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Investigation, modelling and reviewing the effective parameters in microwave-assisted transesterification

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ABSTRACT

Synthesis of biodiesel using so-called microwave (MW) energy at a frequency of 2.45 GHz is investigated in this work. In this frequency, energy can transfer in the scale of molecular size. Dipolar rotation and ionic conduction are two important mechanisms of energy transformation; Thus, an efficient and localized high temperature is produced that can assist reaction. In this study, we focused on effective parameters during transesterification. It was found that methanol produces a higher yield than the other alcohol types. It is due to methanol reorientation ability under the microwave irradiation, which may result in a better microwave absorption. Furthermore, the requirement for catalyst in this situation was reduced about ten-fold. Besides, an empirical model was generated to analyze and predict the effect of operating parameters. The model was based on fitting a wide range of different experimental results for homogeneous alkalic catalysis. The predictive power of developed model was within the temperature range of 40 and 80 °C, reaction time between 5 and 15 min and alcohol to oil molar ratio between 3 and 12. The optimum values in the mentioned ranges included the alcohol to oil molar ratio of between 1:6 to 1:9 in homogenous catalyst systems and 15:1–18:1 in heterogeneous one, reaction time within 3–5 min and the temperature within 65–90 °C. Finally a very good agreement between the model and experimental data was observed with error of ± 8% even with the other catalysts types.

Contents

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1. Introduction

In recent decades, increasing consumption rate of fossil fuels has resulted in discharge of these resources. Thus, alternative fuels have attracted much attention and among them Fatty Acid Methyl Ester (biodiesel) is one of the best choices. Biodiesel is a clean burning fuel which is produced from renewable sources [1]. This fuel is biomass-based with excellent lubricating properties. It does not contain toxic compounds such as aromatic hydrocarbons, metals, sulfur or crude oil residues [2]. Therefore, it is a good replacement for petroleum based diesel by reducing Volatile Organic Compounds (VOC) emissions and Green House Gases (GHG) [3]. It can be blended with fossil diesel at any ratio and used for diesel engines without any modification [4]. Furthermore, biodiesel is safer than petroleum diesel since it is non-flammable and non-explosive, with the flash point of 150 °C in contrast to petroleum diesel with the flash point of 64 °C [5]. Several methods have been suggested to produce biodiesel such as: Thermal cracking (pyrolysis), Microemulsification, Direct use of vegetable oil and Transesterification. In thermal cracking, one substrate is converted into another using heat along with a typical catalyst or only heat in absence of oxygen or air. In microemulsification, the viscosity of vegetable oils decreases by mixing them with solvents, such as alcohols and ionic or non-ionic amphiphiles. Both these procedures may result in imperfect combustion because of their low cetane number. The biodiesel obtained from the direct usage of vegetable oil, suffers from high viscosity which can damage the actual diesel engine [6]. Transesterification (or alcoholysis) is the most common and simplest process, which is widely studied [6–8]. This method contains three steps for exchanging the alkoxy group of an alcohol with the alkoxy group of an ester compound. In the first step, triglyceride molecule existing in animal fats or vegetable oils reacts with an alcohol in the presence of a catalyst and leads to diglyceride and one molecule of ester. In the next step, diglyceride with another alcohol molecule converts to monoglyceride. Finally, monoglyceride with the third alcohol molecule produces glycerin. In each step, one fatty acid ester molecule is generated [6,9,10]. Today, the majority of biodiesel in industry is produced by transesterification. However, there are some obstacles related to this method:

- Most commercial processes are done in a batch system which lessen some advantages of continuous mode.
- Transesterification may take 1–24 h to reach a high fatty acid methyl ester yield or oil conversion.
- Generally, it is nearly 1.5 times more expensive than petroleum diesel fuel [11].
- There is an upper conversion limitation in the absence of product removal since transesterification is a reversible reaction [4,11].
- The immiscible nature of reactants is another limitation of mass transfer [12].
- The other problem within the biodiesel production is energy consumption.

There are several techniques to compensate for these weaknesses such as increasing alcohol to oil molar ratio and catalyst concentration as well as adding co-solvent in the reaction, such as tetrahydrofuran or working under supercritical conditions (temperatures above 300 °C and pressures above 40 MPa). All these mentioned factors are used to increase the mass transfer between the two immiscible phases (called oil and alcohol as reactants) [12]. However, the addition of co-solvents increases the number of process steps and energy consumption. In supercritical process, methanol needs high temperature and pressure for a long time, which may result in significant loss of unsaturated fatty acid ethyl ester (FAEE) due to degradation reaction. Based on the report of Patil et al. [7], the alkyl esters and oil/lipid tend to become thermally unstable or decompose in transestrification with temperature above 255 °C at a fixed pressure of 1200 psi [7]. In the above mentioned methods (of transestrification), the required energy of the reaction is provided by convection, conduction and radiation of heat energy from the surfaces of the reactor to the reactants; it is an inefficient heat transfer [13]. Recently, several technologies have been introduced to attain a precise mixing and mass transfer in the reaction system to decrease the need of energy resources. These new technologies are based on the use of alternate energy sources in a special wavelength such as microwave or ultrasound energy. In essence, the microwave energy interacts with the molecules at a very fast rate, thus localized superheating is generated. Therefore, the real reaction temperature is higher than the average temperature of the medium [14]. In consequence, both of the reaction time and energy consumption are reduced by means of microwave irradiation [13]. Then microwave heating becomes more efficient over conventional methods (Table 1). Because by these methodes energy is transferred into a sample depends upon convection currents and the thermal conductivity of the reaction mixture, which is relatively slow and inefficient [15]. In addition, it can overcome the major problems of conventional heating such as limitations depend on the thermal conductivity of materials, heterogenic heating of the surface, specific heat and density [11]. It also requires less energy input for heating compared with the conventional heating method [16].

However, there is no doubt that microwave heating suffers from some challenges. Microwave radiation cannot support a very large reaction vessel due to its penetration depth limitations. Therefore, scaling up the new technique is still an unsolved problem. For example, Groisman and Gedanken reported that the efficiency of laboratory batch ovens is higher than a continuous flow system at various microwave powers [17]. Uncontrolled heating is another problem, which may lead to safety concerns in industrial vessels. Unfortunately, there are few published works in this field, thus this field has not received sufficient attention [13]. In this paper, we have gathered the result of the majority of published papers in microwave systems and investigated the effect of key parameters such as temperature, microwave irradiation power, alcohol to oil molar ratio, catalyst and its concentration. Besides highest and most optimal results of all published works, containing different alcohols and catalysts (homogenous or heterogeneous) are summarized in several tables for a better judgment. For the other information from more than 1000 of experimental tests (with optimum or non-optimum results), an empirical correlated equation has been developed for a wide range of parameters. The model predicts satisfying agreement with the experimental data and can be useful for the other authors to be able to estimate their own experimental result before doing the test.

2. Microwave irradiation

Microwaves are non-ionizing radiations i.e., electromagnetic waves that can be transmitted, reflected or absorbed [15]. Thus,

Table 1
Comparison between convection and microwave heat transfer.

Microwave energy	Conventional energy
Energetic coupling	Conduction/convection
Coupling at the molecular level	Superficial heating
Volumetric	Superficial
Rapid	Slow
Dependent of the properties of the material	Less dependent
Selective	Nonselective