The interplay of phase equilibria and chemical kinetics in a liquid/liquid multiphase biodiesel reactor

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HIGHLIGHTS

▶ Countercurrent liquid/liquid phase biodiesel reactor.
▶ Distributed methanol injection strategy.
▶ Improve reactor performance, yielding ASTM quality biodiesel and 90% separation efficiencies.
▶ A model that simulates the experimental results and provides insight into the reactor behavior.

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ABSTRACT

A countercurrent liquid/liquid phase biodiesel reactor achieved 99% triglyceride to methyl ester conversion at the same time as separating 90% of the produced glycerin. However, a low inverse sensitivity of the conversion to the glycerin separation efficiency led to biodiesel that did not meet ASTM quality standards in previous work. A distributed methanol injection strategy is demonstrated herein to improve reactor performance, yielding ASTM quality biodiesel and 90% separation efficiencies. Preliminary data on feed rate changes yields counterintuitive results where conversion increases as feed rate increases. A model that assumes equilibrium between the reacting oil phase and the settling glycerol phase simulates the experimental results and provides insight into the reactor behavior.

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1. Introduction

1.1. Background

Alternative renewable fuels are becoming increasingly important due to diminishing petroleum reserves and the negative environmental impact of fossil fuels. Numerous studies have shown that triglycerides, including virgin vegetable oil, waste vegetable oil, and animal fats can be converted into promising alternatives for diesel engine fuels via transesterification [1–4].

The chemical processing strategy for the production of biodiesel originated in the 1940s [5,6] and currently biodiesel production via base catalyzed transesterification is mainly performed using batch processes on small scales although new technologies are being developed for continuous processing including continuously stirred tank reactors [7], turbulent flow tubular reactors [8], re-circulating reactors containing long pathways of static mixers [9], and sub- and supercritical processes [10].

The overall reaction scheme for the methanolysis of triglycerides, illustrated in Scheme 1, is comprised of three sequential reactions.

$$TG + MeOH \rightleftharpoons DG + FAME \tag{R.1}$$

$$DG + MeOH \rightleftharpoons MG + FAME \tag{R.2}$$

$$MG + MeOH \rightleftharpoons G + FAME \tag{R.3}$$

where triglycerides, diglycerides, monoglycerides, methyl esters, and glycerin are represented by TG, DG, MG, $FAME$, and G respectively. The conversion can be enhanced by the continuous removal of the products during the reaction. While there are several current

strategies for simultaneously producing biodiesel and separating the glycerol phase [11–14], they require elevated temperatures and pressures and/or extra equipment for the separation process. A simpler combined process would decrease capital and operating costs.

There is a strong incentive to raise the conversion to 99% or above during the production of biodiesel, and that is the ASTM Standard definition of commercial grade biodiesel fuel, ASTM D6751. The chemical quality of the biodiesel is defined by a sub-test of ASTM D6751, ASTM D6584-10a, called the free and total glycerin test. Free and total glycerin values are derived from a gas chromatography (GC) analysis of the fuel. The free glycerin measures the amount of glycerin byproduct left in the biodiesel, and is an assessment of how well the biodiesel has been purified of contaminants. The total glycerin combines the free glycerin and "bound glycerin", a nomenclature referring to remaining tri-, di-, and mono-glycerides in the biodiesel that were not converted to the methyl-esters via reactions R.1–R.3. To pass this ASTM test, the production process must remove the byproduct glycerin and attain a chemical conversion of approximately 99%. If the chemical conversion in the reactor is too low, expensive separation steps are required to sufficiently purify the biodiesel to pass the ASTM tests.

1.2. Laminar flow reactor/separator concept

The combination of liquid–liquid extraction with chemical reaction has long been used in processes ranging from metal recovery from leach liquors to aromatic nitrations to methyl acetate synthesis. The majority of literature published in this area, however, has been directed toward turbulent flow [15] and/or packed bed reactors [16] sometimes requiring multiple units [17]. The use of such a process for biodiesel production is unique in that the current reactor utilizes laminar flow in one column to simultaneously achieve very high conversion and separation.

In previous work, preliminary results with this reactor were introduced and performance questions were raised. In this paper, the performance of this laminar flow reactor/separator is examined under several operating conditions and a simple model proposed to explain the counterintuitive results obtained. In previous studies by others, it was shown that intense mixing is required to achieve high conversions in biodiesel production due to the limited miscibility of triglyceride oils and methanol [18]. The current reactor, however, takes advantage of the large change in miscibility that occurs once a small amount of the methyl ester product is formed. The reactor/separator has been proven to attain high conversion of triglycerides to methyl esters while separating more than 90% of the glycerol formed by reaction [19–21]. The reactor/separator contains an upward moving reacting phase that eventually exits the top of the reactor as biodiesel and a downward flowing raw glycerol phase that accumulates and exits at the bottom of the reactor/separator.

Unker et al. [21] examined the relationship between the gravity vector, the flow vector, and the reactor performance at various tilt angles, θ, of the reactor (Fig. 1). Glycerin separation efficiency showed strong dependence on the reactor angle. Only 35–50% of the glycerin separated from the reacting stream when the reactor was vertical, but 90% of the glycerin separated when the reactor was tilted to an angle of 30° from the horizontal. The conversion of triglycerides was observed to be insensitive to changes in reactor angle, decreasing from roughly 99% at 90° to 97% at 30° tilt angle. The produced biodiesel passed the ASTM D6584-10a free and total glycerin test when the reactor was vertical (90°) but failed the ASTM D6584-10a free and total glycerin test at tilt angles of 45° and 30°. Thus, a small change in the conversion attained in the reactor can have a major impact on the overall performance of the process.

It is hypothesized in this investigation that the decrease in conversion at tilted reactor orientations is caused by the increase in glycerin separation efficiency. As the glycerol byproduct stream flows countercurrently to the reacting mixture, it may scrub the methoxide from the reacting mixture. When the reactor is tilted and the glycerol flow increases substantially due to much higher separation efficiency, more methoxide may be removed from the upward flowing reacting mixture, resulting in less methoxide to interact with the vegetable oil than originally intended. One possible solution to this problem is to simply increase the methoxide injection rate, but that would decrease the overall efficiency of the reactor and place a larger waste load on the overall process. The proposed solution described below is to change the reactant injector design to divert some of the methoxide to a higher point in the reactor (Fig. 1) in an effort to alleviate the scrubbing problem, restore conversion to higher values, and allow the reactor to separate a large fraction of the glycerin that forms.

Injector design plays a vital role in reactor performance. The effect of geometrical positioning of injectors on reactor performance has been documented in processes ranging from nitride deposition during chemical vapor deposition [22] to gas hydrate formation [23]. Injector selection is particularly important in the current study due to the laminar flow in the reactor/separator. A static mixer was chosen for the primary injector to overcome miscibility limitations of methanol with triglycerides [20] and a countercurrent misting nozzle was chosen for secondary injection to disperse methoxide into the flow without disturbing the reacting flow.

2. Materials and methods

2.1. Equipment setup

As seen in the schematic in Fig. 2, the equipment consists of three major components; a glass reactor/separator, a methoxide mixing/storage tank, and a water heater. The reactor/separator, labeled 1 in Fig. 2, consists of a 1.2 m long glass column with a 0.15 m ID. Two brass caps enclose the ends of the tube and each is fitted with its respective injection unit. The primary injection unit is attached to the bottom end cap and consists of a 0.3 m length static mixer that leads to a 0.15 m length static mixer within the glass tube. A perforated metal disk covers the opening of the inner static mixer to disperse incoming flow radially. The top end-cap was fitted with an additional injection unit. This injection unit consists of a 0.35 m long stainless steel tube with a 3 mm ID. A stainless steel full-cone misting nozzle, with a 0.5 mm orifice, was mounted onto the end of the tube in order to disperse methoxide flow against the upward moving reacting flow.

Labeled 2 in Fig. 2 is the mixing/storage unit for the potassium hydroxide–methanol (methoxide) solution. It consists solely of a sealed 190 L PVC tank plumbed to supply methoxide to the reactor/separator. Labeled 3 in Fig. 2 is the 450 L water heater (Vanguard 240/280 V) used for heating the raw oil feedstock. The water heater is equipped with a 4.5 kW heating element and a thermostat for temperature control. The thermostat was too inaccurate for the experiments described below. Constant monitoring and manual control was required to keep the feed temperatures consistent throughout the experiment.

As indicated in Fig. 2, temperatures (T), liquid phase levels (L), and liquid flow rates (F) were measured at various locations. A National Instruments PCI-6221 DAQ board with a SCC-68 I/O connector block was used to record flows and temperatures at given time intervals. A LabVIEW control system with a PI algorithm in conjunction with the electronic proportional valves, V_{1A} and V_{2A}, controlled the flows of incoming methoxide and vegetable oil, respectively. Biodiesel was allowed to exit the top of the reactor