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Calcium Oxide as an Efficient Heterogeneous Catalyst for Production of Biodiesel

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الملخص

أجريت هذه الدراسة لإنتاج وقود الديزل الحيوي من مخلفات زيت الطهي باستخدام أكسيد الكالسيوم التجاري والمحضر. تم تحضير أكسيد الكالسيوم عن طريق حرق مخلفات عظام الدجاج عند درجة حرارة 800 درجة مئوية لمدة 7 ساعات، ثم تم تشخيص العينات المحضرة باستخدام جهاز الأشعة تحت الحمراء (FT-IR)، والمسح المجهري الإلكترون (SEM)، ومطيافية تشتت الطاقة الأشعة السينية (EDX) وامتزاز غاز النتروجين عند 77.3 كلفن. وتم فحص النشاط التحفيزي لهذه المحفزات عن طريق أسترة مخلفات زيت الطهي مع نوعين من الكحول (الإيثانول والميثانول). وكانت إنتاجية وقود الديزل الحيوي باستخدام أكسيد الكالسيوم المحضر 73% مع الميثانول و65.5% مع الإيثانول، بينما استخدام أكسيد الكالسيوم التجاري 71% و63%. وأشارت النتائج إلى أن محفزات أكسيد الكالسيوم المشتقة من مخلفات عظام الدجاج أظهرت إمكانية عالية لاستخدامها كمحفزات لإنتاج وقود الديزل الحيوي في أسترة زيت الطهي باستخدام الميثانول والإيثانول.

الكلمات المفتاحية: كالسيوم اكسيد، المحفزات الغير متجانسة، مخلفات عظام الدجاج، الأسترة التبادلية، إنتاج وقود الديزل الحيوي.

Abstract

This study was carried out on biodiesel production from waste cooking oil using commercial and synthesized calcium oxide. Synthesized calcium oxide was prepared by calcination of the waste chicken bones at 800 C^o for 7 hours. The prepared samples were characterized using FT-IR, SEM, EDX and N_2-sorption at 77.3 K. The catalytic activity of these catalysts was investigated by transesterification of waste cooking oil with two types of alcohol (ethanol and methanol). The yields of biodiesel using synthesized CaO were 73% with methanol and 65.5% with ethanol, while using commercial CaO were 71 % and 63 %. The results indicated that the CaO catalysts derived from waste chicken bones showed high potential to be used as biodiesel production catalysts in transesterification of cooking oil with methanol and ethanol.

Keywords: Calcium oxide, heterogeneous catalyst, wastes chicken bones, transesterification, biodiesel production.

1. INTRODUCTION

Transesterification is a reaction that uses a catalyst to create alkyl esters, or biodiesel from vegetable oils and alcohols. Homogeneous Brønsted acid catalysts, such as sulfuric acid, sodium hydroxide, and potassium hydroxide are typically used to carry out the transesterification reaction. However, using such catalysts presents a number of advantages, including equipment corrosion, waste generation, difficulty separating the catalyst from the reaction, and environmental issues [1]. It was resorting to using the heterogeneous catalysts, which have many advantages such as this catalyst. It can help to reduce waste generation, give cleaner technologies, easily separated, recyclable and high catalytic activity [1,2,3]. There are several types of heterogeneous catalysts have been used in biodiesel production, and metal oxides such as calcium, magnesium, strontium, zirconia and zinc oxides have been widely used [4].

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Among these oxides, the calcium oxide CaO which is a strong base oxide with high catalytic activity, long life activity, low temperature and short time of the reaction conditions, as well as low cost [4,5,6]. The Bioresource bone waste is a good source of calcium oxide, which has been used extensively as heterogeneous catalysts for many types of organic synthesis, due to their favourable properties such as low cost, thermal stability, selectivity, large specific surface area, ease of separation, as well as environmentally friendly [7]. The calcium oxide can obtain from bone waste i.e., chicken [8,9,10]. Calcium oxide is also available from other biological sources like mussels, scallops, and eggshells [11,12]. Bones are one of the most bio-resources, which consist of cells, fillers and fibres. These bones contain proteins, mineral salts, calcium phosphate, calcium carbonate, magnesium phosphate, calcium fluoride, water, and red and yellow marrow. These bones contain protein, mineral salts, calcium phosphate, calcium carbonate, magnesium phosphate, calcium fluoride, water, red bone marrow, and yellow bone marrow. Removal of these organic substances by heat does not cause any changes in the bone structure, but the weight of the bone decreases due to the decrease in water content [13]. Rashid et al., 2015 [14] have studied the production of biodiesel from waste cooking oil using CaO derived from waste eggshells as catalysts. The calcium oxide has been prepared from waste eggshells by the calcination at different temperatures (700,750,800,850 and 900 C°) for periods of time (1, 2, 3, 4 and 5 hours). The transesterification of waste cooking oil with methanol under the conditions of 30:1 alcohol to oil molar ratio, 65 C° of reaction temperature, catalysts amount 3 wt% and reaction time 3 hours. Under these conditions, the catalyst showed a high biodiesel yield of about 96.11%. Lesbani et la., 2015 [10] in their study, they used calcium oxide obtained by the thermal decomposition at different temperatures of 400,500, 800.900,1000 and 1100 C° of chicken and goat bone. Then the prepared CaO for biodiesel synthesis from discarded cooking oil was used. The biodiesel product showed the biodiesel applied to the chicken bone catalyst had a fatty acid number of 0.56 mg/KOH, iodine number of 22.41 g I2/100 g KOH, the density of 0.88 g/cm^3 and viscosity of 5.91 mm^2/s, while biodiesel applied the goat's bone catalyst has an iodine number of 21.57 g I 2/100 g KOH, the density of 0.88 g/cm^3 and viscosity of 6.34 mm^2/s. 0.56 mg/KOH. The aim of this study is to produce a synthesis of calcium oxide from chicken bones, and biodiesel production from waste cooking oil using commercial and synthesized calcium oxide as a heterogeneous catalyst for transesterification reaction with two different types of alcohols (methanol, ethanol).

2. MATERIALS AND METHODS

2.1 Calcium oxide preparation

Calcium oxide was prepared by collecting the waste chicken bone, then washing and drying it in a normal oven for 30 min. Chicken bones are ground until it becomes a powder. The powder is placed in a burning oven to dry for 7 hours at 800 C°. The prepared calcium oxide was characterized by FTIR, SEM, EDX and the surface area analysis using BET analysis.

Figure 1. Stages of synthesis of the calcium oxide

2.2 Catalytic activity of the catalyst

The catalytic activity of the prepared CaO (synthesis from waste chicken) bone was studied by conducting the transesterification reactions. A reaction was carried out in a 250 mL two-neck round bottom flask equipped with a condenser and a magnetic stirrer. For all reactions, the reaction mixture, which consisted of approximately 18.7 g of waste cooking oil, 0.5 g of catalyst (synthesized and commercial calcium oxide), a molar ratio of alcohol to oil 2:1 in a water bath at 60 °C for 3 h according to the method by [15]. After the reaction was completed, the mixture was filtered to remove the catalyst. Then, the filtrate mixture was transferred to separating funnel samples and left for one night to separate the two layers. The upper layer was the biodiesel, and the lower layer was the glycerol .

The yields of biodiesel were calculated using the equation below [16].

$$\% \; yield = \frac{volume\ of\ biodiesel}{volume\ of\ waste\ cooking\ oil} \; x \; 100$$

3. Results and Discussion

3.1 FT-IR Spectroscopy

Figure 2 below shows the FTIR of spectra of CaO from 4000 to 500 cm^{-1}. In addition, the figures show peaks at 3496 and 3570 cm^{-1}; these peaks correspond to the OH functional group which indicated the presence of physisorbed and coordinated water in CaO. This is due to the hygroscopic property of CaO, and also calcium oxide can easily absorb water vapor from the air [2]. The figure also showed no sharp absorption in the range from 700-900 cm^{-1}, this indicated that the calcium carbonate, which is the major component in the chicken bones, is already converted to calcium oxide [12]. Peak at 1415 cm^{-1} corresponding to O-C-O attached to the calcium oxide surface [10, 17]. Other peaks at 472, 876 cm^{-1} attributed to the bond of Ca-O [18, 19].

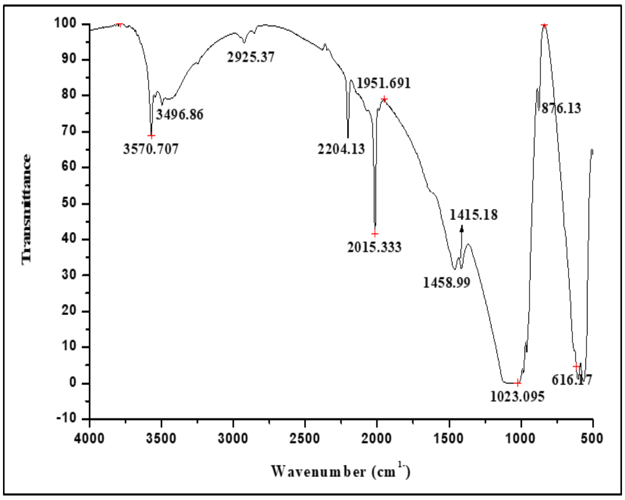

Figure 2. FTIR spectra of prepared CaO

3.2 Scanning Electron Microscopy (SEM)

The surface morphology of CaO sample was identified using SEM at a magnification of 1.50 k as shown in Figure 3. The SEM images showed that the Calcium carbonate from chicken bones form calcium oxide at calcification temperature and this was relevant with previous work [10]. The SEM images of CaO from chicken bones calcined at 800 °C showing that the surface of CaO has irregular particles (a non-uniform size of particles) that contain small flaky particles and large particles, which indicated the formation of CaO [1, 9]. The small particles observed due to the large amount of CO_2 gas produced during the calcination process (the decomposed of $CaCO_3$ to CaO and CO_2), this was also observed by Mmusi et al., 2021 [1].

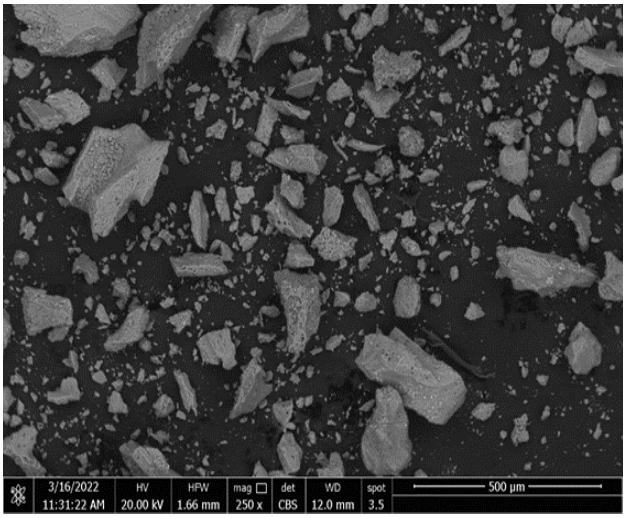

Figure 3 SEM images of unmodified CaO and modified samples with magnification of 1.50 K

3.3 Energy Dispersive X-ray Spectroscopy (EDX)

The energy dispersive x-ray spectroscopy EDX can identify the elements in the sample. The percentage atomic compositions in all samples showed existence of nine elements, i.e carbon (C), oxygen (O), sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), potassium (K), and calcium (Ca). These elements represented the components of chicken bone waste. The results indicated the presence of CaO in the chicken bones and also indicate that CaO was formed in high concentration [1]. It can be seen from Table 1 that the mean composition of elements in chicken bone waste (CaO) was Ca^{2+} and O^{2-} which was in the range of 28.96 and 47.53 %.

Table1 Elemental compositions (%) from EDX analysis of CaO

Elemental compositions (%)	CaO
Ca	28.96
O	47.53
C	16.44
Na	1.18
Al	0.67
K	0.57
Mg	0.78
P	12.64
Si	0.26

3.4 Textural Properties

3.4.1 Nitrogen Sorption Isotherms

The textural characterizations of CaO which consist of the surface area, pore volume and pore size distribution were determined using BET analysis. Figure 4 showed the nitrogen sorption isotherm of the CaO. It was clear that the isotherm of CaO isotherm belonged to Type IV according to the BET classification. Type IV isotherm can be associated to the mesopores type [12]. The samples had a closure point at P/Po (~ 0.4), this means that the complete monolayer formation took place slowly, and there was also an effective contribution of micropores to the adsorption on the samples. Consequently, these features of the sorption isotherms reflected the mesoporous character of the samples.

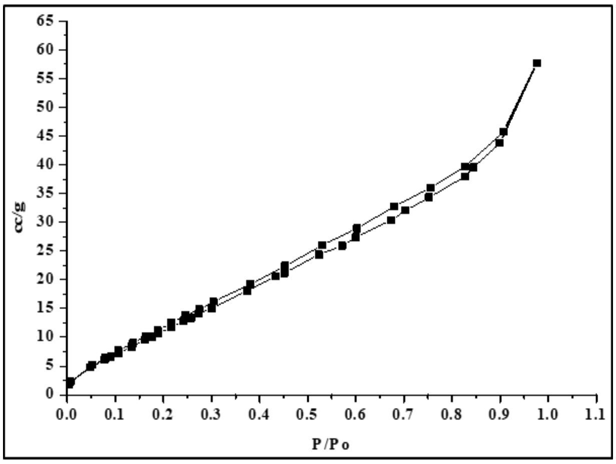

Figure 4 Nitrogen sorption isotherms of CaO

3.4.2 Surface Area Measurement

The textural data of the CaO including the BET surface area, pore volume and pore radius obtained from the conventional analysis of nitrogen isotherms, were showed in Table 2. From the table, it can be seen that the CaO had the high BET surface area (45.3318 m²/g). Zarubica et al. (2015) and Widiarti et al. (2017)[2,20] suggested that the higher calcination temperature from 800 to 1000 ºC will increase the crystal size, where the higher calcination temperature will break the crystal structure of calcium oxide.

Table 2 Textural properties of CaO

Sample	Surface area (m^2/g)	Pore volume (cc/g)	Pore radius (nm)
CaO	28.214	0.0895	48.3318

3.4.3 Pore Size Distribution

Pore size distribution (PSD) was calculated by the BJH method developed by the Barret, Joyner and Halenda model. Pore size distribution curves from adsorption isotherm of the unmodified and modified CaO sample which is illustrated in Figure **5**. As discussed previously, the isotherm of the samples belonged to the mesoporous type with pore sizes between 2-50 nm. According to IUPAC, the definition of these pores are related to the mesopores range, the material micropore (<2 nm), mesoporous (2-50 nm), and macropore (> 50 nm) (Mohadi et al., 2016).

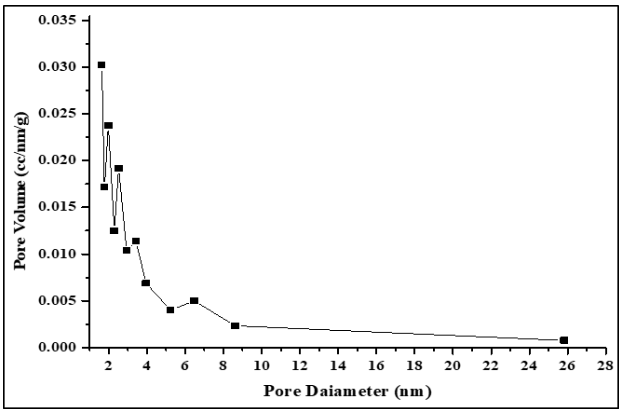

Figure 5 Nitrogen sorption isotherms of CaO

3.5 The catalytic activity

The biodiesel was produced using basic materials of waste cooking oil (WCO), the types of alcohol, ethanol and methanol. The yield of biodiesel produced was calculated from the equation 1. The yields percentage of biodiesel produced at the reaction conditions; 3 hours, 60 ºC , 2:1 alcohol to oil and 0.5 g of catalyst, these are shown in Figure 6. Higher biodiesel yield with methanol around 73% and 71.3% using synthesised and commercial calcium oxide respectively, compared to the reaction with ethanol at 65 % and 63% using synthesised and commercial calcium oxide respectively. The higher biodiesel yield using methanol has been reported in previous works. Studies conducted by Hossain et al. 2010[21] reported that the methanol gave highest biodiesel yield and this can be ascribed to the shorter chain length of methanol and its high polarity, whereas increasing the carbon atom number of alcohols will decrease the –OH molar concentration and polarity of alcohol. The formation of ethyl ester is difficult compared to the formation of methyl ester. In the case of methanol decomposition, the emulsions form rapidly forming a low glycerol-rich layer and a methyl ester-rich layer. Whereas in the decomposition of ethanol, the emulsions are more stable and complex and thus difficult to separate and purify the esters [21].

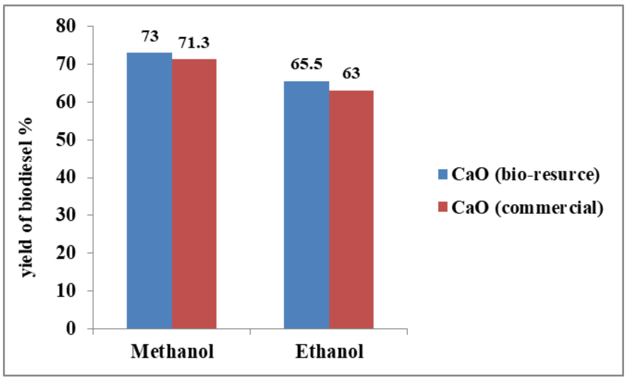

Figure 6. The yield of biodiesel produced using methanol and ethanol

4. CONCLSION

Calcium oxide (CaO) was successfully synthesized from bio-resources (waste chicken bones). The catalysts showed outstanding results in the biodiesel production using waste cooking oil with two types of alcohol. The catalyst was able to give high yield of biodiesel up 71 % and 65 % with ethanol and methanol respectively at the reaction conditions; 3 hours, 80 ºC, 2:1 alcohol to oil and 0.5 g of catalyst. The prepared catalysts showed closer and higher results compared to the commercial calcium oxide. It can be concluded that the calcium oxide proved to be inexpensive, efficient, and potential heterogeneous catalyst to replace the usage of potentially hazardous homogeneous catalyst. This was in addition to the advantages of CaO, such as low cost, eco-friendly with the use of calcium oxide as a catalyst for many of organic synthesis**.**

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