



Synthesis and kinetics of biodiesel formation via calcium methoxide base catalyzed transesterification reaction in the absence and presence of ultrasound

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HIGHLIGHTS

- ▶ Biodiesel synthesis from soybean oil using calcium methoxide as solid base catalyst.
- ▶ Studied effects of catalyst concentration, methanol/oil mole ratio, reaction temp.
- ▶ Biodiesel yield >90% in 1.5 h using 1% catalyst, 9:1 methanol/oil and 65 °C temp.
- ▶ Effect of catalyst storage time and ultrasound (20 and 611 kHz) on biodiesel yield.
- ▶ Kinetic parameters derived for pseudo first order with two-step reaction mechanism.

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ABSTRACT

The transesterification of soybean oil using calcium methoxide as solid base catalyst and the process parameters affecting the yield of biodiesel such as the catalyst concentration, methanol/oil molar ratio and the reaction temperature were investigated in detail. The results showed that the yield of biodiesel in excess of 90% was achieved within 90 min using 1% catalyst loading, 9:1 methanol/oil molar ratio and 65 °C reaction temperature. In addition, the effects of catalyst storage time on its activity for transesterification reaction and ultrasound at 20 kHz and 611 kHz frequencies on the yield of biodiesel were also evaluated. TGA–DSC and BET studies showed that the catalyst has good thermal stability and high surface area, respectively. Furthermore, the mechanism of this heterogeneously catalyzed transesterification system with and without ultrasonication was demonstrated to be a two-step reaction in which mass-transfer controlled regime is accompanied by kinetically controlled regime with both regimes following pseudo first order reaction kinetics.

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1. Introduction

Biodiesel also called fatty acid methyl ester (FAME) is a clean-burning, renewable fuel produced from vegetable oils, animal fats and recycled cooking oil and greases, etc. [1–3]. Sodium and potassium hydroxides are the most studied and industrially used catalysts for biodiesel production. These catalysts allow transesterification to be performed in a shorter reaction time under moderate operating conditions. However, removal of the base catalyst after reaction is a major problem since aqueous quenching results in the formation of stable emulsions and saponification, making separation of the methyl ester difficult with increased production costs. The solid catalysts can be easily separated from the reaction products with much more simplified product separation steps resulting in high yields of methyl esters and decrease of catalyst

cost due to catalyst regeneration [4]. Heterogeneous systems operate in a continuous mode and are designed to give higher catalyst activity, selectivity and longer lifetimes, increasing the production capacities and lowering associated costs [5,6].

Many types of heterogeneous basic catalysts, such as zeolites and modified zeolites [7–9], alkaline earth metal oxides [10–14], supported alkaline earth metal oxides [15–19], supported alkali metals [20–23], alkali and alkaline earth mixed [24–26], hydrotalcites/layered double hydroxides [27–29], rare earth/lanthanide based [30–32], ion exchange resin [33], zirconia based [34–36] and various other compounds showing active basic sites [37–39] have been proposed or studied in the literature. Biodiesel synthesis by using most of these catalysts have shown promising results with good-to-high yields, but the majority of these methods suffer at least from one of several disadvantages. These include low activity, use of solvents, need for high temperature, long reaction time, high methanol/oil molar ratio, high catalyst loading, high cost and catalyst toxicity. Alkaline earth metal oxides are the most studied

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solid-base catalysts for transesterification of vegetable oils in the literature. The existence of basic sites on the alkali earth oxides have been attributed to the presence of $M^{2+}-O^{2-}$ ion pairs in different coordination environments [40]. The basic strength of alkaline earth metal oxides and hydroxides was observed to increase in the order of $Mg < Ca < Sr < Ba$ [41]. From the economical and ecological point of view, calcium derived bases were found to be the most promising as they are inexpensive, exhibit low methanol solubilities, and are the least toxic of most of the catalysts studied to date.

Calcium methoxide represents a potential alternative to homogeneous alkaline catalysts as it showed higher activity and very low solubility compared to calcium oxide catalyst in the transesterification of rapeseed oil with methanol. Under the reflux condition, 93% yield of FAME was obtained in 150 min using 4.5:1 methanol/oil molar ratio and catalyst loading of 1.25% [11]. Liu et al. [14] investigated the transesterification of soybean oil with methanol using calcium methoxide as solid base catalyst and found it to exhibit excellent catalytic activity and stability. Yield of 98% was obtained under the derived optimum conditions of 65 °C reaction temperature, 2% catalyst, reaction time of 120 min and 1:1 volumetric (or 22:1 molar) methanol/oil molar ratio. The catalyst maintained its activity for 20 cycles in a recycling experiment with only slight decrease in the biodiesel yield. The use of calcium ethoxide at 12:1 molar ratio of methanol to oil, 3% catalyst, and a reaction temperature of 65 °C yielded 95% FAME in 90 min. The used calcium methoxide and ethoxide catalysts were observed to have surface areas in the range of 15–19 m²/g [42].

Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems due to its ability to improve mixing and mass transfer especially in biphasic systems and allow operation at mild conditions of temperature and pressure [43]. It has been successfully used to increase the conversion and the yield of reactions, change reaction pathway and/or initiate reaction in biological, chemical, and electrochemical systems [44,45]. The enhancement of biodiesel synthesis resulting via ultrasonic cavitation in homogeneous catalytic systems have been reported by several prior investigators [46–49]. However, studies in heterogeneous catalysis involving ultrasound are still limited [50–52]. Gryglewicz [11] found that in the methanolysis of rapeseed oil using calcium methoxide catalyst, reaction time reduced from 150 min to 45 min for 93% FAME yield when ultrasonic bath (25 kHz, 300 W) without temperature control was used compared to the conventional reaction under refluxing condition. Georgogianni et al. [51] studied the ultrasonic transesterification (24 kHz, 200 W) of rapeseed oil using Mg/MCM-41, MgAl hydrotalcite and K/ZrO₂ catalysts. At 60 °C and 10% catalyst loading, and very high methanol/oil mole ratio of 285:1, biodiesel yields of 89%, 96% and 83% were obtained after 300 min using Mg/MCM-41, MgAl hydrotalcite and K/ZrO₂ catalyst, respectively. Mootabadi et al. [50] also studied the ultrasonic transesterification (20 kHz, 200 W) of palm oil and obtained improvement of 75%, 47% and 30% over magnetically stirred system for CaO, SrO and BaO catalysts, respectively. Kumar et al. [48] observed a significant reduction in reaction time with a 98.53% biodiesel yield obtained in 15 min for the transesterification of Jatropa oil in the presence of ultrasound (24 kHz, 200 W) using Na/SiO₂ (3% wt/wt of oil) compared to the conventional stirring process, both at 9:1 methanol/oil mole ratio. The results of these prior studies suggest that ultrasound has different influence on transesterification reactions depending on the different feedstock and catalyst systems used.

In the present study, high surface area calcium methoxide catalyst is used for the transesterification of soybean oil in a cylindrical jacketed glass reactor. A detailed parametric experimental study was performed to select the best parameters (or conditions) for the specified purpose of this investigation. The effect of storage time on the activity of the catalyst was also evaluated by carrying

out the transesterification reaction with fresh catalyst as well as the catalyst stored for 160 days. Transesterification in the presence of ultrasound at both low (20 kHz) and high (611 kHz) frequencies were also studied. Finally, the kinetics of this calcium methoxide base-catalyzed transesterification of soybean oil with and without ultrasound was evaluated for the first time using a previously reported kinetic and mass transfer model for heterogeneous systems [53].

2. Experimental

2.1. Chemicals

Calcium methoxide [$Ca(OCH_3)_2$ >90%, balance methanol] was obtained from STREM Chemicals (Newburyport, MA). Pure soybean oil was obtained from MP Biomedicals, LLC (Solon, OH). The certificate of analysis from the supplier shows that FFA content of the oil was 0.03%, iodine value was 130/100 g of soybean oil, and peroxide value was 0.2 meq/g. Methanol of ACS grade was obtained from Fisher Scientific (Somerville, NJ).

2.2. Catalyst preparation

The calcium methoxide obtained from the supplier was in the form of flakes. It was ground manually using mortar and pestle and passed through 100 mesh screen to obtain the fine powdered catalyst, which was stored in a dark, well closed, glass bottle in a desiccators containing silica gel.

2.3. Catalyst characterization

The BET surface area, total pore volume and pore size distribution of the catalyst were determined with AUTOSORB-1C, Chemisorption-Physisorption analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Surface area was calculated by using BET equation from the adsorption branch of the isotherm in a relative pressure range of 0.07–0.3. The pore size distribution was calculated from desorption branches using the Barrett-Joyner-Halenda (BJH) method [54]. The total pore volume was derived based on the amount of N₂ adsorbed at a relative pressure close to unity. Thermo-gravimetric (TGA) and differential scanning calorimetry analysis (DSC) were carried out using a SDT Q600 V20.4 Build 14 system (TA Instruments, New Castle, DE, USA). The heating was carried out in a nitrogen environment. The nitrogen flow rate was maintained at 100 ml/min and the heating rate was 10 °C/min. The FTIR spectra were obtained using an FTIR spectrometer (SENSOR 27, Bruker Optics, Inc., Billerica, MA). The XRD patterns were recorded on D8 DISCOVER X-ray diffractometer from Bruker (Bruker Optics, Inc., Billerica, MA) with a PSD detector using Cu K α radiations generated at 40 mA and 40 kV at the scanning rate of 0.01°/s.

2.4. Transesterification reaction procedure

The reaction was carried out in a cylindrical jacketed glass reactor with four necks. It was equipped with condenser to reflux the methanol evaporated during the reaction. A thermocouple with digital temperature indicator was used to measure the temperature of the reaction mixture. The stirring was carried out using a magnetic stirrer (396 W, StableTemp, Cole Parmer) at 1000 rpm. To start the experiments, the measured quantities of oil and methanol were added to the reactor. The mixture was heated by circulating the hot water through a reactor jacket with continuous stirring to get required temperatures. Then the measured quantity of catalyst was added to start the reaction. Samples (1 ml aliquot) were

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