does not produce water, which can cause the catalyst to be inactive [7].

Beef tallow is a byproduct of the food industry, so it is a low-cost and abundant feedstock. Beef tallow can be converted into renewable gasoline and renewable diesel at lower production costs when compared to other biofuels [8]. The main properties of the beef tallow are oleic acid (C₁₈), stearic acid (C₁₈), palmitic acid (C₁₆), palmitoleic acid (C₁₆), and myristic acid (C₁₄) [9].

Pyrolysis of waste animal fats at the temperature of 500 °C showed a complex mixture such as alkanes, alkenes, cyclic compounds, carboxylic acids, aldehydes, ketones, and esters [10]. Catalytic decarboxylation can be done at a temperature of 300 °C, catalytic and thermal reactions can be done at the temperature of 350 °C, and thermal reaction can be done at the temperature above 400 °C [7].

The MgO catalyst is useful for the dehydrogenation of alkanes into cyclic and aromatic carbon compounds [11]. The MgO catalyst is also useful for deoxygenation of fatty acid into alkanes, alkenes, and cyclic carbon compounds [5, 6]. The MgO catalyst helps in the oxygen removal and CO₂ absorbance in the gas phase through catalytic deoxygenation [12].

Thus, the present study highlights the usage of solid base catalysts MgO prepared from low-cost MgCO₃ industrial grade for the conversion of beef tallow with MgO catalyst for renewable hydrocarbon biofuels production. Decomposition thermal of magnesium carbonate can produce porous magnesium oxide [13].

The research on commercial MgO as a catalyst for the catalytic beef tallow has been done by our group and have reported [14]. The resulting product still requires development because the product can freeze at 0 °C temperature, and it is not good as fuel. This research conducted the manufacture of porous MgO catalysts from the MgCO₃ industrial grade that costs much cheaper and environmentally friendly raw material. The MgO catalyst was characterized by XRD, BET, and SEM-EDX. Chemical compositions of products from the conversion of beef tallow into biofuels were analyzed using GC-MS.

2. Materials and method

MgO was prepared from MgCO₃ industrial grade with a calcination temperature of 700 °C for 90 min under atmosphere condition. Beef tallow in the study was obtained from the household industry in Kemang, Bogor, Jawa Barat, Indonesia. Tallow is a product of beef fat hydrolysis that has been separated from the residue of muscle tissue, meat and bones.

2.1. Catalyst characterization

The powder X-ray diffraction (XRD) analysis was conducted to determine the crystallography of the mixed metal oxide catalysts. The XRD analyses were carried out by the Shimadzu diffractometer model XRD-7000. The specific surface area and pore distribution of the catalysts were identified with Brunauer-Emmet-Teller (BET) method with N₂ adsorption/desorption analyzer using ASAP 2020 Micromeritics Instrument Corp. The identification of elemental compositions of Mg, O and C on the catalysts surface were determined by SEM-EDX mapping analysis using JED-2300 Analysis Station.

2.2. Activity test

Catalytic deoxygenation of beef tallow was conducted in a 150 mL stainless steel bath reactor and connected to a distillation system [14]. Around 25 g of beef tallow using 2 wt.% and 4 wt.% of MgO
catalyst was inserted into the reactor. The deoxygenation reaction of beef tallow was carried out with heating at 300 °C for 60 min. The cracked/deoxygenated product was then collected in a receiver flask, and the liquid products were immediately weighed and analyzed with gas chromatography-mass spectrometry (GC-MS) Perkin Elmer Clarus 600.

3. Results and discussion

3.1. Physicochemical properties of catalysts
MgO catalyst was synthesized with calcination of industrial-grade magnesium carbonate at temperature 700 °C for 90 min under atmosphere condition. When the MgCO3 heating occurs, the release of CO2 gases causes pore formation in MgO material [13]. MgCO3 is an excellent raw material for making MgO porous. The lost weight is calculated based on the material weight difference before and after material calcination. Between 500–700 °C, CO2 escapes and emits out from the sample MgCO3 [13]. From the calculation of stoichiometry, % lost weight of MgCO3 to MgO is 52.20 %, and % conversion is 47.80 %. In this study, % lost weight of MgCO3 calcination at 700 °C for 90 min is 53.32 %, this weight reduction occurs due to the formation of CO2 gases and water loss.

After calcination at 700 °C, the acquired powder was characterized by XRD, as shown in figure 1. The three highest peaks at 2θ value of MgO are at 42.80; 62.19 and 78.49°, according to JCPDS 75-0447, and all peaks show the character of cubic MgO periclase. There is no other conspicuous phase in the XRD pattern, which implies the high purity of MgO particles.

After calcination at 700 °C, the acquired powder was characterized by XRD, as shown in figure 1. The three highest peaks at 2θ value of MgO are at 42.80; 62.19 and 78.49°, according to JCPDS 75-0447, and all peaks show the character of cubic MgO periclase. There is no other conspicuous phase in the XRD pattern, which implies the high purity of MgO particles.

Morphology and compositional analysis of the synthesized MgO derived from MgCO3 were done by using electron microscopy. Figure 2 shows the scanning electron microscopy (SEM) image of MgO, which exhibits a flakes-like structure. Based on the results of SEM-EDX analysis in table 1, it shows the MgO atom composition of 43.50 % Mg and 56.50 % O, close to the atomic ratio of 1:1 from MgO.

Surface area and pore size of material were characterized using BET. In this study, MgO derived from MgCO3 has a surface area of 53.42 m²/g and an adsorption average pore width of 17.76 nm. These results show bigger than MgO being synthesized by Cai et al. [15], respectively 47.85 m²/g and 12.15 nm is prepared using Mg(NO3)26H2O.

3.2. Catalytic conversion of beef tallow
The beef tallow contents used for catalytic conversion were identified by GC-MS. The contents are shown in table 2, and the main content is octadecanoic acid, 11-octadecenoic acid and hexadecanoic acid.

![Figure 1. XRD pattern of MgO obtained from the MgCO3 calcination at 700 °C.](image-url)
The assay activity of 2 wt.% MgO catalyst shows all fatty acids derived from beef tallow converted into 38.24 % liquid; 27.20 % gas fraction and 34.56% black paste residue that has a boiling point of more than 300 °C, while the assay activity using 4 wt.% MgO shows the results of 41.52 % liquid, 30.96 % gas fraction and 27.52 % black paste residue, as shown in table 3. These results show more catalysts used, resulting in more liquid and gas fractions produced, on the contrary to the black paste residue.

![Figure 2. SEM images of MgO with (a) 10,000x and (b) 20,000x magnification.](image)

**Table 1.** Elemental ratio of MgO.

| Element | wt.% | atom % |
|---------|------|--------|
| Mg      | 53.92| 43.50  |
| O       | 46.08| 56.50  |

**Table 2.** The contents of beef tallow used for catalytic conversion.

| Retention time (min) | Percentage (%) | Fatty acid                    | Formula       |
|----------------------|----------------|-------------------------------|---------------|
| 20.29                | 5.29           | Tetradecanoic acid            | C_{14}H_{28}O_{2} |
| 23.02                | 1.71           | 9-Hexadecenoic acid           | C_{16}H_{30}O_{2} |
| 23.33                | 25.04          | Hexadecanoic acid             | C_{16}H_{32}O_{2} |
| 25.66                | 1.41           | 9,12-Octadecadienoic acid     | C_{18}H_{32}O_{2} |
| 25.76                | 26.57          | 11-Octadecenoic acid          | C_{18}H_{34}O_{2} |
| 25.83                | 1.84           | 13-Octadecenoic acid          | C_{18}H_{34}O_{2} |
| 25.88                | 3.08           | 16-Octadecenoic acid          | C_{18}H_{36}O_{2} |
| 26.10                | 26.86          | Octadecanoic acid             | C_{18}H_{36}O_{2} |

**Table 3.** Products distribution of beef tallow conversion using MgO catalyst.

| Products (wt.%) | 2 wt.% MgO | 4 wt.% MgO |
|-----------------|------------|------------|
| Liquid fraction | 38.24      | 41.52      |
| Gas fraction    | 27.20      | 30.96      |
| Black paste     | 34.56      | 27.52      |
Table 4. Product composition based on petroleum range of liquid fraction.

| Products (wt.%) | Catalyst          |
|----------------|-------------------|
|                | 2 wt.% MgO | 4 wt.% MgO |
| Gasoline (C5–C11) | 22.28     | 28.84     |
| Kerosene (C12–C15) | 30.13     | 35.50     |
| Diesel (C16–C26)   | 47.59      | 35.66     |

Table 5. The organic compound composition of liquid fraction.

| Products (wt.%) | Catalyst          |
|----------------|-------------------|
|                | 2 wt.% MgO | 4 wt.% MgO |
|                |            |            |
| Alkanes        | 45.61      | 55.56      |
| Alkenes        | 4.12       | 8.94       |
| Alcohol        | 3.96       | 5.27       |
| Ketones        | 8.55       | 13.73      |
| Esters         | 23.42      |            |
| Cyclic         | 14.34      | 16.50      |

The liquid fractions products obtained from catalytic deoxygenation and cracking processes are bright yellow and do not freeze at 0°C. The liquid fractions were analyzed using GC-MS and grouped into three lumps [16], gasoline (C5–C11), kerosene (C12–C15), and diesel fraction (C16–C26) as indicated in table 4. The resulting composition of liquid fractions depends on the percent of the given MgO catalyst. The using of 2 wt.% catalysts results in the gasoline, kerosene, diesel fraction of 22.28 %; 30.13 % and 47.59 %; respectively, while by using of 4 wt.% catalyst results are 28.84 %; 35.50 % and 35.66 %, respectively. The using of 4 wt.% catalyst results in the gasoline and kerosene much more 2 wt.% catalysts, indicating many cracking reactions, of all fatty acid from beef tallow.

As a comparison with commercial MgO (5 wt.%) reported [14], catalytic cracking of tallow showed C7–C11 fraction of 17.85 %, and C12–C19 fraction of 82.15 %. The result in using MgO catalysts from MgCO3 industrial-grade indicated more gasoline fraction than commercial MgO. Solid base catalysts of MgO from MgCO3 industrial grade is an environmentally friendly and low-value precursor.

The product characterization based on organic compounds is shown in table 5. The using of MgO catalysts and feeds 2 wt.% results of liquid fraction contain the alkanes (45.61 %), alkenes (4.12 %), alcohols (3.96 %), ketones (8.55 %), esters (23.42 %), and cyclic compounds (14.34 %), while at the ratio of 4 wt.%, liquid fraction contain the alkanes (55.56 %), alkenes (8.94 %), alcohols (5.27 %), ketones (13.73 %) and cyclic compounds (16.50 %). The results are lower than by using the MgO catalyst and feed 4 wt.%, however, no ester product was found. The products at the ratio of MgO catalyst and feed 4 wt.% did not contain ester products. Ester products have successfully cracked either through carboxylation and carbonylation reactions.

4. Conclusion
This study has been successfully confirmed that beef tallow is valuable raw materials for bio-oil production using MgO catalyst. The assay activity of MgO synthesized from MgCO3 as a catalyst at temperature 300 C for 60 min, show all fatty acids derived from beef tallow converted into gas, liquid fraction, and black paste residue. The composition of the liquid fraction depends on the percent of the given MgO catalyst. The much more catalysts used in the conversion of beef tallow will give a higher result of gasoline and kerosene but not for diesel products. The industrial-grade MgCO3 can be used as
a precursor for an environmentally friendly and low-value MgO production. The MgO as active catalysts for the deoxygenation and cracking hydrocarbons of tallow with different results depend on the reaction conditions.

Acknowledgments
The authors thank to The Indonesia Endowment Fund for Education Ministry of Finance Republic of Indonesia (LPDP Kementerian Keuangan RI) for the fund through the Scholarships and Research Grants.

References
[1] Bezergianni S and Dimitriadis A 2013 Renew. Sustain. Energy Rev. 21 110-6
[2] Guo J-H, Xu G-Y, Shen F, Fu Y, Zhang Y and Guo Q-X 2015 Green Chem. 17 2888-95
[3] Chen S, Zhou G and Miao C 2019 Renew. Sustain. Energy Rev. 101 568-89
[4] Knothe G 2010 Prog. Energy Combust. Sci. 36 364-73
[5] Edeh I, Overton T and Bowra S 2019 Renewable diesel production by hydrothermal decarboxylation of fatty acids over platinum on carbon catalyst Biofuels doi:10.1080/17597269.2018.1560554
[6] Li D, Xin H, Du X, Hao X, Liu Q and Hu C 2015 Sci. Bull. 60 2096-106
[7] Roh H-S, Eum I-H, Jeong D-W, Yi B-E, Na J-G and Ko C H 2011 Catal. Today 164 457-60
[8] Esteves V P P, Esteves E M M, Bungenstab D J, Feijo G L D, Araujo O de Q F and Morgado C do R V 2017 J. Clean. Prod. 151 578-91
[9] Ito T, Sakurai Y, kakuta Y, Sugano M and Hirano K 2012 Fuel Process. Technol. 94 47–52
[10] Ben Hassen-Trabelsi A, Kraiem T, Naoui S and Belayouni H 2014 Waste Manag. 34 210-8
[11] Elkhalfiu E A and Friedrich H B 2018 Arab. J. Chem. 11 1154-9
[12] Asikin-Mijan N, Lee H V, Juan J C, Noorsaadah A R and Taufiq-Yap Y H 2017 RSC Adv. 7 46445-60
[13] Morozov S A, Malkov A A and Malgyn A A 2003 Russ. J. General Chem. 73 41-6
[14] Riyadba A and Syahrullah 2016 Integrated Lab Journal 4 125-38
[15] Cai Y, Li C, Wu D, Wang W, Tan F, Wang X, Wong P K and Qiao X 2017 Chem. Eng. J. 312 158-66
[16] Demirbas 2015 Petrol. Sci. Technol. 33 1703-11