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Alcohol effect on microwave-ultrasound enhanced transesterification reaction

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ABSTRACT

The effect of alcohol on transesterification of used vegetable oil under simultaneous microwave and ultrasound irradiations was studied. Ethanol or methanol was used as an alcohol. The synergistic effect of microwaves and ultrasound was evaluated and compared through a series of experimental studies. A molar ratio of 9:1 (alcohol to oil) was found to be optimum for both ethanol and methanol with approximately 98% and 96% biodiesel yields respectively. Similarly, a catalyst weight of 0.75% resulted in maximum biodiesel yields of 97% and 96% for methanol and ethanol respectively. A reaction time of 2 min was adequate for the transesterification reaction either using methanol or ethanol as a reactant. Higher reaction time severely affected the biodiesel yields when ethanol was used as a reactant. The synergistic effect studies showed that an equal rate of microwave and ultrasound exposure resulted in higher biodiesel yields for both reactants while ethanol produced superior results when microwaves or ultrasound irradiations were used as energy sources individually. There were more polyunsaturated fatty acids in the biodiesel composition for FAMEs compared to FAEEs. Power density tests optimized energy utilization by matching the energy output rates and the reaction volumes for transesterification reaction.

1. Introduction

Biofuel production through energy-efficient processes has become a major priority for sustainable development of renewable energy sources considering current fossil fuel consumption and resource depletion issues. Among the potential renewable biofuel sources, biodiesel is a more promising fuel since it can be produced in liquid form suitable for use as a transportation fuel. Biodiesel refers to the production of mono alkyl esters by a chemical process called transesterification, which is the reaction of oil (fatty acids) with a monohydric alcohol [1]. Commonly used alcohols are ethanol and methanol which result in production of fatty acids ethyl esters (FAEEs) and fatty acids methyl esters (FAMEs) respectively, i.e., biodiesel through transesterification reaction. Various lipid and oil sources categorized as first generation (e.g., vegetable and edible oils), second generation (e.g., used oils, animal fats and other non-edible crop oils) and third generation (e.g., microbial and algae derived lipids and oils) feedstock have been studied as potential raw materials for biodiesel production [2]. While transesterification reaction is simple and efficient, the process condition severities by conventional methods reduce the net energy benefit from this conversion reaction [3,41]. Process intensification using novel equipment or methods (process schemes and techniques) could help these processes become energy-efficient [42].

Process intensification refers to development of novel equipment and/or methods that produce significantly higher yields or superior benefits in comparison with the existing equipment and/or methods in practice. These benefits can be realized in the form of dramatic reduction in processing times, significant improvements in product quality or quantity and decreasing the equipment size, reducing complexity of the production schemes, improving energy efficiency, minimizing waste production, and finally resulting in cheaper and sustainable technologies [4]. The process intensification developments in equipment could focus on developing novel reactor design with intense mixing to promote heat- and mass-transfer while developments in methods could focus on integrating the reaction-separation processes (minimizing process steps), use of alternative energy sources, and new process control techniques. In the context of biodiesel production, process intensification efforts refer to increasing mass and heat transfer rates among the reaction products whether in extraction and/or transesterification and/or separation and/or purification stages. Several methods to enhance the biodiesel production

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reactions were reported. The most notable results were obtained when microwave or ultrasound energy sources were employed as process intensification methods [5]. These two novel methods have distinct features in that microwaves are a result of electromagnetic irradiation while the ultrasound is based on high frequency acoustic waves [6,7]. Many studies involving these two process intensification methods have reported higher biodiesel reaction yields, superior biodiesel quality and reduced chemical, energy consumption, and reaction times [8]. Although these results are impressive, both microwave and ultrasound have their own drawbacks. For example, microwaves have mass transfer limitations and ultrasound does not possess the ability to generate high thermal energy for chemical synthesis [9]. Therefore, a combination of both techniques [9–11] may result in a complementary effect that could provide energy efficient biodiesel production. Ultrasonication will provide the mechanical mixing effect required by microwaves to improve mass and heat transfer, and microwaves will generate thermal energy that ultrasound lacks; thereby, intensifying the process and maximizing the benefits. The combination of microwave with ultrasound technique can improve the process chemistry by increasing the yields, and by reducing the process time by 10–15 folds as compared to the individual operation [12,13].

While many studies reported on the individual process intensification effects of microwaves or ultrasound on transesterification reaction, very few recent studies reported on the combined effect of these two novel methods on biodiesel production through transesterification reaction [9,14]. Moreover, the effect of reactants, i.e., the alcohol and the combined effect of these two novel methods has not been reported to date. Therefore, in this study, we investigated the effects of alcohols, methanol and ethanol, under simultaneous microwave and ultrasound irradiations. The effect of alcohol to oil ratios, catalyst amounts, and reaction times were studied through process parametric evaluation studies. Finally, the effect of ultrasound and microwave power densities was investigated. A comparison of the methanol and ethanol based transesterification reaction under simultaneous microwave and ultrasound conditions were presented.

1.1. Ethanol and methanol in biofuel production

Ethanol and methanol can be used directly without requiring major changes in the structure of a car engine, and both alcohols are known as the most suitable fuels for spark ignited engines [15]. Ethanol has been used as a fuel, and it is usually blended with gasoline to reduce emissions. According to the Energy Information Administration, nearly all gasoline sold in the U.S. contains some ethanol. One of the drawbacks of ethanol production is the use of edible corn or other sugars; therefore, several studies report on the production of bioethanol from cellulosic material to be used as a biofuel source [16–18]. Also, ethanol has been proven to be efficient in enhancing biodiesel production; however, its major disadvantage when compared to methanol is its cost. During the first two months of 2015, the price of ethanol has been $1.44 per gallon [19] while for methanol, the reported price was $1.25 per gallon [20]. However, regardless of their prices, both alcohols are being used in great quantities either for biodiesel production or for blending with gasoline. Major part of the United States is proposing to change from E10 (10% ethanol) to E15 [21] while China has already set standards for M85 (85% methanol), and they have been using M15 for several years [22]. Both ethanol and methanol have advantages and disadvantages; methanol is more cost-effective than ethanol, but ethanol has better environmental acceptance. Nevertheless, both alcohols are capable of producing high quality biodiesel.

1.2. Effects of microwave and ultrasound irradiations

Microwaves interact with alcohol by dipole rotation, and alcohols, such as ethanol and methanol are pure polar reactants whose molecules are hydrogen bonded in the liquid state. Therefore, the heat transfer limitations during the transesterification process are overcome due to the swift dipolar moment of polar molecules [23–25]. On the other hand, ultrasound efficiency could be attributed to proper mass and heat transfer provided by the physical and chemical effects during intensification reaction caused by turbulence in the reaction medium and free radicals [26]. Ultrasound efficacy depends on the local temperature, pressure effect, and better emulsification characteristics due to the cavitational events generated locally in the reactor [27]. Methanol and ethanol are strong mediums in absorbing microwaves, and thus the excess of alcohol may absorb microwave energy and reduce the microwave power. The medium absorbing capabilities of a reactant are determined by its loss factor ($\tan \delta$), which is obtained from the division of the dielectric loss (ε'') by the dielectric constant (ε') [28]. The loss factor for methanol and ethanol is 0.659 and 0.941 respectively at 2.45 GHz [28]. The higher the loss factor of a solvent, the quicker is its absorption capability, which indicates that ethanol is more efficient in converting microwave energy into thermal heat. Furthermore, the auto ignition temperature for methanol (385 °C) is only 20 °C higher than that of ethanol (365 °C); however, the auto ignition of methyl esters (464 °C) is 131 °C higher than ethyl esters (333 °C), but both are higher than regular diesel (315 °C) [29].

2. Materials and methods

2.1. Materials

The waste oil was collected from the Mississippi State University cafeteria. The acid value of the waste cooking oil was low suitable for base catalyzed transesterification reaction. The calculated molecular weight for the waste cooking oil was 842.58 g/mol, which was obtained through gas chromatograph flame ionization detector (GC-FID). Ethanol, methanol, and catalyst (sodium hydroxide, NaOH) 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-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 unit combines microwave generator and an ultrasound horn in a single facilitating simultaneous application of both irradiations with inclusion of a thermocouple and a reflux condenser as described previously [9]. A set of conditions were selected to test the effect of microwave and ultrasound irradiations (MW/US) from our previous experience. A sample volume of 20 mL of waste vegetable oil (WVO) and the power output of MW/US (100/100 W) were fixed for the process parametric evaluation studies, i.e., while varying catalyst loads from 0.25 to 1.25% (wt./wt.) by increments of 0.25%; the molar ratio of methanol or ethanol to oil tested were, 4.5:1, 6:1, 9:1, and 12:1; and the reaction times ranging from 1 to 4 min at one minute interval. The three-neck reactor vessel was equipped with a reflux condenser and a temperature probe. The reflux condenser allowed cooling down the evaporating reactant and keeping it in the mixture.