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Synergistic effect of simultaneous microwave and ultrasound irradiations on transesterification of waste vegetable oil

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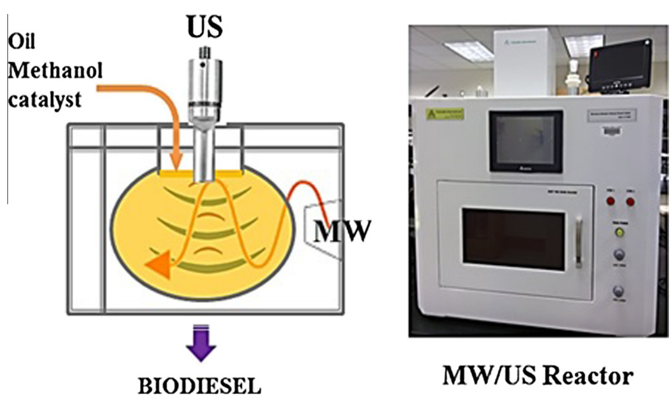
HIGHLIGHTS

- Synergistic effect of simultaneous microwave/ultrasound irradiations was evaluated.
- Synergistic effect enhances biodiesel process performance and yields significantly.
- Yields were higher for the MW/US reactions compared to MW or US individually.
- Optimum power density must be determined for energy-efficient biodiesel production.

GRAPHICAL ABSTRACT



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ABSTRACT

This study presents a novel application of simultaneous microwave and ultrasound (MW/US) irradiations on transesterification of waste vegetable oil. Experiments were conducted in three phases to evaluate: (1) the effect of process parameters on the transesterification reaction mediated by simultaneous MW/US irradiations at a fixed power output rate; (2) the individual and synergistic effects of the two technologies (by changing the power output rates); and (3) the synergistic effect on the power density (by changing the sample volume for a fixed MW/US power output). From the process parametric optimization study, the following conditions were determined as optimum: 6:1 methanol to oil ratio, 0.75% sodium hydroxide 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 (~98%) when compared to MW (87.1%) or US (89.8%) irradiations individually. The power density tests revealed that an optimum power output rate must be determined for energy-efficient biodiesel production. This study concludes that the combined irradiations result in a synergistic effect that enhances the biodiesel process performance and yields significantly. Identification of optimal parameters and hindrances concerning both techniques will further allow for large-scale application of the combined technology for biodiesel production.

1. Introduction

One of the twelve green chemistry principles introduced by Anastas and Warner includes "design for energy efficiency", which suggests that energy requirements of chemical processes should be

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recognized for their environmental and economic impacts and should be minimized [1,2]. If possible, synthetic methods should be conducted at ambient temperature and pressure. Biodiesel can be produced from a variety of feedstock containing triglycerides through a well-known transesterification process [3]. Current biodiesel conversion processes range from room temperature and ambient pressure conditions to sub- and super-critical solvent conditions requiring high temperatures and pressures and high energy inputs. Severe process operating conditions often suggest high capital investments and process safety concerns. Reactions at room temperatures and ambient pressures require longer reaction times with excess solvent and catalyst quantities. Conventional heating is a well-practiced method to conduct various chemical, industrial and pharmaceutical processes. However, this method poses many limitations such as mass and heat transfer related issues (poor heat transfer ability), low product conversion and low energy efficiency and higher by-product yield.

It is well accepted by now that microwaves and ultrasound produce superior results in many chemical syntheses attributed to both thermal and specific non-thermal effects induced by these irradiations. More specifically, microwaves provide rapid and convenient heating for chemical synthesis but have mass transfer limitations whereas the ultrasound produces intense physical mixing by cavitation but lacks the ability to generate/induce high thermal energy for chemical synthesis. These heat and mass transfer limitations and/or requirements can be addressed collectively by combining the two different techniques in a single reactor. Microwaves require mechanical mixing to enhance mass/heat transfer and to reduce localized superheating whereas an increase in the reaction temperature enhances ultrasound mediated reactions. While the two technologies were utilized individually to improve the biodiesel synthesis process in numerous studies thus far, the combined effect of these two non-conventional methods has not been studied in detail to date [4–12]. Chemat et al. demonstrated the first study of esterification of propanol using microwave and ultrasound reactor and pyrolysis of urea [13]. In that study, they reported an increase in the yields for both the reactions. Cravotto et al. reported the combined use of the two mechanisms on transesterification of vegetable oil and algal oil extraction [14]. They reported that the ultrasound and microwave either alone or combined have greatly improved the extraction yields along with higher yields and shorter reaction times. However, the combined effect of these two technologies on transesterification reaction has not been reported so far. In addition, none of the studies have attempted to compare the synergistic effect of these non-conventional technologies in terms of their performance. Synergism can be defined as a phenomenon resulting from the effect of a combination of technologies, tools, or reagents that exceeds the sum of their individual effects [14,15].

In this paper, we studied the combined (simultaneous) effect of microwave and ultrasound irradiations on the transesterification reaction of waste vegetable oil to convert into biodiesel. Three different sets of experiments were conducted: (1) to verify the combined effect of the microwave and ultrasound irradiation on the transesterification reaction parameters (by fixing the power output rates and sample volume); (2) to identify the individual and synergistic effects of the two technologies (by changing the power output rates); and (3) to determine the synergistic effect on the power density (by changing the sample volume for a fixed power output rate). Various parameters responsible for transesterification reaction namely reaction time, catalyst concentration, methanol to oil ratio and the power effect were tested on different sample volumes. The effect of power density and a comparison between the microwave and ultrasound effects and their combined (synergistic) effect on the transesterification reaction were evaluated.

2. Materials and methods

2.1. Materials

The waste vegetable oil (WVO) was obtained from a local restaurant in Starkville, MS. The acid value of WVO was found to be 3.5 mg KOH/g, corresponding to a free fatty acid (FFA) level of 1.7%. The calculated molecular weight for the waste vegetable oil used is 837 g/mol (from GC-FID analysis) which was used to calculate the reactant to oil molar ratio. 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 schematic of the experimental procedures is shown in Fig. 1. The photo image of the microwave/ultrasound unit is shown in the graphical abstract. 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 but by changing the process conditions. For the first set of tests, 20 mL of WVO was added to the mixture of methanol and NaOH (catalyst) and was then subjected to MW/US (100/100 W) irradiations. A

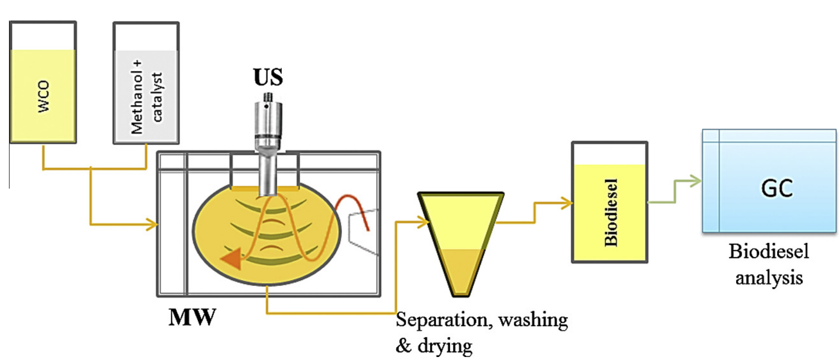

Fig. 1. Schematic of the experimental set-up for transesterification reaction mediated by simultaneous microwave and ultrasound irradiations (temperature probe and reflux condenser are not shown in the schematic).