# Comparative study of natural dolomitic rock and waste mixed seashells as heterogeneous catalysts for the methanolysis of palm oil to biodiesel

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## ARTICLE INFO

## ABSTRACT

Natural dolomitic rock and waste mixed seashells were investigated as renewable sources for preparing heterogeneous catalysts for the methanolysis of palm oil to biodiesel as fatty acid methyl esters (FAME) at 60 °C and ambient pressure. After calcination at 800 °C, the dolomite as the mixed CaO·MgO catalyst possessed smaller CaO crystallites, a higher thermal stability and higher basicity than the pure CaO catalyst derived from the seashells. Although both catalysts gave the FAME yield >98% (w/w), the calcined dolomite exhibited a faster methanolysis rate and higher stability in use than the likewise calcined seashells. The linear correlation of the FAME yield to the amount of CaO phase containing in both catalysts supported that CaO was the active site. The catalyst deactivation was relevant to the formation of calcium glyceroxides. The presence of MgO dispersed in the CaO matrix was important for the superior physicochemical and catalytic properties of the natural dolomite calcined at 800 °C.

## 1. Introduction

Biodiesel, an alternative fuel for diesel engines, is of increasing research and commercial interest because of the depleting reserves of the non-renewable fossil fuels of the world and the need to mitigate the greenhouse gas effects caused by increasing atmospheric carbon dioxide ($CO_2$) levels. The primary advantages of using biodiesel are that it is one of the most renewable, non-toxic and biodegradable fuels available, and can be used directly in diesel engines without requiring engine modification. Biodiesel is usually produced by the catalytic transesterification of vegetable oils or animal fats with methanol, so-called methanolysis. Industrially, biodiesel production by transesterification is most frequently performed in the presence of basic catalysts, such as NaOH, KOH or $NaOCH_3$, due to the fast reaction rate they induce [1]. However, the use of homogeneous catalysts requires extensive conditioning and purification steps for the reaction products (fatty acid methyl esters (FAME) and glycerol) to separate the soluble catalysts and impurities. This produces around 120 L of contaminated and alkaline wastewater per 100 L of biodiesel, which requires treatment prior to discharge. These drawbacks contribute to a significant additional economic and environmental costs to biodiesel production.

Replacement of the homogeneous catalyst with a heterogeneous catalyst has, therefore, received considerable attention since the process can be simplified by facilitating the catalyst separation and purification steps. A number of heterogeneous catalysts for the methanolysis of oils have been proposed. For example, $Al_2O_3$-supported potassium salt catalysts, prepared by impregnation method, were reported to be active in the methanolysis of palm oil at 60 °C [2,3]. However, since the active oxide species of alkali metals are easily leached by the methanol, supported alkali catalysts exhibit a short service lifetime. A superior stability of $Ca(NO_3)_2/Al_2O_3$, compared to the alkali metal oxide catalysts, prepared by incipient-wetness impregnation was reported for the transesterification of palm kernel oil and coconut oil with methanol [4]. Despite its strong basicity ($H\_26.0$) [5], the availability and low cost of calcium precursors have motivated the research on the transesterification over pure CaO catalyst [6] as well as the development of CaO mixed with other metals through simple preparation methods [7—13].

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Although high purity and yield of FAME product can be achieved by the heterogeneous catalysis, the molar ratio of methanol: oil and the catalyst amount required are relatively high when compared to the conventional homogeneous system.

In attempting to move towards a more environmentally benign heterogeneous process of biodiesel production, many researchers have attempted to screen various renewable sources for preparation of active solid base catalysts. The waste shells of mussel [14], *Turbonilla striatula* [15], cockle [16], mollusk [17], capiz [18] and eggs [17] calcined at high temperatures (>800 °C) were all found to be active in the methanolysis of vegetable oils into the corresponding FAME. Moreover, the use of calcined limestone as a heterogeneous base catalyst for the methanolysis of soybean oil has been reported [19,20]. Dolomite, as $CaMg(CO_3)_2$, is a naturally abundant and cheap carbonate rock that is industrially utilized in cement manufacturing [21]. The $CaO \cdot MgO$ mixed oxide derived from natural dolomitic rock was also a good solid catalyst for the biodiesel production [22]. Wilson et al. reported the MgO nanoparticles dispersed on CaO as the active sites responsible for the transesterification [23], while the study on the property and activity improvement of calcined dolomite by the hydration-dehydration technique suggested that CaO had higher basicity and catalytic activity than MgO [24].

In the present work, the use of natural dolomite from the South of Thailand and waste mixed seashells from a Thai frozen food industry were used as calcium precursors for the preparation of heterogeneous base catalysts by calcination and then compared with each other for the physicochemical properties and the ability to catalyze the methanolysis of palm oil to biodiesel. Moreover, the reusability and deactivation of the catalysts derived from the natural calcium materials were investigated.

## 2. Experimental

### 2.1. Catalyst preparation

A natural dolomitic rock and a mixture of five different seashell species (*Amusium pleuronectes*, *Anadara granosa*, *Paphia semirugata*, *Paphia undulata* and *Perna viridis*) were donated from the Thai Dolomite Co. Ltd., Surat Thani Province, Thailand. Before being used as catalysts, they were ground in a mortar and sieved to reduce the particle sizes to less than 10 μm, followed by calcination in air using a muffle furnace from room temperature to the desired temperature (600, 700 or 800 °C) at a heating rate of 2 °C min$^{-1}$ and then held at this temperature for 2 h. The calcined materials were then cooled down to room temperature in a desiccator and used in the methanolysis reaction immediately.

### 2.2. Catalyst characterization

The elemental composition of the as-received materials was analyzed with a JEOL ED-2000 energy dispersive X-ray fluorescence spectrometer (XRF). The crystalline structure of the dolomite and the waste mixed shells before and after calcination was determined by means of powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer equipped with Cu Kα radiation with a 0.02° step size range at room temperature and recording the spectra over a 2θ range of 5−80°. Assignments of diffraction peaks were performed after consulting the JCPDS powder diffraction files. The crystallite size of the oxide phases was calculated using the Debye-Sherrer equation [25]. Scanning electron microscopy (SEM) was performed using a JEOL JSM-5410 LV scanning electron microscope to observe the morphological change of the natural calcium materials upon heat treatment.

**Table 1**
Elemental composition of the as-received natural dolomite and waste mixed seashells, as determined by XRF spectroscopy.

| Catalyst | Composition (% (w/w)) | | | | | |
|---|---|---|---|---|---|---|
| | CaO | MgO | $Al_2O_3$ | $SiO_2$ | Others[a] | Total |
| Dolomite | 32.1 | 20.8 | 0.0 | 0.0 | 47.1 | 100.0 |
| Seashells | 68.6 | 0.5 | 0.2 | 0.8 | 29.9 | 100.0 |

[a] $CO_2$ as the major component.

Thermogravimetric and differential thermal analysis (TG/DTA) of the as-received materials and the spent catalysts, using a sample weight of ~10 mg, were simultaneously performed on a Perkin Elmer Diamond thermogravimeter with a temperature ramp rate of 8 °C min$^{-1}$ under a nitrogen ($N_2$) flow at a rate of 20 mL min$^{-1}$. The textural properties of the dolomite and waste mixed seashells thermally treated at different temperatures were measured by $N_2$ adsorption-desorption using a Micromeritics ASAP 2020 surface area and porosity analyzer. The catalysts were degassed at 200 °C for 2 h prior to the measurement. Calculation of the specific surface area was based on the Braunauer-Emmett-Teller (BET) equation using the linear-relationship data attained in the $P/P_0$ range of 0.02−0.2. Temperature-programmed desorption of $CO_2$ ($CO_2$-TPD) was applied to determine the basic properties of the catalysts using a Micromeritics AutoChemII 2920 chemisorption analyzer. The calcined materials were pretreated at 400 °C for 1 h under an Ar flow (50 mL min$^{-1}$), after which the adsorption of $CO_2$ (10% (v/v) in Ar) was performed at 100 °C and the temperature was increased to 900 °C at 10 °C min$^{-1}$ for desorbing the $CO_2$.

### 2.3. Methanolysis procedure

Refined bleached deodorized palm oil, referred to hereafter simply as palm oil, was provided by the Pratum Vegetable Oils Co. Ltd. Methanol was commercial grade with >99.5% purity. A 100-mL three-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was used as a batch reactor for the methanolysis of the palm oil. In a typical reaction, 0.6 g of the calcined catalyst sample was suspended in methanol and the slurry was maintained at 60 °C using a water bath. Subsequently, the palm oil (10 g) was poured into the flask under vigorous stirring. The methanol: oil molar ratio was maintained at 30:1 in all runs as demonstrated by previous optimization study [22]. After the course of the methanolysis (3 h), the catalyst was recovered from the reaction mixture by centrifugation, and the excess methanol was removed in a rotary evaporator.

The composition of the FAME product was analyzed by gas chromatography (GC) using a Shimadzu 14B gas chromatograph equipped with a 30-m DB-Wax capillary column and a flame ionization detector (FID). The column temperature was initially set at 110 °C, followed by elevating to 200 °C at a ramp rate of 8 °C min$^{-1}$. The FAME yield (% (w/w)) was calculated based on the external standard method (EN 14103) using methyl heptadecanoate ($C_{18}H_{36}O_2$, >99%, Aldrich) as the reference standard. The amounts of mono-, di- and tri-glycerides remaining were quantified according to the internal standard method (EN 14105) by GC using an Agilent 7890A gas chromatograph equipped with an auto-injector, a 15-m DB-1ht capillary column and a FID. The initial and final column temperatures were 50 and 370 °C, respectively. The oven heating rate was 10 °C min$^{-1}$. Prior to the analysis, N-methyl-N-(trimethylsilyl)tri-fluoroacetamide (MSTFA, >97%, Fluka) was used to convert the monoglycerides and diglycerides to more volatile derivatives in which n-heptane was added as solvent. The internal standard used for calibration was tricaprin ($C_{33}H_{62}O_6$, >98.5%, Aldrich).