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Transesterification of used vegetable oil catalyzed by barium oxide under simultaneous microwave and ultrasound irradiations

Edith Martinez-Guerra, Veera Gnaneswar Gude *

Civil and Environmental Engineering Department, Mississippi State University, Mississippi State, MS 39762, United States

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ABSTRACT

This study presents a novel application of simultaneous microwave and ultrasound (MW/US) irradiations on transesterification of used vegetable oil catalyzed by barium oxide, heterogeneous catalyst. Experiments were conducted to study the optimum process conditions, synergistic effect of microwave and ultrasound irradiations and the effect of power density. From the process parametric optimization study, the following conditions were determined as optimum: 6:1 methanol to oil ratio, 0.75% barium oxide catalyst by wt.%, and 2 min of reaction time at a combined power output rate of 200 W (100/100 MW/US). The biodiesel yields were higher for the simultaneous MW/US mediated reactions (~93.5%) when compared to MW (91%) and US (83.5%) irradiations individually. Additionally, the effect of power density and a discussion on the synergistic effect of the microwave and ultrasound mediated reactions were presented. A power density of 7.6 W/mL appears to be effective for MW, and MW/US irradiated reactions (94.4% and 94.7% biodiesel yields respectively), while a power density of 5.1 W/mL was appropriate for ultrasound irradiation (93.5%). This study concludes that the combined microwave and ultrasound irradiations result in a synergistic effect that reduces the heterogeneity of the transesterification reaction catalyzed by heterogeneous catalysts to enhance the biodiesel yields significantly.

1. Introduction

The persisting global energy crisis and the escalating greenhouse gas emissions at global levels from fossil fuel consumption have provided impetus for research and development in the areas of renewable energy and fuels production. Several renewable energy sources such as solar, nuclear, geothermal, wind, and biomass have been explored and appropriate technologies have been developed in the past few decades to serve as carbon–neutral energy sources. Among these renewable energy sources, energy production from biomass and its derived feedstock (i.e., oil) appears to be a very attractive option since the energy/fuel derivatives from these sources possess high energy content/density with minimum environmental emissions. Biodiesel produced from biomass derived oils is also an excellent example of carbon–neutral transportation fuel. As such, it is critical to develop energy-efficient technologies for biodiesel production to enhance the environmental benefits, as well as the net energy benefits of the overall process.

For long-term sustainability of biodiesel production, the following must be considered: (1) developing the best scientific, engineering and technological solutions for converting the feedstock into energy/fuel sources; (2) minimizing the environmental impact by reducing the water and energy consumption; and (3) addressing long-term availability of the feedstock supplies, preferably from local production/sources [1,2]. Accordingly, in this research a novel application of simultaneous microwave and ultrasound irradiations was evaluated for biodiesel production with the goal of understanding their synergistic effect on the transesterification reaction. Microwaves and ultrasound have been used as constructive, rapid and safe methods for biodiesel production [3,4]. Used vegetable oil was utilized as feedstock since it is often available at a very low cost or even free locally for biodiesel production [2,5–10]. Feedstock costs usually account for up to 80% of the total biodiesel costs [11]. Biodiesel from virgin or used oil feedstock is usually produced through a well-known method called "transesterification reaction". The transesterification reaction, also known as alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. The result is that triglyceride molecules (90–98% of the oil), which are long and branched, are transformed into smaller esters whose size and properties are similar to those of diesel oils [12,13]. The transesterification reaction can be conducted

* Corresponding author.
E-mail address: gude@cee.msstate.edu (V.G. Gude).

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by using various catalysts categorized as homogeneous or heterogeneous catalysts [14]. Homogeneous catalysts such as "sodium hydroxide" or "potassium hydroxide" dissolve in the biodiesel, and their separation process produces large quantities of wastewater impacting the environment, adding to the treatment processes and finally increasing product costs. These issues can be circumvented by employing heterogeneous catalysts that do not dissolve or sparingly dissolve in oil or methanol phases and eliminate the extensive cleaning, separation, and drying processes. Heterogeneous catalysis has many advantages such as non-corrosiveness, being an environmentally benign process, fewer disposal problems, and better biodiesel production economics [15]. They are also much easier to separate from liquid products and can be designed for higher activity, selectivity, and long catalyst lifetimes [16,17]. Many types of heterogeneous catalysts, such as alkaline earth metal oxides, and various alkaline metal compounds supported on alumina or zeolite can catalyze transesterification reactions [18–20].

This paper presents the simultaneous effect of microwave and ultrasound irradiations on transesterification of used vegetable oils catalyzed by heterogeneous catalyst, barium oxide (BaO). The effect of various process parameters such as methanol to oil ratio, catalyst amount, and the reaction time were evaluated. The synergistic effects [21] of the two novel technologies on the heterogeneously catalyzed transesterification reaction were investigated. The following sections present the experimental studies and the results with a discussion in detail.

2. Materials and methods

2.1. Materials

The used vegetable oil (UVO) was obtained from a local restaurant in Starkville, MS. The acid value of UVO was found to be 3.5 mg KOH/g, corresponding to a free fatty acid (FFA) level of 1.7%. Although the solid acid catalysts are preferred for simultaneous esterification and transesterification of feedstock possessing high acid value (free fatty acids, FFA%), we have used solid base catalyst (BaO) which has higher catalytic performance for transesterification than solid acid catalyst. Also, it should be noted that the base catalyzed transesterification is suitable for feedstock with FFA content less than 4% [22]. The molecular weight of the used vegetable oil was calculated to be 837 g/mol from GC–FID analysis. Methanol and catalyst (barium oxide, BaO) were purchased from Fisher Scientific and are of analytical grade. The transesterification experiments were conducted in a microwave/ultrasound reactor with temperature and power control functions manufactured by Columbia International Technologies®, USA. Microwave irradiation at 2.45 GHz frequency was applied while the ultrasound frequency was at 25 kHz. This ultrasound frequency was chosen because most of the previous biodiesel research studies have reported superior results at this frequency [4]. Microwave-transparent, three-neck custom-fabricated reaction vessels made of borosilicate glass (provided by Columbia International Technologies) were used as reaction vessels.

2.2. Methods

The experimental setup consists of a microwave unit combined with ultrasound horn and a thermocouple and a reflux condenser. To identify the combined effect of the microwaves and ultrasound (MW/US), a matrix of conditions was evaluated by fixing a sample volume and energy output rate and by changing the process conditions. For the first set of tests, 20 mL of UVO was added to the mixture of methanol and BaO (catalyst) and was then subjected to MW/US (100/100 W) irradiations. A three-neck reactor equipped with a reflux condenser and a temperature probe was used. The reflux condenser allowed for cooling of the evaporating solvent (methanol) and returning to the reaction mixture. Temperature and power readings were recorded every 10 s for all the experiments. The molar ratio of methanol to oil tested were 4.5:1, 6:1, 9:1, and 12:1, while the catalyst loads ranged from 0.25% to 1.5% (wt./wt.) by increments of 0.25%. Different reaction times and different power output rates were also evaluated. For 100/100 W (MW/US) power output rates, the reaction times of 1–5 min at one minute intervals were tested. After the exposure of the reaction mixture to MW/US irradiation and before measuring the yield, the samples were allowed to settle for 12 h and then washed with warm deionized water in a pear-shaped separatory funnel to eliminate any soap and unreacted methanol in the biodiesel. The Glycerol layer was separated from the biodiesel (fatty acid methyl esters – FAMEs) layer prior to washing. The samples were then placed in an oven at 60 °C before measuring the yield. The biodiesel quality was confirmed by the GC–FID analysis by standard ASTM B100 method. 1, 3-DBC was used as an internal standard and 193 BHT was used as antioxidant [8].

For the microwave and ultrasound individual and synergistic effect tests, the power output rate of 100/100 W, 2 min reaction time, 1% catalyst, and 6:1 methanol to oil molar ratio were fixed during the experiment. For the power density tests, different sample volumes (20, 40, 60, and 80 mL) were evaluated using a 6:1 methanol to oil ratio, reaction time of 2 min, and catalyst of 0.75 wt.% for 100/100, 200/0, and 0/200 Watts of MW/US power output rates.

2.3. Heterogeneous catalysis mechanism

The main mechanism of heterogeneous catalysis follows the principle similar to homogeneous catalysis of either acid or base systems [23,24]. The important factor in homogeneous base catalyzed reaction is to create nucleophilic alkoxide from the alcohol to attack the electrophilic part of the carbonyl group of the triglycerides [25], while in acid catalysis the carbonyl group in triglycerides is protonated, and the alcohol attacks the protonated carbon to create a tetrahedral intermediate. The catalyst efficiency depends on several factors such as specific surface area, pore size, pore volume and active site concentration [26]. The order of activity among alkaline earth oxide catalysts is BaO > SrO > CaO > MgO [27–29]. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acidity, i.e. they behave as electron acceptors, and negative oxygen ions (anions) which behave as proton acceptors and are thus Brønsted bases. This has consequences for adsorption. In methanolysis of oils, it provides sufficient adsorptive sites for methanol, in which the (O–H) bonds readily break into methoxide anions and hydrogen cations (Fig. 1). The methoxide anions then react with triglyceride molecules to yield methyl esters [30,31].

Barium oxide catalyzes the transesterification reaction by forming barium methoxide with methanol. Due to its very low methanol-solubility, barium methoxide acts mainly as a heterogeneous catalyst. Pure barium methoxide, which is strongly basic, shows high catalytic activity. It is not soluble in methanol but it forms a suspensoid, whereby its active surface is very well developed. Metal alkoxides can be homogeneous catalysts if they are well soluble in methanol or if they can constitute active centers on the surface of heterogeneous catalysts. The alkalinity of a given compound is a key factor, which determines its catalytic activity in alcoholysis. Alkaline-earth metal compounds are heterogeneous catalysts and the degree of their dispersion in the reaction system has a considerable influence on the level of their catalytic activity, which is determined by diffusion. The classic mechanism of base-catalyzed