



High performance heterogeneous catalyst for biodiesel production from non-edible oil

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In this study biodiesel production by transesterificating *Silybum marianum* oil with methanol was done using KF-Atta-2M-5 catalyst prepared from low-cost attapulgite clay. This effective heterogeneous catalyst was prepared by dehydroxylating raw attapulgite at 130°C for 6 h and treating it with 1.5 M H₂SO₄. Following washing and drying, the acid-activated attapulgite was soaked in 2 M KF for 24 h, then dried at 100°C for 12 h and finally calcined at 400°C for 5 h. The catalyst was characterized using Hammett indicators, Fourier transform infrared (FTIR), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and scanning electron microscopy (SEM). The optimum conditions for the transesterification reaction include methanol to oil ratio of 12:1, catalyst amount of 12 wt.%, reaction temperature of 65°C and reaction time of 5 h. The optimum yield was 93.5%. The catalyst could be cheap and have superior activity for which reason it may be a potential candidate for biodiesel production. The properties of the biodiesel were also comparable to American-ASTM D6751-03 and European-EN 14214 standards.

Introduction

Increase in greater quantities of biodiesel production is currently the global target given that it is the most valuable form of renewable energy that can be used directly in any existing, unmodified diesel engine. However, the conventional technology used in the industrial production of biodiesel employs basic homogeneous catalysts on transesterification of refined oils [1,2]. There are problems associated with the use of the homogeneous catalysts and these include cost of purification of the product and the residues that are generated [3]. These and many others are generating interest in the field of heterogeneous catalyses to explore for low cost, suitable and economical solid catalysts with high activity for biodiesel production.

Different materials have been used as heterogeneous catalysts for transesterification of vegetable oils to biodiesel [4,5]. However,

majority of the homogeneous catalyst have limited use and application. Others are also expensive and complicated to prepare.

Clays are very cheap materials that offer a lot of potential options including the removal of organic and inorganic contaminants [6,7]. Natural clays are readily available and have good cation exchange capacity. Clays have been used to adsorb metallic and organic contaminants including pesticides, phenols and chlorophenols in water [8–11]. Clays are also used as catalysts or catalytic support. The catalytic capacity of clays is due to the relatively high surface area and the net negative charge [12]. Attapulgite is one of such clays with similar functions but different structure. Attapulgite is needle shaped silicate. Its particles are approximately 20 nm in diameter with length of varying range spanning hundreds of nm to μm. It is hydrated magnesium aluminium silicate that contains ribbons of 2:1 phyllosilicate structure [12,13]. Recent studies indicate that attapulgite can be used either as catalyst or support in various chemical processes [12,14–17]. Its unique morphology and structure provides potential for such diverse applications. However, our understanding on

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the structure and morphology of attapulgite as well as methods and tools needed to make it a better material for heterogeneous catalysis (e.g., synthesis, characterization, and reaction kinetics) is nascent. In this context, high-throughput experimentation appears to be one of the most effective for studying the environmental friendliness, catalyst recovery and process integrity of attapulgite. In this study, potassium loaded attapulgite was used as heterogeneous catalyst in the transesterification reaction of *Silybum marianum* (density (kg/m^3)) at 15°C 921.4, saponification no. 191.54, molecular weight (g) 887.9 and FFA content (% w/w) 0.68 with high proportion of unsaturated fatty acids primarily, linoleic acid (65.68%) and a lower amount of saturated ones, typically palmitic (15.04%) and arachidic acid (5.93%) oil with methanol to biodiesel.

Silybum marianum is widely cultivated in Africa and grows wild particularly in Ghana. The medicinal and pharmaceutical aspects of the plant have received attention from researchers [18,19]. For example, the extract from the seeds can be used traditionally for treatment of hepatotoxicity, acute and chronic liver diseases [18,19]. Recent studies have revealed that the seeds of the plant contain much oil [20,21]. Ghavami et al. [20] reported that the content of the oil is more than 28%. Recent study by Li et al. [21] revealed that the oil content to be more than 45%. Also in silymarin industrial oil production, the oil is considered a by-product and not much used. Parameters such as methanol/oil molar ratio, catalyst concentration, reaction temperature and time effects were studied. The possibility of reusing the catalyst for continuous biodiesel production was also investigated.

Experimental

Materials and methods

Attapulgite, H_2SO_4 , K_2CO_3 , $\text{C}_4\text{H}_4\text{O}_6\text{HK}$, KOH, KF and KI were obtained from Sinopharm Chemical Reagent Co., Ltd. (China) [22,23] and Ryte Aid Chemicals (Ghana). The chemicals were all of analytical reagent (AR) and used without any purification.

Synthesis and characterization of activated Atta-based catalyst

The attapulgite particles were first dried in an oven at 130°C for 3 h. 5–10 g of the attapulgite nano-powder (10–30) mesh was then treated with 50 mL H_2SO_4 , thus 1.5 M for 1 h at 85°C . This was followed by washing with distilled water until pH of 7 was detected by 0.1 mol/L AgNO_3 aqueous solution. Following centrifugation, the activated attapulgite was dried at 120°C for 12 h to obtain H_2SO_4 -activated attapulgite. About 3.5 g of the dried H_2SO_4 -activated attapulgite was then soaked in 2 M KF solution at atmospheric temperature and pressure for 24 h. The product was subsequently dried at 120°C for 12 h and then calcined at 400°C for 5 h.

Hammett indicator, FTIR, XRD, SEM and BET were used to characterize the changes in structure and morphology of fresh catalysts [23].

Biodiesel synthesis

Biodiesel synthesis was done by transesterifying 20 g of *S. marianum* oils in excess methanol using the procedure modified from Wang et al. [24]. Typically, 12:1 methanol to oil ratio, 11% catalyst amount at 65°C in 5 h using 125 mL round bottom flask was refluxed. A stirring rate was maintained at 600 rpm. After

completion of the reaction, the mixture was washed with n-hexane to remove any absorbed biodiesel from the solid catalyst. The mixture was then centrifuged at 5000 rpm for 10 min to ensure the separation of the solid catalyst from the liquid layer made of biodiesel and the n-hexane. The transesterification process was performed in triplicate for each set of parameters.

Yield and chemical analyses of the *S. marianum* biodiesel

The biodiesel samples were analyzed using 7890A gas chromatograph (Agilent Technology Inc., USA), equipped with a flame-ionization detector (FID) and a HP-5 capillary column (30 m \times 0.25 mm i.d., film thickness 0.25 μm ; Restek, Bellefonte, PA). Helium was used as the carrier gas. The oven temperature ramp program was similar to Takase et al. [22,23] with slight modification. Thus, the flow rate of hydrogen was 40 mL/min and that of air was about 400 mL/min. Temperatures of the injector and detector were 280 and 300°C , respectively. The injection was performed in split mode with a split ratio of 80:1. Biodiesel yield was quantified in the presence of tetradecane as an internal standard. The analysis of biodiesel for each sample was carried out by dissolving 1 mL of biodiesel sample into 5 mL of n-hexane and 0.5 μL of the solution injected into GC. The biodiesel yield was calculated using the following equation [25]:

$$\text{FAME}(\text{wt.}\%) = \left(\frac{\text{area of all FAME}}{\text{area of reference}} \times \frac{\text{weight of reference}}{\text{weight of biodiesel sample}} \times \frac{f_{\text{FAME}}}{f_r} \right) \times 100$$

where f is the correction factor for transforming area% to weight% obtained from calibration.

Results and discussion

Catalyst characterization

FTIR spectra of raw attapulgite and KF-Atta-2M-5 are shown in Figure 1. In the spectrum of KF-Atta-2M-5, the absorbance at 3344 and 1002 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations of Atta=O bond of the raw attapulgite. New strong bands are observed at 1663 and 1369 cm^{-1} on the spectra of KF-Atta-2M-5 and this could be considered the symmetric and asymmetric stretching vibrations of Atta-O-K groups due to K^+ ions which could replace Atta-O-Atta groups at the high calcination temperature [26]. The FTIR spectra of KF-Atta-2M-5 revealed

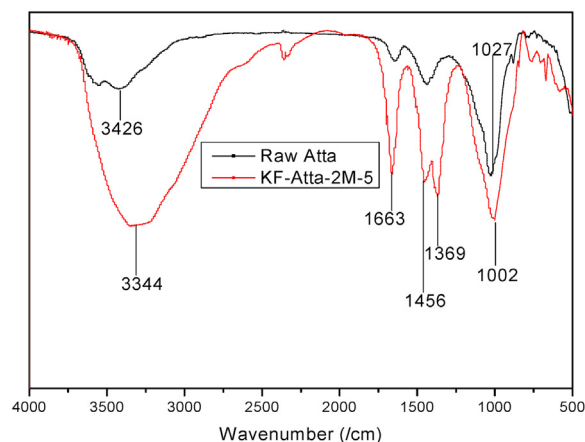


FIGURE 1
FTIR spectra of Atta and KF-Atta-2M-5.

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