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Optimization of methyl ester production from waste cooking oil in a batch tri-orifice oscillatory baffled reactor

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ABSTRACT

Transesterification of vegetable oils is a common route for the production of biodiesel. This reaction is a slow mass transfer limited reaction that has been shown to benefit from process intensification reactors such as the Oscillatory Baffled Reactor (OBR). The use of waste cooking oil as a resource is an attractive alternative to other virgin vegetable oils that will enable the capital costs of biodiesel production to be largely decreased, thereby making biodiesel an affordable and competitive fuel. In this study, optimization of biodiesel, or fatty acid methyl ester (FAME) production from waste cooking oil (WCO) was investigated using a batch OBR (diameter = 0.06 m, height = 0.55 m) with multi-orifice baffles, which have been recommended for scale-up. Response Surface Methodology (RSM) was applied to study the effects and interaction of different operating parameters: oscillation frequency (in the range 2.4–4.9 Hz), inter-baffle spacing (in the range 0.05–0.09 m) and reaction temperature (in the range 40–60 °C). It was found that temperature is the main factor influencing reaction yield and the interaction between temperature and oscillation frequency is non-negligible. Inter-baffle spacing does not, however, have a significant effect on the reaction. This is different from the design recommendations of OBRs in the literature, which were originally developed for single orifice baffles. An optimal reaction yield of 81.9% was obtained with an oscillation frequency of 4.1 Hz and an inter-baffle spacing of 5 cm (i.e. approximately $1.5d_e$) at a temperature of 60 °C. However, similar reaction yields could be obtained for different values of inter-baffle spacing.

1. Introduction

Biodiesel is promoted as a renewable and sustainable supplement for petroleum diesel and has received much attention in research over the last decades as it is a biodegradable and non-toxic fuel source. Biodiesel, often referred to as fatty acid methyl ester (FAME), is characterized as the alkyl esters of long chain of fatty acids derived from vegetable oils or animal fats. Indeed, the feedstock plays the most important role in biodiesel production process cost, comprising 70–90% of the biodiesel price. Therefore, waste cooking oils (WCOs), which are two or three times cheaper than virgin vegetable oils, are of high interest in biodiesel production [1,2], thereby potentially making it a sustainable substitute for petroleum diesel. Furthermore, collecting and reusing WCOs as a biodiesel feedstock or other bio-sourced derivatives, such as bio-lubricants [3,4], bio-asphalts [5] and bio-based surfactants [6], instead of discarding them into sewers can significantly decrease costs of treating waste waters [3]. It should be pointed out that however, the use of WCO for biodiesel production may require extra pre-treatment processing due to the presence of free fatty acids (FFA), water and other impurities which can hinder the performance of the FAME producing reaction.

Amongst different biodiesel production technologies, including such as pyrolysis, alcoholysis, co-feeding with petroleum feedstock etc., transesterification has been one of the most common and preferred chemical modification processes [7,8]. In this reaction, glycerides react with a short chain alcohol, such as methanol or ethanol, in presence of an alkaline, acid or enzyme catalyst. At the beginning of the reaction, oil and methanol form an immiscible liquid-liquid mixture that is mass transfer controlled due to the low solubility of these reactants. As the reaction occurs, however, the intermediates (diglycerides, monoglycerides) and methyl ester act as an emulsifier and the reaction medium is an emulsion of fine drops (or pseudo-homogeneous phase) [9–12]. In the final stage of the reaction, the products (methyl esters and glycerol), which are immiscible, for two distinct liquid phases

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again. The high difference in densities between glycerol and methyl ester causes phenomena such as stratification, which can lead to an incomplete reaction if there is no sufficient mixing, since most of the catalyst resides in glycerol phase [13,14]. The most important limitation in biodiesel production, however, is the mass transfer process and it is therefore vital to mix the reactants, which have significantly different viscosities, effectively such that high interfacial area is created and mass transfer is enhanced. Previously, some important issues in biodiesel synthesis reaction, such as modeling of reaction kinetics and mass transfer, effects of different feedstocks and alcohols as well as other main reaction parameters have been investigated comprehensively in a mechanistic approach [14,15].

An oscillatory baffled reactor (OBR) is composed of a tube containing equally spaced orifice plate baffles. The oscillatory flow generates vortices near the baffles and thereby improves radial mixing and plug flow [16,17] and enhances heat and mass transfer [18,19]. In OBRs, the amplitude and frequency of oscillation are independent parameters that control the mixing process. The governing dimensionless groups for oscillatory flow mixing are [20]:

$$\mathrm{Re}_o = \frac{2\pi f x_0 \rho d_e}{\mu} \tag{1}$$

$$\mathrm{St} = \frac{d_e}{4\pi x_0} \tag{2}$$

where Re_o is the oscillatory Reynolds number, ρ is the fluid density, μ is the fluid viscosity, f is the oscillation frequency, x_0 is the center-to-peak oscillation amplitude and St is the Strouhal number. d_e is the effective tube diameter for OBRs with multi-orifice baffles [21]:

$$d_e = \sqrt{\frac{d^2}{n}} \tag{3}$$

where d is the tube diameter and n is the number of orifices in the baffle. Re_o describes the nature of the flow generated by the maximum oscillatory velocity $2\pi f x_0$. For $Re_o < 250$, the flow in the OBR is essentially axi-symmetrical and mixing intensity is low; for $Re_o > 2000$, the flow becomes turbulent; at intermediate values of Re_o, the flow is 3-dimensional and mixing is more intense than the laminar flow [22]. The Strouhal number (St) is a measure of vortex propagation inside each inter-baffle zone relative to the tube diameter: larger oscillation amplitudes cause smaller St values and improve the vortex formation. Mixing and eddy propagation within the OBR is also inherently related to the inter-baffle spacing. For a given oscillation amplitude, the inter-baffle space should be large enough for vortices to expand and propagate. If the inter-baffle distance is too large, the vortices will not propagate through the full volume of the inter-baffle zone and produce stagnant regions [23]. Generally, the most adapted inter-baffle spacing is that which covers the maximum length of eddies without causing suppression or stagnation [23,24]. Several early studies on OBRs with single orifice baffles have investigated the effect of baffle spacing on single phase mixing quality using qualitative flow visualization [25,26]; and gas-liquid mass transfer [24]. The results of these studies indicate an 'optimal' baffle spacing of 1.5 and 1.8 times the tube diameter, although an optimization approach was not used in their experiments. A baffle-spacing of 1.5 time the tube diameter is now considered as a basic design rule for OBRs. Later, in 1999, Smith used this recommendation for the design of multi-orifice baffled reactors, whereby he replaced the tube diameter by the effective tube diameter as given in Eq. (3) [27].

Amongst the different studies on OBRs, several have focused on biodiesel and FAME production. Harvey et al. [20], evaluated the feasibility of a continuous OBR in the intensification of biodiesel production from rapeseed oil using single-orifice baffles in the presence of NaOH catalyst. Although no optimization process was done on the experimental factors (operating conditions or reactor geometry), it was found that the OBR allows methyl esters to be produced in much shorter residence times than the traditional batch stirred tank. The study shows that a product with a cetane number of 45 at 50 °C in just 30 min. In another study, Phan et al. [28] used continuous mesoscale OBRs in the laminar flow regime for the screening process conditions. They also studied the effect of baffle design and found that the sharp edged helical baffle design significantly improves the mixing of immiscible oil and methanol phases in the laminar regime, compared with the single orifice baffled reactor. At 50 °C and after a residence time of 10 min, the authors obtained methyl ester yields in the range of 78–85% depending on the methanol-to-oil ratio. Mazubert et al. [29] studied the process intensification of biodiesel production from waste cooking oil in a continuous glass OBR for relatively low temperatures and a few different oscillation conditions. At low temperature (27 °C), the Re_o in the range of 28–42 does not have a significant effect on reaction yield, which is between 82.3 wt% and 87.3 wt%. However, for low amplitude oscillations (Strouhal number equal to 0.16), reaction conversion was greatly diminished (38.1 wt%). At the highest achievable temperature in the reactor 44 °C (due to limitations of the glass), 92.1 wt% conversion was obtained in 6 min for a methanol-to-oil of 6:1 and 1% KOH catalyst. Syam et al. [30] used a mechanistic approach to investigate the effect of different operating parameters (temperature, catalyst type, methanol-to-oil molar ratio) on biodiesel production from Jatropha oil in a pulsed loop reactor with annular baffles. The methanol to oil molar ratio of 6:1, the potassium hydroxide catalyst with the recommended amount of 1% (per oil weight), and the reaction temperature of 60 °C were suggested as optimal operating parameters. Under these conditions, the authors obtained 99% yield of methyl esters in 10 min.

In all of the above-mentioned studies, the effect of OBR baffle spacing on biodiesel synthesis has not been investigated. Indeed, in these experimental set-ups, the baffle spacing was fixed at the so-called optimal value that was determined visually many years ago [22,23,24]. The effects of oscillation frequency and amplitude on methyl ester production are also not entirely straightforward. The objectives of this study are therefore to explore the effects of oscillation frequency and baffle spacing on FAME yield (after 5 min of reaction time) in a temperature range 40–60 °C. To do this, we have used RSM for experimental design and then to model the system and find the optimal operating parameters amongst those studied.

2. Material and methods

2.1. Materials

Methanol of 99% purity and potassium hydroxide of 98% purity (Merck) were used in methoxide production. Ethyl acetate (Fluka) and BSTFA (Sigma-Aldrich) were used for gas chromatography (GC) sample preparation. The waste cooking oil (WCO) with < 1% FFA, was obtained from the TMU University restaurant in Iran. Prior to the reaction, WCO was filtrated and preheated at 100 °C for about 3 h to vaporize its water content. The composition of WCO was determined by GC and is composed principally of oleic acid (32.9%wt), palmitic acid (30.4%wt) and linoleic acid (21.0%wt) with small amounts of stearic, linolenic and other fatty acids.

2.2. Experimental equipment

A vertical batch Oscillatory Baffled Reactor (OBR) with 0.06 m internal diameter and 0.55 m height and tri-orifice baffles (Fig. 1) following the dimensions given by Nogueira et al. [21] was fabricated in-house. The baffles had the capability of moving along the rod. The inter-baffle spacing, l, was varied between 0.05 m, 0.07 m and 0.09 m, corresponding to $1.45d_e$, $2d_e$ and $2.6d_e$, respectively. The multi-orifice baffle was chosen since multi-orifice baffles were initially designed for the scaling up of OBRs [27]. Indeed, this baffle type has shown to reproduce the fluid mechanics and axial dispersion, which are observed in lab-scale reactors, in larger scale equipment [31]. It is also expected to