Biodiesel Production from Fats and Oil Feedstocks Catalyzed by Calcined Bovine Bone
การผลิตไบโอดีเซลจากน้ำมันและไขมันโดยใช้กระดูกวัวเผาเป็นตัวเร่งปฏิกิริยา

Wilasinee Lerdrittipong (วิลาสินี เลิศฤทธิพงศ์)* Dr.Suwilai Chaveanghong (ดร.สุวิไล เฉวียงหงส์)**
Dr.Christopher B. Smith (ดร.คริสโตเฟอร์ บรู๊ค สมิธ)*** Dr.Siwaporn M. Smith (ดร.ศิวพร มีจู สมิธ)****

ABSTRACT

Biodiesel can be effectively produced from transesterification of methanol and oil (or fat) feedstocks with the requirement of a base catalyst. This study aims to investigate the catalytic activity of a heterogeneous base catalyst derived from waste bovine bone towards biodiesel production from vegetable oils and animal fats. Calcination of bovine bone particulates at 750°C for 5 h resulted in nanoparticles containing crystalline hydroxyapatite and CaO (catalytically base sites). The acid value and saponification number of oil and fat feedstocks, soybean oil, sunflower oil, palm oil, chicken fat, and pork lard, were determined. High biodiesel yields (> 92%) were achievable after 3 hour methanolysis of soybean oil, sunflower oil, palm oil, chicken fat, or pork lard at 65°C using 8 wt.% of catalyst loading, and a methanol:oil molar ratio of 6:1. On the other hand, using identical catalyst loading and methanol:oil molar ratio, high reaction temperature (120°C) was required to achieve high biodiesel yields from coconut oil and sesame oil feedstocks. In conclusion, the calcined bovine bone can be utilized as an effective base solid catalyst in methanolysis of all studied feedstocks having acid value $\leq$ 3.3 mg KOH/ g oil.

บทคัดย่อ

ไบโอดีเซลสามารถผลิตได้อย่างมีประสิทธิภาพจากปฏิกิริยาทรานส์เอสเทอริฟิเคชันของเมทานอล กับ น้ำมัน ภายใต้ตัวเร่งปฏิกิริยาที่มีความเป็นเบส การทดลองนี้ต้องการศึกษาความสามารถในการผลิตไบโอดีเซลของตัวเร่งปฏิกิริยาวิวิธพันธ์ที่สังเคราะห์จากวัสดุกระดูกวัวเหลือทิ้งที่มีความเป็นเบส กับน้ำมันพืชและไขมันสัตว์ การเผาตัวอย่างผงกระดูกวัวเหลือทิ้งที่ 750 องศาเซลเซียส เป็นเวลา 5 ชั่วโมง พบว่าเกิดอนุภาคระดับนาโน ซึ่งประกอบด้วย ผลึกไฮดรอกซีอะพาไทต์ และแคลเซียมออกไซด์ จากการทดลองพบว่าผลผลิตไบโอดีเซลมากกว่า ร้อยละ 92 สามารถสังเคราะห์ได้จากการทำปฏิกิริยากับเมทานอลเป็นเวลา 3 ชั่วโมง ที่อัตราส่วนของตัวเร่งปฏิกิริยาต่อน้ำมันเป็น ร้อยละ 8 และอัตราส่วนของเมทานอลต่อน้ำมันเป็น 6 ต่อ 1 ที่อุณหภูมิ 65 องศาเซลเซียส สำหรับน้ำมันถั่วเหลือง น้ำมันทานตะวัน น้ำมันปาล์ม น้ำมันไก่ และน้ำมันหมู และที่ 120 องศาเซลเซียส สำหรับน้ำมันมะพร้าวและน้ำมันงา ในการทดลองนี้ได้ทำการหาค่าความเป็นกรดของน้ำมันทุกชนิดที่ใช้ และสามารถสรุปได้ว่าตัวเร่งปฏิกิริยาจากการเผา กระดูกวัวเหลือทิ้ง มีประสิทธิภาพในการสังเคราะห์ไบโอดีเซล จากน้ำมันที่มีค่าความเป็นกรดน้อยกว่าหรือเท่ากับ โพแทสเซียมไฮดรอกไซด์ 3.3 มิลลิกรัม ต่อน้ำหนักเป็นกรัมของน้ำมัน

Keywords: Bovine bone, Heterogeneous catalyst, Biodiesel
คำสำคัญ: กระดูกวัว ตัวเร่งปฏิกิริยาวิวิธพันธ์ ไบโอดีเซล

** Student, Master of Science Program in Chemistry, Department of Chemistry, Faculty of Science, Mahidol University*

*** Student, Post-Doctoral, Materials Science and Engineering Graduate Program, Faculty of Science, Mahidol Unversity*

**** Lecturer, Faculty of Science, Mahidol University*

***** Associate Professor, Center of Sustainable Energy and Green Materials and Department of Chemistry, Faculty of Science, Mahidol University*

Introduction

Biodiesel, derived from vegetable oil or animal fat, has been accepted as an environmentally friendly fuel having similar properties to petrodiesel, however producing less harmful gas emission (Dennis et al, 2010). As it consists of mono-alkyl esters such as methyl, ethyl, or propyl esters, high cetane number and high combustion efficiency, biodiesel can be used alone (as B100) or blended with petrodiesel (as B5, B10, B25) in diesel engines (Sivaramakrishnan, 2017). Therefore, biodiesel has shown a great promise as a high potential greener energy source, and as a replacement of fossil fuel. Transesterifications of triglycerides (TG), in oil or fat feedstocks and an alcohol leading conversion of TG to fatty alkyl esters, the major chemical constituents in biodiesel. When methanol is used, expected reaction products from transesterification (or methanolysis) are fatty acid methyl ester (FAME) and glycerol (Dennis et al, 2010).

Base catalysts are generally required in transesterification to ensure high FAME yields within a short time. Two classified catalysts, based on their phases in the reaction, include homogeneous- and heterogeneous catalysts. Homogeneous base catalysts (NaOH, KOH), dissolved well in methanol, catalyzed transesterification of TG at faster rate under mild conditions (Borge et al, 2012). However, product separation and purification is complicated, and suitable wastewater treatments are necessary. Hence, using heterogeneous catalysts are considered more environmentally friendly systems with no requirement of special handling of corrosive reaction stream. Calcium oxide (CaO) has been extensively reported as an effective and reusable solid-base catalyst in producing FAME under mild conditions (Islam, 2014). Sources of CaO in nature include $CaCO_3$ containing minerals, marine and aquatic shells, and animal bones. In previous studies (Smith et al, 2013), reusable base catalyst systems (CaO/hydroxyapatite and Sr-CaO/hydroxyapatite) derived from waste bovine bone were utilized in transesterification of soybean oil (food grade) and methanol, achieving high FAME yields at low reaction temperatures (35-65°C). However, undesirable soap formation may occur, resulting in low FAME yields obtained from base catalyzed methanolysis of feedstocks having high FFA content and acid value (Talebian-Kiakalaieh et al, 2013). Hence, it is interesting to explore the practicality of the bone catalyst in conversions of other feedstocks to biodiesel.

Objectives of the study

To investigate the catalytic activity of calcined bovine bone for FAME production using several oil and fat feedstocks, the acid value and saponification number of each feedstock were determined, as these properties may influence the reaction parameters of FAME productions.

Methodology

Materials

Fresh bovine bone (denoted as BV) was purchased (retail price < US 1$ per kilogram) as particulates from Rung Ruang Co., Ltd. (Samutprakarn, Thailand), a company sourcing raw bone from many parts of Thailand. Methanol (Burdick & Jackson, reagent plus, Korea) were used without further purification. All of virgin vegetable oils such as soybean oil, sunflower oil, coconut oil, palm oil, and sesame oil, were purchased from supermarket in Bangkok, Thailand. Chicken fat was obtained from a local fresh market in Bangkok, Thailand. Pork lard was obtained from a local fresh market in Nakhonratchasima, Thailand. The acid value and saponification number of oil and fat feedstocks were determine by using the AOCs official of method Cd-3d-63 and ASTM D 1962, respectively.

Sample preparation and characterization

Fresh BV powder was dried at 120°C overnight, and then ground and sieved to obtain fine particles (400 mesh). Next, the dried bone was calcined at 750°C for 5 hours with a heating rate of 5°C/min using a MEMMERT furnace. Phases of BV materials were identified by powder x-ray diffraction (PXRD), while its chemical composition and morphology were studied by using, Fourier transformed infrared spectrometer equipped with attenuated total reflectance (FTIR-ATR), and scanning electron microscope (SEM), respectively. Diffraction patterns were recorded on a diffractometer (Bruker, Germany) equipped with Cu K_{α}, lamp at 40 kV and 35 mA in the 2-theta range of 20° – 80° with increment of 0.075°. FTIR-ATR spectra were measured on a spectrophotometer (Perkin Elmer) within the range of 4000 to 370 cm^{-1}, at $4cm^{-1}$ of resolution and 16 accumulation scans. Each sample was dried and coated by gold plasma prior to observe the morphology on a microscope (SEM, Philips: XL30&EDAX) using magnification of 8,000 at 15 kV.

Catalytic activity test

Methanolysis catalyzed by the calcined bone was carried out using fats or oils mentioned above as feedstock in an ace-pressured tube, being used as reactor equipped with a magnetic stirrer. Firstly, the bone catalyst and methanol were mixed in the reactor and heated to required temperature of 65°C in oil bath under a stirring condition for 5 minutes. Then, a feedstock was added into the mixture (methanol to oil ratio = 6: 1, 8 wt.% of catalyst. The reaction was terminated after 3 hours, and the top liquid layer was collected for of FAME yield analysis by using a previously reported ^{1}H-NMR method (Knothe, 2000). The percent biodiesel conversion was calculated by the integral of methyl ester peak at 3.7 ppm divided by integral of α–CH_2 peak in the ester molecule at 2.3 ppm and proton ratio of these methyl and methylene.

Results

Table 1 shows the acid value and saponification number of the fats and oils studied. PXRD profiles (Fig. 1), FTIR-ATR spectra (Fig. 2) and SEM images (Fig. 3) represent characteristics of the fresh BV and calcined BV materials. Catalytic activity of the calcined BV in methanolysis of oil and fat feedstocks are reported in terms of biodiesel yields, as shown in Figs. 4-5.

Table 1 Acid value and saponification number of oil feedstocks

Feedstock	**Acid value (mg KOH/ g oil)**	**Saponification number (mg KOH/ g oil)**
Soybean oil	0.32 ± 0.03	178.62 ± 3.24
Sunflower oil	0.08 ± 0.00	218.94 ± 1.95
Palm oil	2.02 ± 0.02	219.12 ± 0.32
Coconut oil	3.10 ± 0.06	161.47 ± 1.64
Sesame oil	2.22 ± 0.03	212.27 ± 3.01
Chicken fat	1.89 ± 0.01	312.13 ± 0.67
Pork lard	1.23 ± 0.03	230.44 ± 0.28

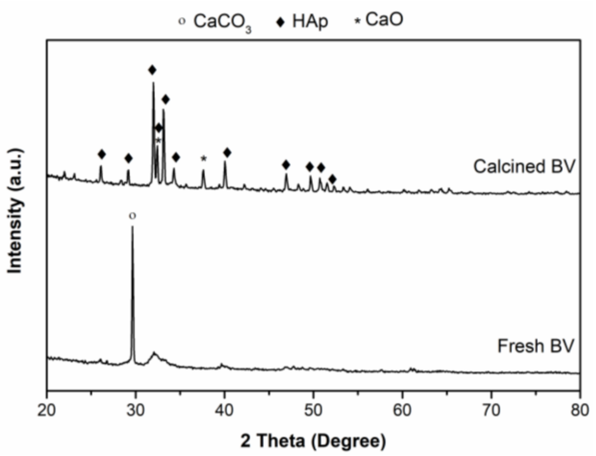

Figure 1 Diffraction patterns of the fresh and calcined BV, with the presence of $CaCO_3$, hydroxyapatite (HAP), and CaO phases

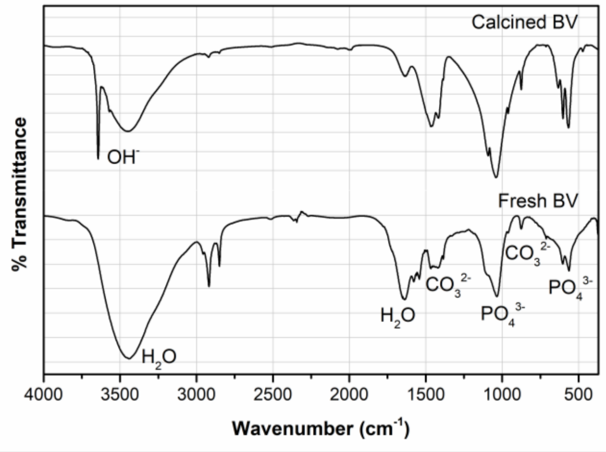

Figure 2 IR spectra of the fresh and calcined BV

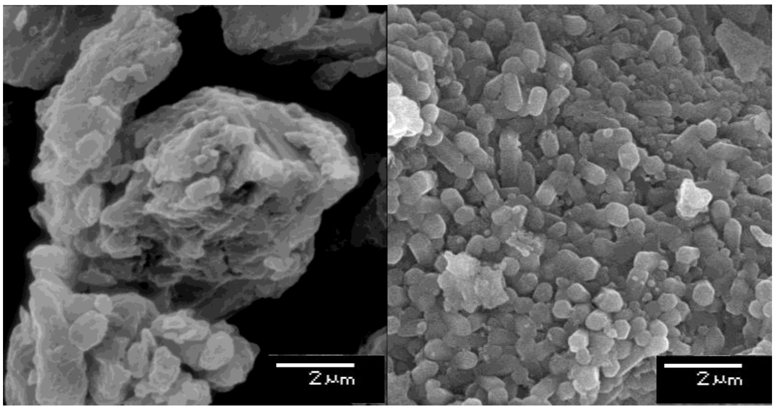

Figure 3 SEM images of fresh (left) and calcined BV (right)

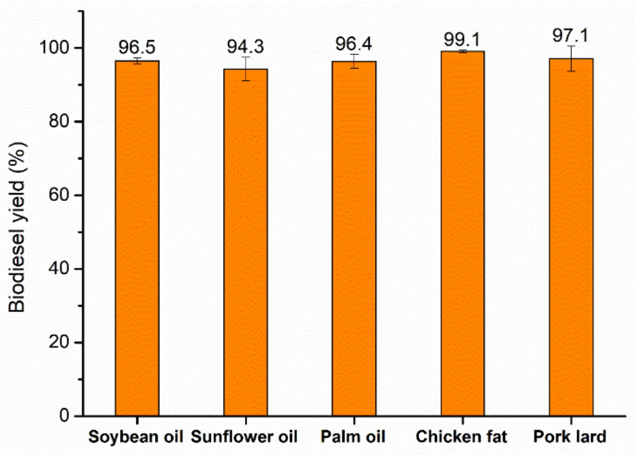

Figure 4 Biodiesel yield (%) from 3 h methanolysis at 65°C of soybean oil, sunflower oil, palm oil, chicken fat, and pork lard catalyzed by the calcined BV using 8 wt.% of catalyst loading, methanol to oil molar ratio of 6:1

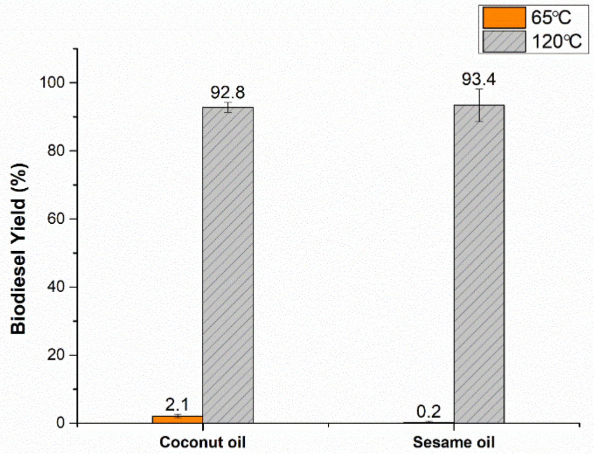

Figure 5 Biodiesel yield (%) from 3 h methanolysis at 65 and 120°C of coconut oil and sesame oil catalyzed by the calcined BV, using 8 wt.% of catalyst loading, methanol to oil molar ratio of 6:1

Discussion

Calcination resulted in changes in phase and morphology, and chemical compositions of bovine bone as evidenced from PXRD, FTIR-ATR, and SEM results. The diffraction pattern (Figure 1) of fresh BV demonstrated a peak with highest intensity at 2θ = 29.6°, which can be assigned to $CaCO_3$ (Smith et al, 2013). Additional broad, low intensity peaks, 2θ = 33° and 40°, correspond to hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$). In contrast, after calcination of fresh BV at 750°C for 5 hours, PXRD of the calcined BV shows sharp, and high intensity diffraction peaks corresponding to HAP, implying some crystallinity enhancement upon calcination. The observed peak at 2θ = 37°, corresponding to CaO, suggested a conversion of $CaCO_3$ to CaO at 750°C.

FTIR-ATR spectra of the fresh and calcined BV, shown in Fig. 2, confirm the presence CO_3^{2-} (at 1463, 1417, and 880 cm^{-1}) in $CaCO_3$, and PO_4^{3-} (at 1092, 1039, 602 and 566 cm^{-1}) in HAP. Note that these two functional groups were also observed in the calcined BV, however with lower intensity of CO_3^{2-} peaks. The absorption peaks at 2918 and 2850 cm^{-1} assigned to organic carbon in the fresh BV seems to disappear after calcination suggesting a complete decomposition of organics in bone at high temperature. It is unclear that the Ca-O vibrational peak (around 560 to 500 cm^{-1}) is also present due to phosphate-peak overlapping. Furthermore, the broad peak around 3500 cm^{-1} corresponding water content in the fresh BV was removed after calcination, leading to the appearance of sharp peak (at 3574 and 3650 cm^{-1}) corresponding to OH group. These characteristics may be contributed to OH^- absorbed to CaO or $Ca(OH)_2$ particles (Kalinkin et al., 2005). The variation in morphology of the fresh and calcined BV (SEM image in Fig. 3) was observed. Irregular granular structures with random size and agglomeration of fresh BV sample changed, after calcination, to uniform rod-like particles.

The CaO phase in calcined bovine bone acts as catalytically base active sites (Smith et al, 2013). High biodiesel yields (>94 %), reported in Fig. 4, from transesterification catalyzed by the calcined bone at 65°C, when soybean oil, sunflower oil, palm oil, chicken fat, and pork lard were employed as feedstocks. Nevertheless, a higher reaction temperature (120°C) was required to achieve high biodiesel yields (>92%) from coconut and sesame oils as seen in Fig. 5. From Table 1, the coconut oil has the highest acid value of 3.1 mg KOH/ g oil, followed by that of sesame oil (2.2 mg KOH/ g oil). The acid values of other oil and fat feedstocks utilized in this work are around 2.0 mg KOH/ g oil or lower. As results, the calcined bovine bone can be applied as an effective catalyst for productions of biodiesel from both low- and high- acid value feedstocks, with the values ranged from 0.08 to 3.1 mg KOH/ g oil, while a higher temperature is required for the acid values even or higher than 2.22 mg KOH/ g oil, to ensure high biodiesel yields under identical conditions. From this work, the acid value of feedstocks seems to play a significant role to the reaction temperature required for high biodiesel yields, greater than the saponification number of feedstocks. Other properties of feedstocks, such as moisture content, iodine value, and peroxide value, are probably important influencing the required reaction parameters of heterogeneous base catalyzed biodiesel productions.

Conclusion

It was possible to employ calcined waste bovine bone as an effective catalyst in transesterification of methanol and several oil and fat feedstock although high temperature is required for feedstocks with high acid value (>2.0 mg KOH/ g oil). The findings from this work suggested that calcined bovine bone has high potential to be used as a catalyst for biodiesel production. Its advantages are low cost, simple-to-prepare solid catalyst for large scale biodiesel production, in which the catalyst can be easily separated for recycling purpose. Further chemical modifications *via* doping acid sites on the bone material may result in the catalyst being suitable for production of biodiesel from high acid value feedstocks under milder conditions.

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