Waste Management 34 (2014) 2611–2620

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

# Transesterification of waste vegetable oil under pulse sonication using ethanol, methanol and ethanol–methanol mixtures

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ARTICLE INFO

*Article history:*
Received 24 April 2014
Accepted 26 July 2014
Available online 29 August 2014

*Keywords:*
Pulse sonication
Alcohol mixture
Process parameters
Waste vegetable oil
Ultrasound intensity
Power density

ABSTRACT

This study reports on the effects of direct pulse sonication and the type of alcohol (methanol and ethanol) on the transesterification reaction of waste vegetable oil without any external heating or mechanical mixing. Biodiesel yields and optimum process conditions for the transesterification reaction involving ethanol, methanol, and ethanol–methanol mixtures were evaluated. The effects of ultrasonic power densities (by varying sample volumes), power output rates (in W), and ultrasonic intensities (by varying the reactor size) were studied for transesterification reaction with ethanol, methanol and ethanol–methanol (50%-50%) mixtures. The optimum process conditions for ethanol or methanol based transesterification reaction of waste vegetable oil were determined as: 9:1 alcohol to oil ratio, 1% wt. catalyst amount, 1–2 min reaction time at a power output rate between 75 and 150 W. It was shown that the transesterification reactions using ethanol–methanol mixtures resulted in biodiesel yields as high as >99% at lower power density and ultrasound intensity when compared to ethanol or methanol based transesterification reactions.



## 1. Introduction

The United States Energy Information Administration has estimated that about 138 million tons of waste cooking oil is produced per year in the USA with a per capita production of 9 lb per year (Radich, 2006). In Canada, approximately 135,000 tons per year of waste cooking oil produced (Canada, 2006). In the European Union (EU) countries, the total waste cooking oil production is approximately 700,000–1,000,000 tons per year (Kulkarni and Dalai, 2006; Patil et al., 2009) while for the UK, the production is about 200,000 tons of waste cooking oil per year (Carter et al., 2005; Chhetri et al., 2008). These waste cooking oils may pose an environmental threat if they are not reused or disposed properly (Charpe and Rathod, 2011). However, waste cooking oils may serve as local feedstock for biodiesel production (Ramos et al., 2013; Gude and Grant, 2013; Grant and Gude, 2013; Gude et al., 2013a,b). This use will reduce the biodiesel production costs by at least 2–3 times since feedstock costs can count for up to 80% of the total biodiesel costs. The waste cooking oils are sold at a cost 2–3 times lower than fresh or virgin feedstock and are often available free of cost (Ramos et al., 2013). As a comparison, the diesel production from petroleum costs about 1.00 $/L in 2008 which is a very competitive price for biodiesel production from other feedstock as well. Additionally, utilizing waste oil for biodiesel production will mitigate the environmental impacts related to feedstock production (Sivasamy et al., 2009).

Biodiesel from waste cooking oils can be produced by a well-known transesterification reaction. Addition of an alcohol group is required to complete this reaction (Felizardo et al., 2006). The short chain alcohols such as methanol, ethanol, and butanol are frequently used, with methanol being the most common. All of these alcohols possess different physical and chemical properties and therefore exhibit different patterns of transesterification reaction kinetics and biodiesel yield rates. Methanol and ethanol produce superior results in transesterification reactions. Currently, methanol is produced from the fossil sources and mineral oils (Andrade Torres et al., 2013) which impact the availability and cost of the oil resources. For long term sustainability of biodiesel production, use of ethanol provides a more environmentally friendly perspective since it can be derived from natural and renewable sources like plants and crops (Encinar et al., 2002; Andrade Torres et al., 2013). Biodiesel containing ethyl esters are more beneficial compared to methyl esters because ethanol can be derived from renewable sources, and the extra carbon atom in the ethanol molecule slightly increases the heat content and the cetane number. In addition, another important advantage is that the ethyl

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http://dx.doi.org/10.1016/j.wasman.2014.07.023
0956-053X/

esters generally have lower cloud and pour points than methyl esters (Encinar et al., 2007).

Mass transfer issues are often not discussed in the transesterification reactions. The Transesterification reaction is mainly dominated by the mass transfer limitations, then followed by a kinetics controlled region, with oils and methanol (Likozar and Levec, 2014a; Narvaez et al., 2009). Mass transfer between two organic phases (methanol and oil) plays a critical role during the transesterification (methanolysis) and controls the reaction kinetics. In transesterification reaction kinetics, three regimes are well-recognized, that is an initial mass transfer-controlled regime (slow), followed by a chemically-controlled regime (fast), and a final regime, close to equilibrium (slow) (Stamenkovic et al., 2008). Therefore, methanol is not effectively used for the reactions due to the interfacial mass transfer resistance (Kai et al., 2010). The mass transfer limitations on biodiesel production may be overcome with efficient mixing mechanism such as ultrasonic mixing. Ultrasound can enhance the mass transfer between two immiscible liquids (Leung et al., 2010). Cavitation mainly affects the mass transfer rates and ensures a uniform distribution of the reactants, as one concludes from the fact that a significant effect on both the reaction rate and the equilibrium conversion is only observed in the later stages of the reactions when heterogeneity is removed (Likozar and Levec, 2014b).

The rationale for this study can be explained as follows: transesterification reaction using methanol as reactant is a mass transfer limited operation due to poor solubility of oil in methanol. But methanol has a higher equilibrium conversion due to the higher reactive intermediate methyl group. On the other hand, ethanol has better solvent properties and can be obtained from renewable resources (Issariyakul et al., 2007). However, the formation of emulsion after the transesterification of oil with ethanol makes the separation of ester very difficult. When methanol/ethanol mixtures are employed for the transesterification reaction, this combination may benefit from ethanol's better solvent properties and methanol's faster equilibrium conversion kinetics. In addition, esters obtained from the mixture of alcohols possess better lubricating abilities and render as lubricating additive. Finally, replacing methanol with ethanol will also make the biodiesel production sustainable by reducing dependence on non-renewable methanol production (Kulkarni et al., 2007). Moreover, the ultrasound mixing provides superior mixing compared to conventional heating in transesterification reaction promoting mass transfer between the oils and alcohols.

In this paper, we report the transesterification of waste vegetable oils using methanol and ethanol under a pulse sonication effect. Since the two different alcohols have different physical and chemical characteristics, their effect on the transesterification reactions under ultrasound irradiation could be very distinguishable. The molar ratio of alcohol to oil, catalyst amount, and the reaction time were evaluated under direct pulse sonication without any external heating or mixing. Additionally, the effects of power density, ultrasound intensity and power output rates were also evaluated. Finally, the effect of ethanol/methanol mixtures (50%-50%) on the transesterification reaction along with power density, ultrasonic intensity and power output rate are presented.

## 2. Materials and methods

This section provides details on the materials used and experimental procedures followed in this study.

### 2.1. Materials

Waste vegetable oil (Canola) was obtained from a local restaurant near the Mississippi State University (MSU) campus. The acid value of the oil was found to be 3.5 mg KOH/g, corresponding to a free fatty acid (FFA) level of 1.7% and base catalyzed transesterification is suitable for feedstock with FFA content less than 4% (Patil et al., 2010, 2012). Ethanol, methanol and the catalyst (sodium hydroxide, NaOH) were purchased from Fisher Scientific. Methanol used in this study was of ACS (American Chemical Society) certified grade and ethanol was of reagent grade.

### 2.2. Experimental procedures

The pulse sonication of transesterification reaction was performed using a NO-MS100 ultrasonicator manufactured by Columbia International Technologies with a maximum of 1000 W power output capacity. The ultrasonic frequency was 25 kHz. The horn is made of titanium alloy with variable power output rates and a 2.54 cm diameter tapered to 0.254 cm at the tip.

The transesterification process involves direct sonication of the sample mixture (known amount of waste vegetable oil mixed with pre-prepared sodium methoxide solution) to be converted into biodiesel followed by separation/washing/drying cycles. The transesterification reaction was carried out in a 50 ml glass batch reactor (beaker) equipped with an ultrasonic horn and a digital temperature probe (Fig. 1). The reaction sample temperature was recorded using a digital thermometer at every 10 s of reaction time. The molar ratio of methanol and/or ethanol to oil was varied between 4.5:1, 6:1, 9:1, and 13.5:1, while three catalyst loadings

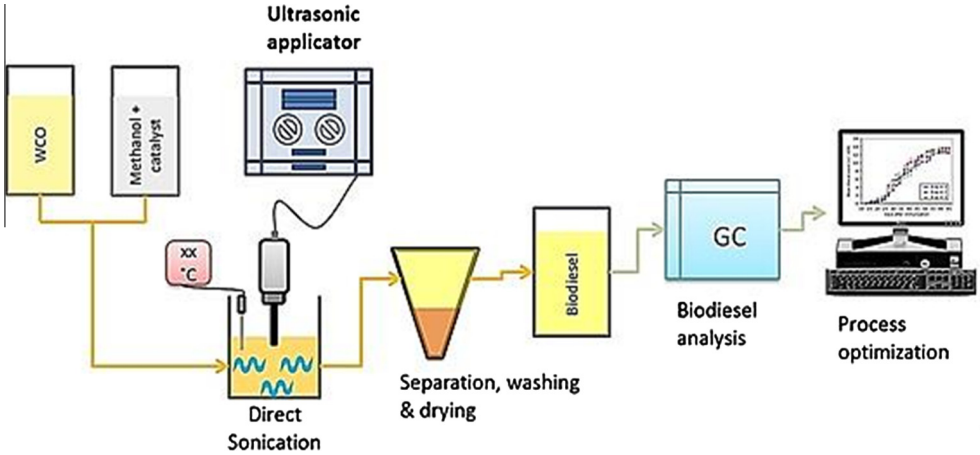


**Fig. 1.** Biodiesel production from waste vegetable oil under pulse-sonication.