



# Synthesis of novel graphene oxide/bentonite bi-functional heterogeneous catalyst for one-pot esterification and transesterification reactions

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## ABSTRACT

Several heterogeneous catalysts have been utilized for biodiesel synthesis from low-grade oils containing free fatty acids (FFA) in a two-stage esterification and transesterification method in previous studies. In this study, NaOH-bentonite impregnated with graphene oxide (GO), as a novel bi-functional heterogeneous catalyst for simultaneous esterification and transesterification was developed and characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, field emission scanning electron microscopy (FESEM), N<sub>2</sub> adsorption measurement to obtain the surface area (BET) and temperature programmed desorption (TPD NH<sub>3</sub> and CO<sub>2</sub>). The effect of reaction time (h), reaction temperature (°C), methanol-to-oil ratio and catalyst amount (wt%) was studied. All experiments were performed at an optimized GO-to-NaOH-bentonite ratio of 1:20. Impressively, the GO-NaOH-bentonite catalyst exhibited excellent catalytic performance and resulted in 89.5 wt% conversion of free fatty acids and 98.5 wt% overall biodiesel yield after 4.5 h reaction time with catalyst amount of 6 wt%, reaction temperature of 62 °C and 6:1 methanol-to-oil ratio. Results showed that the presence of Na<sub>2</sub>O enhanced the low-strength basic sites of the catalyst at 150–200 °C, which played the key role in transesterification of rapeseed oil. It was also found that, the presence of GO on NaOH-bentonite, increased the overall acid strength of the composite catalyst by providing more Brønsted acidic sites. The acidic-basic nature of GO-NaOH-bentonite improved the accessibility of methanol to oil and FFA with the increased pore size of the composite catalyst.

## 1. Introduction

Renewable fuels as an alternative to fossil-derived fuels have attracted many researchers worldwide due to fluctuating oil prices, environmental issues and limited fossil-fuel reserves [1,2]. Expedient population growth along with industrialization has triggered the need of alternative resources to overcome energy paucity. Techno-economic viability of these alternate fuels has been a challenge for scientific community for some time. Among others, biodiesel has attracted a lot of researchers [3–5]. Biodiesel as a sustainable fuel comprises of mono-alkyl esters of long chains fatty acids obtained from vegetable oils and animal fats [6], also known as fatty acid methyl ester (FAME) [7]. Biodiesel has lately become a promising replacement for petroleum diesel fuel because of its renewability, biodegradability and minimized emission of CO<sub>2</sub>, SO<sub>2</sub> and hydrocarbons as compared to petroleum-based diesel [8]. And the best thing about biodiesel is its adaptability to existing engines with or without blending (in variable volumetric ratios

[9]) with petroleum diesel owing to its affirmative combustion properties.

Conventionally, biodiesel is produced via transesterification of vegetable oils with methanol in the presence of acidic and basic homogeneous catalyst. Basic catalysts (NaOH/KOH) give high reaction rate under moderate conditions but the production cost is quite high due to difficulty in separation, purification of the product and in recovery of catalyst [7]. Additionally, basic catalysts cannot be directly employed for oil having more than 2 wt% FFA [10]. Non-edible oils such as Jatropha, rubber seed and waste cooking oils have ≥ 5 wt% FFA which reacts with homogeneous basic catalyst to form undesired soap. Resultantly, FAME yield is substantially reduced and complicates glycerol separation [11]. Use of highly refined vegetable oils resulted in high production costs [12]. Haas et al. [13] calculated that, the feedstock cost effect is up to 88% of the total cost of biodiesel production. Farooq et al. [14] reported the cost reduction up to 60–70% by the utilization of low-quality waste oils which also alleviates the disposal issues.

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Most of the researchers reported two-step process by utilizing homogeneous acid catalysts (HCl, H<sub>2</sub>SO<sub>4</sub>) for esterification to reduce the FFA content up to the desired level followed by transesterification of treated oil in the presence of a basic catalyst for FAME synthesis [15]. Although this method is suited for the utilization of unrefined, non-edible or waste cooking oils as feed stocks but, increased number of separation stages and water washing steps for the removal of corrosive acid and base catalyst make this process more tedious. Consequently, it generates excessive amounts of waste water, in addition to irrecoverable loss of catalyst [16].

Heterogeneous catalysts are the auspicious selection for biodiesel production from vegetable oils and can catalyze esterification and transesterification reactions simultaneously. Catalytic activity for esterification [17,18] and transesterification of vegetable oils [19,20] has been reported widely. Omota et al. [18] studied the utilization of sulphated zirconia as solid catalyst for esterification. Unlike homogeneous catalysts, they have the advantage of easy recovery and reusability [21]. Embong et al. [22] utilized palm fatty acid distillate as feedstock for biodiesel synthesis, esterification reaction was carried out in the presence of SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>-SiO<sub>2</sub> as a solid heterogeneous catalyst. The catalyst showed good catalytic activity and 93.3 wt% conversion was observed at optimum reaction conditions. Several zirconia supported catalysts have been investigated due to their redox properties. Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> (2.6 wt% of Al) and TiO<sub>2</sub>/ZrO<sub>2</sub> (11 wt% Ti) as zirconia based amorphous solid catalysts have been investigated [23] and more than 95 wt% conversion was achieved. Although, conversion efficiency was high but, high reaction temperature (175–200 °C) seems to be the drawback of this reaction. Bala et al. [24] studied the catalytic performance of silicotungstic acid loaded KIT-6 using high FFA feedstock oils. The catalyst showed good stability and 99 wt% FFA conversion to biodiesel was observed at a reaction temperature of 70 °C after 3 h. Santiago-Torres et al. [25] reported high conversion efficiency by utilizing 3% (by weight) of Na<sub>2</sub>ZrO<sub>3</sub> as a basic catalyst for biodiesel by achieving 98.3 wt% FAME conversion after 3 h. Wan Omar and Amin [26] reported 79.7 wt% biodiesel yield by using Sr/ZrO<sub>2</sub> catalyst for waste cooking oil. Rattanaphra et al. [27] achieved 86 wt% methyl ester yield by using sulfated zirconia for transesterification. Thus, it is observed that mostly the catalysts based on zirconia support require high temperature for FAME production.

In recent studies bi-functional heterogeneous catalysts having both acidic and basic sites have been reported. The acidic-basic nature of the catalyst could perform esterification of FFA and transesterification of triglycerides simultaneously to produce FAME at mild reaction conditions [7,28,29]. The purpose of exploring these bi-functional catalysts is to make the process economical by performing simultaneous esterification of FFA and transesterification of triglycerides in a single step. Kulkarni et al. [30] have utilized tungstophosphoric acid supported hydrous zirconia as a solid heterogeneous catalyst for esterification and transesterification of canola oil and 90 wt% biodiesel yield was observed at 200 °C. Rabiah et al. [31] studied lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) supported bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) bi-functional catalyst for simultaneous esterification and transesterification. The Bi<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> catalyst showed good catalytic performance and FAME yield of 93 wt% was observed after 4 h of reaction time, 15:1 alcohol-to-oil ratio, 2 wt% of catalyst amount and reaction temperature of 150 °C. Xu et al. [32] studied Ta<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>-[H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/R] (R = Me or Ph) heterogeneous catalyst for simultaneous esterification and transesterification of soybean oil in the presence of 20% myristic acid as FFA content. The yield of methyl myristate reached up to 99 wt% after 24 h. Endalew et al. [7] studied La<sub>2</sub>O<sub>3</sub>-ZnO catalyst for simultaneous esterification and transesterification by using conventional batch process. The waste cooking oil with 9 wt% FFA content was used as a feedstock. The catalyst showed very low catalyst activity and only 30 wt% yield was observed. The process is not economical because of the expensiveness of lanthanum and the need for higher reaction temperature (160–200 °C) to achieve higher yield. Montmorillonite KSF was studied as a bi-functional acid-base

solid catalyst for simultaneous esterification and transesterification. *Cerbera Odollam* oil with 54 wt% FFA content was used as a feedstock. The catalyst showed better performance and successfully performed esterification and transesterification simultaneously. The recorded FAME yield was found to be 48.3 wt% at optimized parametric reaction condition [33].

Clay materials are also prevalent in nature and can be used as a solid catalytic support for transesterification due to its heterogeneous composition, low cost and porosity [34]. There are many types of clay available naturally such as kaolin, zeolite and bentonite. The most abundantly available clay is bentonite with good adsorption ability. The raw bentonite can be activated by thermal activation and sometimes treated with alkali to increase its basicity [35,36]. The presence of basic sites actively enhances the transesterification reaction rate. Fukuda et al. [37] reported that alkali catalyzed transesterification reaction proceeds 4000 times faster than acid catalyst of same amount. Clay materials can be utilized as a promising heterogeneous catalysts or catalyst supports for biodiesel production. Gitari [38] reported that bentonite clay possessed free alkaline materials. The composition of bentonite (MgO, Na<sub>2</sub>O, CaO, and K<sub>2</sub>O) indicated the presence of exchangeable cations which are responsible for its basicity. However, there is a very scarce utilization of clay materials for biodiesel production [34]. Boz et al. [39] studied the transesterification of canola oil by utilizing bentonite impregnated with KF, KOH or K<sub>2</sub>CO<sub>3</sub>. It was found that KF/bentonite prominently increased the FAME yield as compared to KOH and K<sub>2</sub>CO<sub>3</sub> and the catalytic performance for transesterification reaction was greatly affected by basicity of the catalyst. Soetaredjo et al. [35] performed transesterification of palm oil using KOH/bentonite as a solid heterogeneous catalyst, has achieved 90 wt% biodiesel yield. Several studies reported the utilization of alkaline metal oxides as heterogeneous catalysts for transesterification [21,28,40]. The sensitivity of basic heterogeneous catalysts towards water and FFA (would lead to saponification) made them unsuited for low-grade oil with free fatty acid content more than 3 wt% [28,41]. NaOH/bentonite was reported as an alkaline heterogeneous catalyst for transesterification of rapeseed oil in our previous work [34]. The results showed promising catalytic performance and 92 wt% FAME yield was observed after 3 h of reaction time and catalyst amount of 3 wt%. Indeed, for the simultaneous esterification and transesterification reaction, further modification of the basic catalyst can be achieved by providing acid centers for effective FAME production [40]. However, the high basicity and the scarcity of the acidic site limited the capability of NaOH/bentonite to be implemented in one pot esterification and transesterification reactions.

Carbon-based catalyst is gaining pronounced attention due to its unique surface properties. In recent times, graphene oxide (GO), which is a single atomic layer of graphite oxide, has been highlighted because of its high specific surface area and presence of complex cocktail of oxygen functionalities on edges and basal planes [42]. GO, a delaminated layer of graphite oxide consists of sp<sup>3</sup>-hybridized carbons on the surface and sp<sup>2</sup>-hybridized carbon on the aromatic network and has the ability to donate protons due to the presence of hydroxyl groups on the surface [43]. Graphite oxide supported CaO was developed as a solid heterogeneous catalyst for transesterification [44]. In addition, it has become a promising catalyst because of its easy preparation from cheap graphite powder, low cost, thermal stability and easy exfoliation. The mechanical strength and chemical stability of GO is due to high C–C bond strength and the presence of carbon atoms at higher oxidation states [45]. GO contains Brønsted acidic sites along with carboxyl, hydroxyl and epoxide functionalities [46,47]. It's important to note that, Brønsted acid sites play a pivotal role to esterify FFA content of the oil [21]. It was reported that metal oxides supported GO composites increase the mechanical strength of the solid heterogeneous catalyst [48]. An interesting study demonstrated, microwave assisted biodiesel production by utilizing GO as a solid acid heterogeneous catalyst. The results indicated 95.1% conversion efficiency of lipids to FAME [49].

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