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# Production of biodiesel from palm oil using modified Malaysian natural dolomites

Z.A. Shajaratun Nur, Y.H. Taufiq-Yap *, M.F. Rabiah Nizah, Siow Hwa Teo, O.N. Syazwani, Aminul Islam

*Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*
*Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

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ABSTRACT

Calcined dolomite (AD), produced by calcination of Malaysian dolomite (UD) promotes a potential natural catalyst for biodiesel production from palm oil with the conversion of 99.98%. The catalysts were characterized by using X-ray Diffractometer (XRD), Brunauer–Emmet–Teller (BET) surface area, Scanning Electron Microscopy (SEM) and Temperature Programmed Desorption (TPD) of $CO_2$. All catalysts were then employed for transesterification reaction under different conditions (time, methanol to oil molar ratio and amount of catalyst). $SnO_2$ doped on activated dolomite (SD) shows an optimum conversion (99.98%) at conditions, i.e. 15:1 methanol to oil molar ratio in 4 h compared to ZnO doped on activated dolomite (ZD) and AD. The catalytic activities of these catalysts were found to be depending on the basicity as well as the surface area of the catalyst used.



## 1. Introduction

Biodiesel has become a great attention these days as a good replacement for the conventional diesel derived from fossil fuel [1–3]. Biodiesel consists of fatty acid methyl ester (FAMEs) that usually derived from plant instead of petroleum based fuel. Therefore, it offers a solution to fossil fuel depletion and environmental degradation issues due to its ability to be renewed and biodegraded easily. Unlike conventional fossil fuel, biodiesel has no sulfur content and produces lower emission of carbon dioxide ($CO_2$), carbon monoxide (CO) and nitrogen oxides ($NO_x$) to the atmosphere that can cause pollution [4]. Still, the biodiesel is not comparable with the petroleum based diesel due to its high production cost and feedstock price. Thus, many researchers have investigated on how to reduce the cost of biodiesel production. As a result, one of the efficient ways was introduced which is by using catalytic transesterification reaction.

Normally, homogeneous catalysts such as NaOH, KOH, HCl and $H_2SO_4$ have been used for the production of biodiesel [5–7]. However, one of the main problems of using these catalysts is the separation of the catalyst from the reaction medium. Therefore, attentions have been paid to the invention of heterogeneous catalyst to make it easier to separate from the reaction medium. It may be mentioned that, cost of separation processes represented more than half of the total investment in equipment for the chemical and fuel industry [8]. Therefore, researchers have been directed toward the development of heterogeneous catalyst to simplify the separation, purification and washing stage.

Based-catalyzed transesterification reaction has been claimed to provide better conversion of vegetable oil to biodiesel compared with acid-catalyzed reaction [9]. Dolomite is a type rock that can be found around the world which can be used as non-toxic base catalyst. Chemically, it consists of calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$) and very small percentages of other compounds. In Malaysia, the price of dolomite is very cheap (US $20–40 per metric ton) and it is mainly used in constructions as well as agricultural fields. It is used in agricultural field as fertilizers which supplies Mg mineral to the plants that is necessary for their growth. [10]. Similar to the other natural sources of $CaCO_3$, the active phases of the dolomite were obtained by thermal decomposition of dolomite into CaO and MgO as shown in Eq. (1) [11].

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \quad (1)$$

As reported by Kouzu and Hidaka [12], CaO and dolomite are promising basic solid catalysts to produce biodiesel at mild temperature. However, the catalytic potential of natural CaO is relatively lower than natural dolomite as it requires large amount of catalyst in the reaction.

* Corresponding author. Address: Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia. Tel.: +60 389466809; fax: +60 389466758.
*E-mail address:* taufiq@upm.edu.my (Y.H. Taufiq-Yap).

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A few studies have been focused on the use of dolomite as a catalyst for biodiesel production using different types of feedstock such as palm kernel oil, canola oil and olive oil. Ngamcharussrivichai et al. [11] performed transesterification reaction of palm kernel oil at 333 K for 3 h in 30:1 methanol to oil molar ratio. Using 6 wt.% of catalyst under these conditions, 98% yield of methyl ester was obtained. In another report, Ngamcharussrivichai et al. [13] also studied the transesterification reaction of palm kernel oil catalyzed by modified dolomite catalyst. The reaction was carried out in conditions of 15:1 methanol to oil molar ratio for 3 h at 333 K. The result shows that 99.9% of FAME yield was achieved using 10 wt.% amount of catalyst consumed. Ilgen [14] reported that they achieved FAME yields of 91.78% for the transesterification reaction of canola oil. The study was performed in 6:1 methanol to oil molar ratio at 340.5 K for 3 h with 3 wt.% of catalyst. Wilson et al. [15] also carried out transesterification reaction of olive oil in 30:1 methanol to oil molar ratio at 333 K for 3 h using 15.6 wt.% of dolomite catalyst. Based on the literature surveys, however, the efficiency of the dolomite in transesterification reaction is low, as it consumes large amount of catalyst (up to 10 wt.%) [11,13–15]. Thus, aim of this study is to enhance the efficiency of dolomite by incorporating metal oxide such as $SnO_2$ and ZnO onto the dolomite. The metal oxide provides sufficient adsorptive sites for alcohol in transesterification reaction, as reported by several researchers [8]. In our knowledge, there is no report so far on using $SnO_2$–dolomite and ZnO–dolomite catalysts for transesterification reaction to produce biodiesel. The reusability of the catalyst was performed to evaluate the stability of the catalyst.

## 2. Experimental

### 2.1. Materials

Commercial refined palm oil was purchased from local market in Serdang, Malaysia. A gas chromatography (GC) analysis of palm oil was provided in Fig. 1. Grinded dolomite was supplied by The Division Group Sdn. Bhd. (Malaysia). $SnCl_2$ (98%) and $Zn(NO_3)_2$ (98%) were purchased from Sigma Aldrich. MeOH (99.7%) was obtained from J. Kollin Chemicals while chloroform (99.99%) was acquired from Merck.

### 2.2. Preparation of catalyst

The dolomite was sieved using 250 μm (Toshniwal) and subsequently, calcined at 1173 K in tubular furnace for 8 h, as reported by Taufiq-Yap et al. [16] and Wilson et al. [15]. They suggested that dolomite with high calcite content required more than 1173 K of calcination temperature. Modified dolomite catalysts were prepared by wet impregnation method where the calcined dolomite catalyst was doped with 5% of two different metal salts ($SnCl_2$ and $Zn(NO_3)_2$) separately for 3 h at 333 ± 5 K [19]. The slurry mixtures were then dried overnight in the oven at 373 ± 5 K. Grinded and sieved doped dolomites were then calcined at 773 K for 3 h to produce calcined doped dolomites. $SnO_2$ and ZnO doped dolomites were denoted as SD and ZD respectively whereas undoped dolomite was denoted as AD.

### 2.3. Characterization of catalyst

XRD analysis was performed using Shimadzu XRD-6000 Diffractometer at scanning rate of 2°/min (20–80°). The Cu Kα radiation, generated by Philip glass diffraction X-ray tube (broad focus 2.7 kW type) was employed on the catalyst which was mounted on a plate. The patterns obtained were compared with Joint Committee on Powder Diffraction Standards (JCPDS) files based on the peaks' positions and their intensities.

The surface area of the catalysts was investigated by using Brunauer Emmmet Teller (BET) surface area instrument, Thermo Finnigan Scorptomatic 1900 model. The catalysts were degassed overnight at 423 K to remove moisture and foreign gases adsorbed on the surfaces of the catalyst. Adsorption and desorption process of $N_2$ on the catalyst surfaces were analyzed in a vacuum chamber at 77 K.

TPD-$CO_2$ was carried out by using Thermo Finnigan TPD/R/O 1100 instrument equipped with thermal conductivity detector (TCD). The catalysts (~0.05 g) were pretreated by $N_2$ gas flow for 30 min at 573 K. Then, the catalysts were exposed to $CO_2$ gas for an hour at ambient temperature to allow adsorption of $CO_2$ onto the surfaces. Meanwhile, excess $CO_2$ were subsequently flushed by $N_2$ gas. Desorption of the $CO_2$ from the basic sites of the catalyst were detected by TCD under helium gas flow (30 ml/min) from 323 K to 1173 K and held for 30 min.

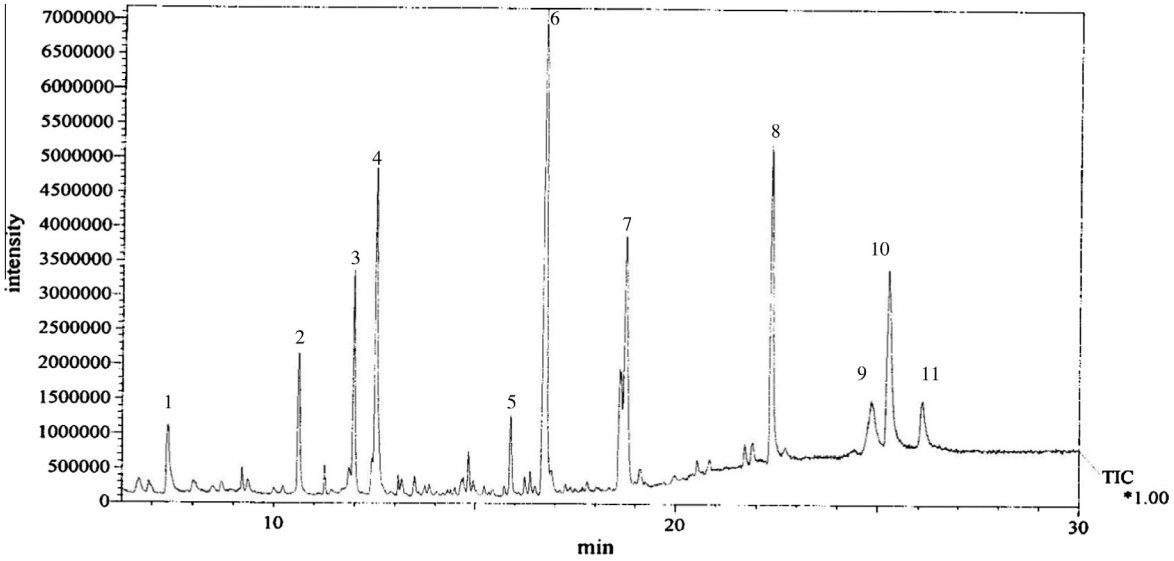


**Fig. 1.** GC analysis of palm oil. 1. Octanoic acid, 2. Tridecenal, 3. 2,4-Decadienal, 4. 2,4-Decadienal, 5. Nonanoic acid, 6. Hexadecanoic acid (palmitic acid), 7. Octadecanoic acid (stearic acid), 8. Hexadecanoic acid (palmitic acid), 9. 2,6,10,14,18,22-Tetracosahexaene, 10. Octadecenoic acid (oleic acid), 11. Octadecadienoic acid (linoleic acid).