



Mechanistic and kinetic investigations in ultrasound assisted acid catalyzed biodiesel synthesis

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ARTICLE INFO

Article history:

Received 11 November 2011

Received in revised form 13 January 2012

Accepted 14 January 2012

Keywords:

Biodiesel

Transesterification

Acid catalyst

Cavitation

Sonochemistry

Kinetics

ABSTRACT

This paper attempts to discern physical mechanism and kinetic aspects of ultrasound irradiation on transesterification of soybean oil with methanol using sulfuric acid as catalyst with approach of coupling experimental results with simulations of cavitation bubble dynamics. Kinetic constants as well as activation energies of transesterification reaction were determined at different alcohol to oil molar ratios and reaction temperatures. The results of this study reveal interesting features of inter-relation between mechanics of ultrasound/cavitation, and the intrinsic behavior (represented by specific rate constant) of the transesterification reaction. The beneficial effect of ultrasound irradiation on transesterification is of physical nature. Several anomalies of ultrasound assisted acid catalyzed transesterification (as compared to conventional system) are: occurrence of reaction at low temperature of 15 °C (albeit with low conversions of 13.45% and 10.2% for alcohol to oil molar ratios of 6:1 and 12:1, respectively); despite higher activation energy, higher rate constant at low alcohol to oil molar ratio of 6:1; and minima shown by reaction rate constant with temperature. The major physical effect of sonication is fine emulsification that generates enormous interfacial area for reaction that overwhelms the effect of specific rate constant. As revealed by simulations, physical effects of cavitation (viz. micro-convection and shock waves) are more pronounced at low temperature, which is primary cause leading to these anomalies.

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1. Introduction

As the prices of crude oil cross \$100 per barrel, in addition to fast depletion of fossil fuel reserves, quest for an alternate renewable source of liquid transportation fuel has become an urgent need of the hour. Another driving force for this quest is the issue of global warming and environmental pollution due to large emission of greenhouse gases (GHG) and other polluting gases (including particulates) during combustion of fossil fuels. Recent years have seen emergence of many alternate liquid fuels, most popular among them being biodiesel, which is essentially fatty acid alkyl esters. Despite several merits such as closed carbon cycle, reduction in both CO and CO₂ emissions, less particulate emissions, complete biodegradability and non-toxicity [1], large scale commercial production of biodiesel from vegetable oils has suffered due to low economy [2–5]. The cost of feedstock contributes to about 60–75%

of the total production cost of biodiesel. Substitution of the conventional feedstock of vegetable oil by low cost feedstock can reduce the production cost of biodiesel. Potential low cost feedstock for biodiesel are waste greases such as yellow grease from cooking oil and animal fats, and brown grease obtained from municipal and commercial wastes. However, these greases have high levels of free fatty acids up to 15 wt% or higher. Due to this feature, conventional base catalyzed transesterification (which can handle free fatty acid content of less than 0.5 wt% even with totally anhydrous alcohol with water content of less than 0.1–0.3 wt%) of these feedstocks leads to soap formation [6]. A solution on this problem is use of acid catalysts (instead of base catalysts) in either homogeneous or heterogeneous form for esterification of the free fatty acids [7–9]. An added advantage of acid catalyzed esterification is higher tolerance toward moisture content of feedstock, which could otherwise trigger the hydrolysis of esters resulting in regeneration of fatty acids. However, a major drawback of the acid-catalyzed esterification is slow kinetics [10–12]. The literature on acid catalyzed transesterification is much limited than the conventional base-catalyzed process. An excellent review of the literature in this area is given by Lotero et al. [13] and Sharma et al. [14]. Some notable contributions in homogeneous acid catalyzed transesterification are by Freedman et al. [15], Liu [16], Canakci and Van Gerpen [7], Crabbe et al. [17], Goff et al. [18], and Miao

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et al. [19]. Conventional technique of mechanical stirring for acid catalyzed transesterification has numerous processing demerits, which hinder effective and economic scale-up. These include high reaction temperature (70–200 °C), high pressure (6–10 bar) and long reaction time (>48 h). The root cause of slow kinetics of the acid catalyzed transesterification is in mass transfer limitation due to biphasic nature of reaction system that affects catalyst accessibility to the triglycerides molecules. The reaction kinetics can be enhanced by increasing the acid concentration (~5 wt%) and alcohol to oil molar ratio (in the range 20:1 to 45:1). However, for large scale process, these remedies are impractical as they increase the operating costs due to excessive usage of alcohol as well as reactor corrosion due to acid. Another solution is to increase the miscibility of the two phases is use of cosolvents such as tetrahydrofuran (THF) [20]; but again, this technique is impractical for large scale application. Use of THF on large scale operation would significantly increase the operating costs due to high cost of THF. Moreover, after reaction all of THF would end up in the aqueous phase (glycerol). Separation, recovery and recycle of this would also be an expensive operation that would add to the production cost.

Recently, ultrasound irradiation of the transesterification reaction system has been attempted as a means of intensification of kinetics. The beneficial effects of ultrasound on the transesterification reaction system are several fold such as marked enhancement in reaction kinetics, high yield at low alcohol to oil molar ratios and reduction in temperature required for high conversion. Published literature reports enhancement effect of ultrasound on biodiesel synthesis from diverse feedstocks. Stavarache et al. [21–24] have studied the transesterification of vegetable oils with several short chain alcohols using ultrasound of two frequencies, viz. 28 kHz and 40 kHz. Significantly smaller reaction times (10–40 min) were observed with catalyst concentrations 2–3 times lower than those required for mechanically agitated processes. 40 kHz ultrasound was found to be more effective in reducing of reaction time, while 28 kHz ultrasound gave better yields (~98%). Shorter reaction time and greater energy efficiency for transesterification with ultrasound and hydrodynamic cavitation has also been reported by Ji et al. [25], Wu and Zong [26], Singh et al. [27], and Georgogianni et al. [28] Colucci et al. [29] have studied transesterification of soybean oil with methanol in presence of ultrasound at 3 levels of temperature and 4 alcohol to oil molar ratios. The reaction rate constants were 3–5 times higher than those reported for mechanical agitation, with excellent yields of fatty acid methyl esters. Increase in interfacial area and activity of microscopic and macroscopic bubbles have been cited as principal causes behind the observed mass transfer and kinetic rate enhancements by Colucci et al. [29]. Kelkar et al. [30] have studied esterification of fatty acids (in range C₈–C₁₀) with methanol using acid catalyst (H₂SO₄) in both ultrasonic processor and hydrodynamic cavitation reactor. Cavitation phenomenon has been found as effective tool for intensification of the esterification of fatty acids. This result was equally applicable to esterification of fatty acids outside C₈–C₁₀ range with methanol, viz. caprylic acid and capric acid. Benitez [31] studied the transesterification reaction between methanol and soybean oil and tallow at various alcohol to oil molar ratios and at different temperatures. The results of the experiment were explained on the basis of the cavitation model using Rayleigh–Plesset equation. However, the model used by Benitez [31] did not take into account the continuous transport of methanol vapor across the cavitation bubble during radial motion. Deshmane et al. [32] have reported synthesis of isopropyl esters from palm fatty acid distillate with ultrasound of 25 kHz and 1 kW power using sulfuric acid catalyst. The optimum process parameters were alcohol to oil molar ratio of 1:5, catalyst concentration of 5 wt% and reaction temperature of 60 °C. The reaction followed first order kinetics and 80% conversion was achieved in 6 h under optimized conditions.

Ultrasound and cavitation render both physical and chemical effects on the liquid medium. The physical effect is in terms of production of high intensity turbulence or convection in the medium while the chemical effect is in terms of production of highly reactive radicals produced through dissociation of entrapped vapor molecules in the bubble, which are subjected to extreme conditions generated at the collapse of the bubble. Although significant literature published in the area of homogeneous acid catalyzed transesterification, the principal focus has been on results than rationale. This means that the exact physical mechanism of the beneficial action of ultrasound on the transesterification reaction is not explored yet. Ultrasound manifests its beneficial effects on homogeneous as well as heterogeneous reaction systems through phenomenon of cavitation, which is nucleation, growth and transient collapse of tiny cavitation bubbles [33]. Transient collapse of cavitation bubbles results in high energy concentration on extremely small spatial and temporal scales [34]. In a previous paper [35], we had explored the physical mechanism of base (NaOH) catalyzed transesterification reaction with methanol as alcohol and soybean oil as the feedstock. In this paper, we address the issue of discernment of the physical mechanism and the kinetic analysis of acid catalyzed transesterification with alcohol and feedstock remaining the same. Our approach is of coupling the experimental results with simulations of cavitation bubble dynamics using a mathematical model. As revealed in following sections, physical effects of ultrasound and cavitation on the transesterification system give rise to peculiar trends in reaction kinetics. Some of these trends are anomalous with the conventional systems in which mechanical stirring of the biphasic reaction mixture is employed. Concurrent analysis of simulations and experimental results sheds light on the physical mechanism of the ultrasonic enhancement of the acid catalyzed transesterification reaction and helps explain these anomalies as explained in subsequent sections.

2. Material and methods

2.1. Materials

Fortune[®] soybean oil (edible grade, procured from local market) with acid value of 0.2 mg/g and average molecular weight of 884.65 g/mole was used in all experiments. Other chemicals used in experiments are: methanol (AR grade 99%, Merck, India), sulfuric acid (AR grade 99%, Merck, India), NaOH (AR grade, 99%, Merck, India). Anhydrous methanol was obtained by further vacuum distillation. Other chemicals were used as received (without any further treatment).

2.2. Experimental setup

A schematic of the experimental setup is shown in Fig. 1. Transesterification reactions were carried out in 50 ml borosilicate glass beakers. In order to conduct reactions at different temperatures, the beaker was placed in the reservoir of a refrigerated circular bath (Jeio Tech, Model: Lab Companion RW 0525G) filled with water. The temperature of the water in reservoir was maintained at different levels, viz. 15, 25, 45 and 65 °C. Internal circulation of water was provided so as to nullify any temperature gradient. The temperature of reaction mixture was monitored with a digital thermometer, and was found to be same as that of the water in the reservoir. A programmable microprocessor based ultrasonic processor (Sonics and Materials Inc., Model: VCX 500) was used for sonication of reaction mixtures. This processor had operating frequency of 20 kHz. The ultrasound probe had a diameter of 13 mm and was fabricated from high-grade titanium alloy (Ti–6Al–4V). The processor was

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