



## Production of fatty acid methyl esters over a limestone-derived heterogeneous catalyst in a fixed-bed reactor



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### ABSTRACT

Production of fatty acid methyl esters (FAME) via the transesterification of different vegetable oils and methanol with a limestone-derived heterogeneous catalyst was investigated in a fixed-bed reactor at 65 °C and ambient pressure. This heterogeneous catalyst, as a 1 or 2 mm cross-sectional diameter extrudate, was prepared via a wet mixing of thermally treated limestone with Mg and Al compounds as binders and with or without hydroxyethyl cellulose (HEC) as a plasticizer, followed by calcination at 800 °C. The physicochemical properties of the prepared catalysts were characterized by various techniques. Palm kernel oil, palm oil, palm olein oil and waste cooking oil could be used as the feedstocks but the FFA and water content must be limited. The extrudate catalyst prepared with the HEC addition exhibited an enhanced formation of FAME due to an increased porosity and basicity of the catalyst. The FAME yield was increased with the methanol/oil molar ratio. The effect of addition of methyl esters as co-solvents on the FAME production was investigated. The structural and compositional change of the catalysts spent in different reaction conditions indicated that deactivation was mainly due to a deposition of glycerol and FFA (if present). The FAME yield of 94.1 wt.% was stably achieved over 1500 min by using the present fixed-bed system.

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## 1. Introduction

Transesterification of vegetable oils or animal fats with methanol in the presence of a homogenous base, such as NaOH or KOH, is the major route for the production of biodiesel as fatty acid methyl esters (FAME) due to the high conversion rate and the mild reaction conditions [1,2]. However, there are some serious drawbacks with homogeneously catalyzed reactions. The process requires neutralization, separation and purification steps that cause a significant increase in the production cycle time, capital investment and operation costs. Furthermore, a large amount of water is consumed and, from the required washing stages, produces environmentally unfriendly alkaline,

biodiesel-contaminated wastewater at significant levels (10% (v/v) the amount of biodiesel produced) that requires detoxification treatment prior to discharge [3]. The use of soluble bases also affects the purity of the glycerol by-product, a versatile trihydric alcohol that is a starting substrate for the syntheses of valuable chemicals.

Recently, Axens commercialized the first heterogeneously catalyzed biodiesel production process, invented by the French Institute of Petroleum (IFP), using a spinel mixed oxide of Zn and Al as a solid base catalyst [4]. The use of this catalyst simplifies the transesterification process by allowing the omission of the catalyst separation and product purification stages. The solid catalyst also reduces the loss of FAME yield from soap formation via the saponification reaction. As a result, a biodiesel with a FAME purity of 98% is produced concomitantly with 99% purity glycerol. Although the transesterification process is operated under high temperature and pressure conditions, resulting in a high operating cost, the plant gains benefit from selling the pharmaceutical grade glycerol.

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Transesterification can be actively performed under milder reaction conditions using an  $\text{Al}_2\text{O}_3$ -supported alkali metal oxide catalysts [5–9]. Unfortunately, the catalytically active centers are easily leached by methanol [10], limiting their economic application at a commercial scale. The use of CaO as an active solid basic catalyst has been widely investigated in alcoholysis [11–17]. In addition to its widespread availability and low cost, it possesses a high basic strength ( $H_- = 26.5$ ) [18] and exhibits a low solubility in methanol [11]. The preparation of CaO can be done by a simple calcination of high-purity limestone at temperatures higher than 825 °C [19], as well as from other natural compounds, such as dolomite, cuttlebone, mollusk shells and eggshells [20,21].

However, CaO has been reported to form colloids of calcium glycerolates ( $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$ ) during the transesterification of rapeseed oil with methanol in a batch reactor [11], and when the column reactor filled with only the calcined limestone was plugged after a long continuous run [22]. Dilution of the catalyst bed by adding active carbon extended the process lifetime. Recently, practical heterogeneous catalysts in an extrudate form were developed via a wet mixing of thermally treated limestone with Mg and Al compounds as binders, and then followed by calcination at high temperatures after extrudate [23]. No colloids were found in the transesterification reaction when performed under both batch and fixed-bed conditions.

In the past decade, there have been a large number of works published on the development of heterogeneous base catalysts for the transesterification of triglycerides [24], of which a few studies have demonstrated the catalytic performance in continuous operation mode conditions [22,23,25]. Here, we reported the production of FAME from different oil feedstocks over a limestone-derived heterogeneous base catalyst packed in a fixed-bed reactor at 65 °C and ambient pressure. Discussion on the system stability and the catalyst deactivation are also provided.

## 2. Experimental

### 2.1. Catalyst preparation

The limestone used in the present study was donated by the Thai Dolomite Company Limited. Elemental analysis by X-ray fluorescence spectroscopy (XRF) indicated the presence of Ca and Mg as the major metals. The transesterification catalyst was prepared as described elsewhere [23] via a physical mixing of calcined limestone with precursors of Mg and Al in the presence of a solvent, followed by calcination. Typically, the limestone powder was calcined in a muffle furnace at 600–800 °C for 2 h, and the required amount of  $\text{Mg}(\text{OH})_2$  and  $\text{Al}_2\text{O}_3$  (AR grade, Ajax Finechem) was then mixed with the calcined rock and deionized water was slowly added under stirring until forming a paste. When hydroxyethyl cellulose (HEC, commercial grade) was used as a plasticizer, the catalyst preparation was carried out in a nitric acid solution. The paste was shaped into a continuous rod with a cross-sectional diameter of 2 mm using a manual extruder and then dried in an oven at 100 °C overnight. Subsequently, the extruded catalyst was cut into 5-mm lengths, followed by calcination in a

muffle furnace at 800 °C for 4 h. Hereafter, the typical catalyst formed from a distilled water paste is designated as CMA-I, whereas the catalysts prepared under the acidic condition without or with adding HEC are denoted as CMA-II and CMA-II-HEC.

### 2.2. Catalyst characterization

The crystalline structures of the catalyst before and after being used in the transesterification were determined by means of powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE X-ray diffractometer equipped with Cu  $K\alpha$  radiation using a 0.02° step size range at room temperature. The diffraction peaks were assigned after consulting the JCPDS powder diffraction files. Elemental analysis was performed by XRF on an Oxford ED-2000 energy dispersive X-ray fluorescence spectrometer. The catalyst morphology was analyzed with a JEOL JSM-5800LV scanning electron microscope (SEM). A Perkin Elmer Pyris Diamond thermogravimetry (TG/DTA) was applied to investigate the catalyst deactivation using a temperature ramp rate of 8 °C  $\text{min}^{-1}$  under a dry air flow at a rate of 20  $\text{mL min}^{-1}$ .

The textural properties of the catalysts were characterized by  $\text{N}_2$  adsorption-desorption measurement at –196 °C on a Micromeritics ASAP 2020 surface area and porosity analyzer. The catalyst was degassed at 200 °C for 2 h prior to the measurement. The total basicity of the catalyst was measured by a  $\text{CO}_2$ -pulse chemisorption using a Micromeritics AutoChem II 2920 chemisorption analyzer. The solid sample (~60 mg) was pretreated *in situ* at 400 °C for 1 h under an Ar flow (50  $\text{mL min}^{-1}$ ), after which  $\text{CO}_2$  (10 vol.% in Ar) was pulsed through the catalyst at 100 °C until reaching the saturation. Some physicochemical properties of the CMA-I, CMA-II and CMA-II-HEC catalysts are summarized in Table 1.

### 2.3. Transesterification reaction

Refined bleached deodorized palm oil (RPO) and palm kernel oil (RKO) were provided by the Chumporn Palm Oil Industry Public Co., Ltd. Food grade palm olein oil (POO) was donated by the Pathum Vegetable Oil Co., Ltd. Waste cooking oil (WCO), after being used for potato and chicken frying, was from Chester's Grill. The fatty acid composition and some properties of the vegetable oils used in the present study are shown in Supplementary Information Tables S1 and S2, respectively, whilst the methanol and ethanol were commercial grade with >99% purity. The transesterification of various oils with methanol or ethanol under continuous conditions was performed in a glass column (20-mm inside diameter and 500-mm height) packed with 78 mL of the calcined catalyst extrudates, and with ca. 2 mm diameter glass beads as the bed support.

In a typical reaction, oil and alcohol were separately fed upwards into the column by peristaltic pumps with a resident time of 60 min (Supplementary Information Fig. S1), maintaining a molar ratio of methanol/oil at 30. In some cases, tetrahydrofuran (THF) at 10% (v/v, based on the oil volume), was added into the oil reservoir to improve the cold flow properties of the feedstocks. The

**Table 1**  
Physicochemical properties of the CMA-I, CMA-II and CMA-II-HEC extrudate catalysts after calcining at 800 °C for 2 h.

Catalyst <sup>a</sup>	BET surface area ( $\text{m}^2 \text{g}^{-1}$ ) <sup>b</sup>	Average pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>b</sup>	Average pore diameter (nm) <sup>b</sup>	Number of basic sites ( $\mu\text{mol g}^{-1}$ ) <sup>c</sup>
CMA-I	34.5	0.148	21.5	45.9
CMA-II	30.3	0.155	20.4	29.2
CMA-II-HEC	24.1	0.239	39.8	35.0

<sup>a</sup> The crystalline phases of all catalysts, as determined by XRD analysis, were CaO,  $\text{Ca}(\text{OH})_2$ , MgO,  $\text{MgAl}_2\text{O}_4$ , and  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ .

<sup>b</sup> Determined by  $\text{N}_2$  adsorption-desorption measurement.

<sup>c</sup> Determined by  $\text{CO}_2$ -pulse chemisorption.

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