PROCESS INTENSIFICATION IN CONTINUOUS BASE-CATALYZED BIODIESEL PRODUCTION

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Abstract

Recent expansion of biodiesel manufacture has resulted in increased interest among commercial enterprises to minimize the cost of feedstock materials and waste production and to maximize the efficiency of production. Oak Ridge National Laboratory has experience in developing process intensification methods for nuclear separations, and this paper will discuss how technologies developed for very different applications have been modified for continuous reaction/separation of biodiesel. In collaboration with an industrial partner, this work addresses the aspect of base-catalyzed biodiesel production that has previously limited it to a slow batch process. In particular, we have found that interfacial mass transfer and phase separation control the transesterification process and have developed a continuous two-phase reactor for online production of a methyl ester and glycerol. Enhancing the mass transfer has additional benefits such as being able to use an alcohol-to-oil phase ratio closer to stoichiometric than in conventional processing, providing opportunities to minimize the amount of solvent that has to be recycled and reduce post-processing clean up. Various technical issues associated with the application of process intensification technology will be discussed, including scale-up from the laboratory to a pilot-scale undertaking.

Introduction

Process intensification is an engineering concept that gained attention through investigations in the 1970s at the University of Newcastle [1]. The goal was to achieve simultaneous reduction in capital cost of a chemical plant through reduced size and inventory, as well operating costs through reduced energy consumption and feedstock required per unit mass of the product. Since the idea was put forward, it has been applied to a number of chemical processes, perhaps most notably the Eastman technology for the esterification of methanol to form methyl acetate, which combines reaction and distillation [2]. More recently, process intensification has been examined as a result of imperatives in chemical safety and safeguards. For instance, the Bhopal incident would not have affected as many people had the inventory of methyl isocyanate been lower. Finally, in the era of dwindling supplies of easily recoverable oil, sustainability depends on dependable supply of both feedstock and energy. Methods of process intensification naturally enhance both environmental and economic sustainability of the chemical industry. Process intensification has been reviewed by Tsouris and Porcelli [3,4], who cite examples including: reactive distillation, static mixers, "HiGee" reactor/separators such as spinning disc [5] and centrifugal contactors [6], fractal technologies to control fluid flow [7], heat-exchanger reactors, microreactors, and process equipment that is enhanced by external fields [8] – electric, sound, magnetic, gravity and microwaves.

Centrifugal phase contact and separation is an example of an intensified technique that enhances mass transfer at high throughput and minimizes inventory of solvents. Such methods are well suited for applications in treatment of nuclear waste [9] and nuclear fuel recycling [10]. Contactors for

such uses are available commercially and have been tested in processing of actual radioactive feeds [11]. Contactor technology has also been tested in the area of oil recovery, enhancing the separation of produced water from the lighter hydrocarbon phase [12]. In all of these solvent extraction applications, the process has been optimized to maximize mixing followed by phase separation with minimal residence time, necessary in nuclear applications to minimize solvent degradation from radiolysis. The work that is discussed in this paper applies the well-known centrifugal contactor/separator technology to a different system that is well suited for process intensification – biodiesel production.

Biodiesel, a mixture of methyl esters, is made commercially from the transesterification of oil [13], often soy oil, Reaction 1. The kinetics of the transesterification process are rapid; however, multiphase separations after the synthesis of the fuel can be problematic and so the process is typically run in batch mode. The biodiesel fuel and the glycerol product take several hours to separate. In addition, to push yields to completion, an excess of methoxide catalyst is typically used, which has to be removed from both the biodiesel and the glycerol phase after reaction. Washing steps are often employed to remove free fatty acids, which can lead to undesirable saponification. Standards for biodiesel purity are based on the removal of contaminants either before the oil feedstock is esterified or separation of unwanted byproducts [14].

$$C_3H_5(CO_2R^1)(CO_2R^2)(CO_2R^3) + 3CH_3OH \rightarrow CH_3O_2R^1 + CH_3O_2R^2 + CH_3O_2R^3 + C_3H_8O_3 \qquad (1)$$

Triglyceride + Methanol ⟶ Methyl Esters + 1,2,3-Propanetriol

Various methods have been examined to enhance either the pretreatment of biodiesel feedstocks or posttreatment of reaction products, including the use of cavitation reactor in the process intensification of the homogeneous acid catalysis of transesterification [15]. Centrifugal mixing has been applied to biodiesel production, using the contactor as a low throughput homogenizer, employing very low flow rates to increase residence times to tens of minutes [16]. In this study, we have combined the reaction of oil and methoxide with the online separation of biodiesel and glyercol into one processing step, using a modified centrifugal contactor. Two distinct phases enter the reactor (reagents) and two distinct phases leave the reactor/separator (products), demonstrating the application of process intensification to high-throughput biofuel production.

Experimental

Based-catalyzed biodiesel synthesis and simultaneous separation of methyl ester and glycerol products was carried out in a modified centrifugal contactor [17][1]. Reagents were food grade soy oil and potassium methoxide, formed from the reaction of KOH (EM Science) and methanol (EM Science 99.8%), at a phase ratio of 5:1 oil-to-methoxide. All reagents were used without further purification. Analysis of reaction products was by gas chromatography flame-ionization detection, GC FID, with a Hewlett Packard 5890 II GC. The analysis procedure followed ASTM D6854 for [18].

Before using the reactor/separator, the kinetics of the based-catalyzed transesterification reaction were studied by sampling a homogenized (IKA Labortechnik model T25) mixture of the oil and methoxide, 120 mL, contained in a 300 mL beaker, and held at $56 \pm 4°C$. Samples of two mL were

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[1] Patent pending

taken after 15, 30, 60, 120, and 240 s, with t = 0 s corresponding to when the reaction started. After sampling, the samples were immediately contacted with 1 mL of 0.1 N HCl to arrest the transesterification reaction. Samples were analyzed by GC.

Once the required residence time was established, the reaction was carried out in a centrifugal contactor, modified to allow a sufficient contact time to permit the reaction to go to completion. The reagents, introduced through separate ports, were combined in a centrifugal contactor with the internal rotor spinning at 3600 rpm, Figure 1. Mixing to enhance mass transfer and reaction occurred, followed by separation of products according to their densities. Products were collected from the "light" side and "heavy" side outlet streams. The whole assembly was heated to 60°C in a temperature-controlled water bath, and the reagents were likewise preheated. Samples were taken after 1, 3, 6, and 10 min intervals and, as in the case of the kinetics experiments, were immediately contacted with a solution of 0.1N HCl. The samples were analyzed by GC to assess the extent of the reaction.

Figure 1: Picture of reactor/separator experimental apparatus in the water bath.

Results and Discussion

Results of the kinetics experiments are shown in Figure 2. The yield was calculated from the total GC signal for C16, C18, C20, C22, and C24, indicating the chain length of the hydrocarbon chain on the ester. GC signal included peaks from unsaturated as well as saturated methyl esters. The same data are presented in two different ways on the graph, the ratio of methyl ester-to-oil signal from the GC, and the second showing the same data converted to mole % biodiesel. There is a rapid increase in biodiesel fraction up to about 1 minute, and then the signal levels off. Although there appears to be a slight decrease in signal over the remaining data points, this is not statistically significant as the GC precision is about ±10%. The uncertainty in the abscissa is ±2s, during which grab samples were taken.

The analyses of product streams from the centrifugal contactor synthesis are shown in Figures 3 and 4. The bars show the fraction of unreacted oil versus methyl ester coming from the "light" and "heavy" fractions respectively. The flow of glycerol-rich dense phase was much slower than that of the

biodiesel, and so during the initial stages of the experiment, methyl ester was found in both of the streams. After a minute the flows settled down, and the methyl ester and glycerol were well separated.
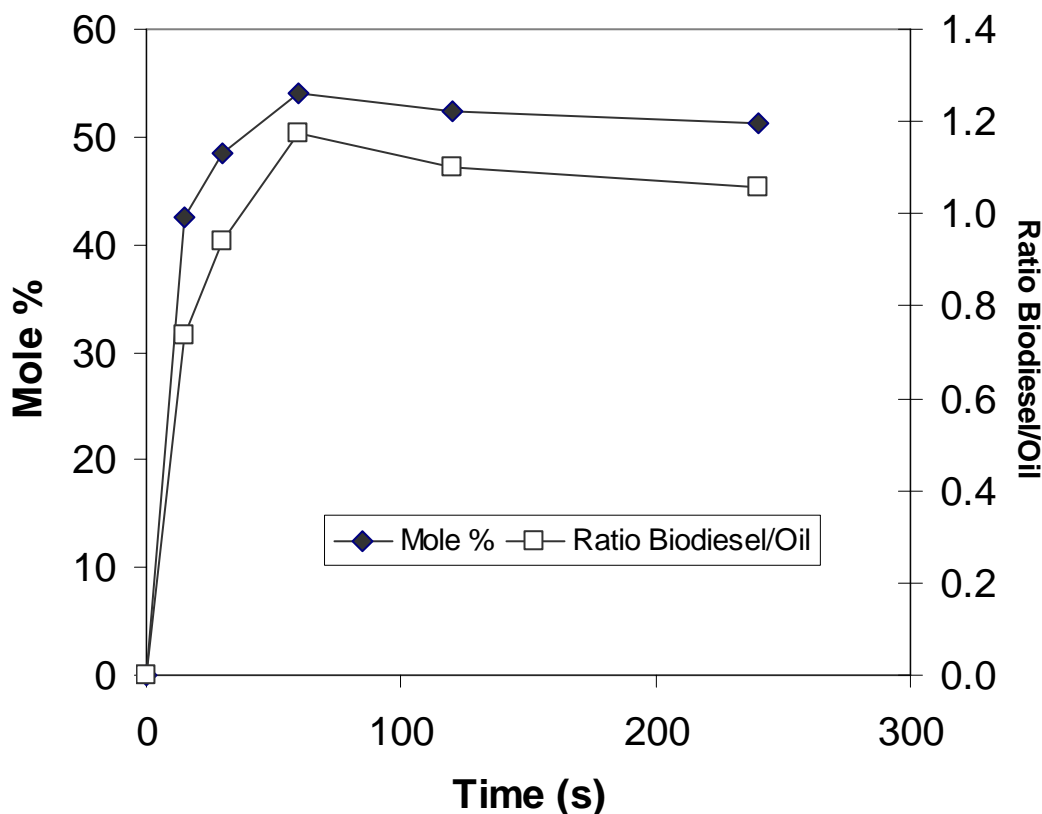

Figure 2: Mole % Biodiesel and Biodiesel-Oil Ratio as a Function of Time Determined from GC Analysis of Homogenized Samples.

Except at the beginning of the experiment, where mixing and flows were being established, no unreacted oil was present in the "light" side fraction. The data in Figure 4 show that over time, the fraction of methyl ester in the "heavy" side flow decreased dramatically as the flow of glycerol was established. However, because the system was configured to achieve the highest purity on the "light" side, some oil and methyl ester were entrained in the "heavy" side. The residual samples were taken well after the timed experiment was complete, and arose from the phases that were drained out of the bottom of the reactor. These samples showed that the centrifugation process was more effective than what could be achieved in a mixer settler relying on several hours of gravity settling for separation of the product and reagent phases. The effective separation in the contactor arose because of enhanced mass transfer from application of centrifugal forces equivalent to approximately 300 times that of gravity. The slight drop in signal at 6 and 10 minutes after the experiment started, as shown in Figure 3, is likely indicative of the precision of the GC method for methyl ester sampling, or about ±10%, as there was no deliberate variation in mixing speed or any other experimental parameter.
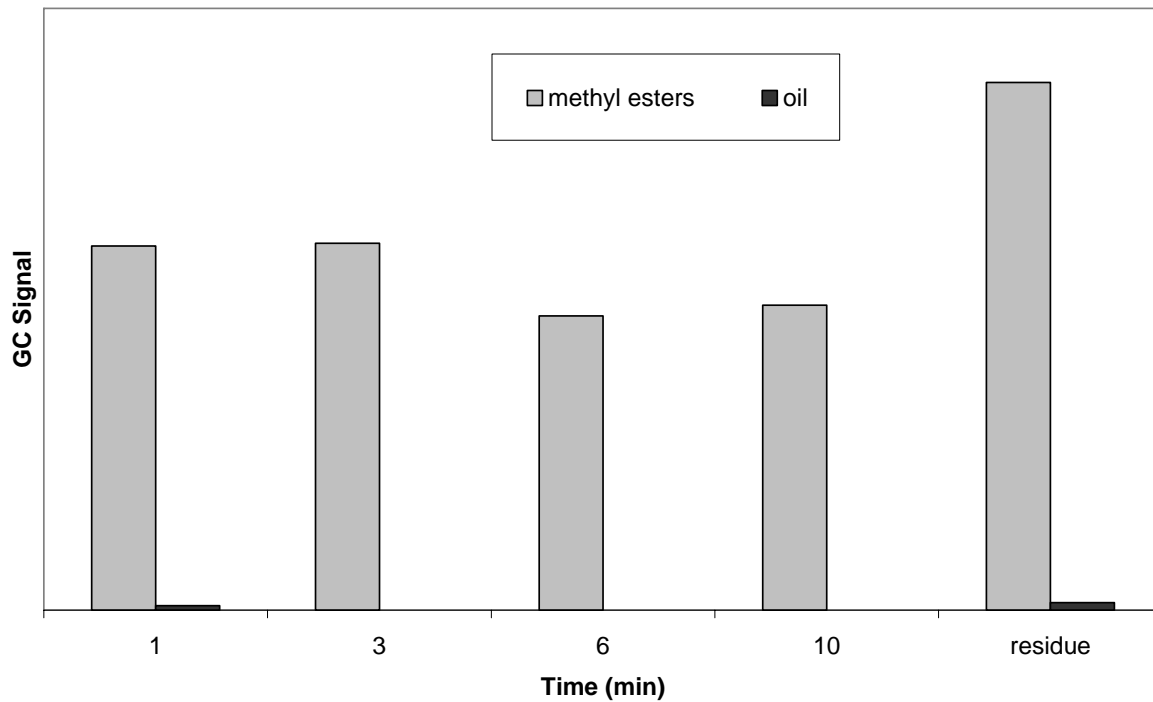
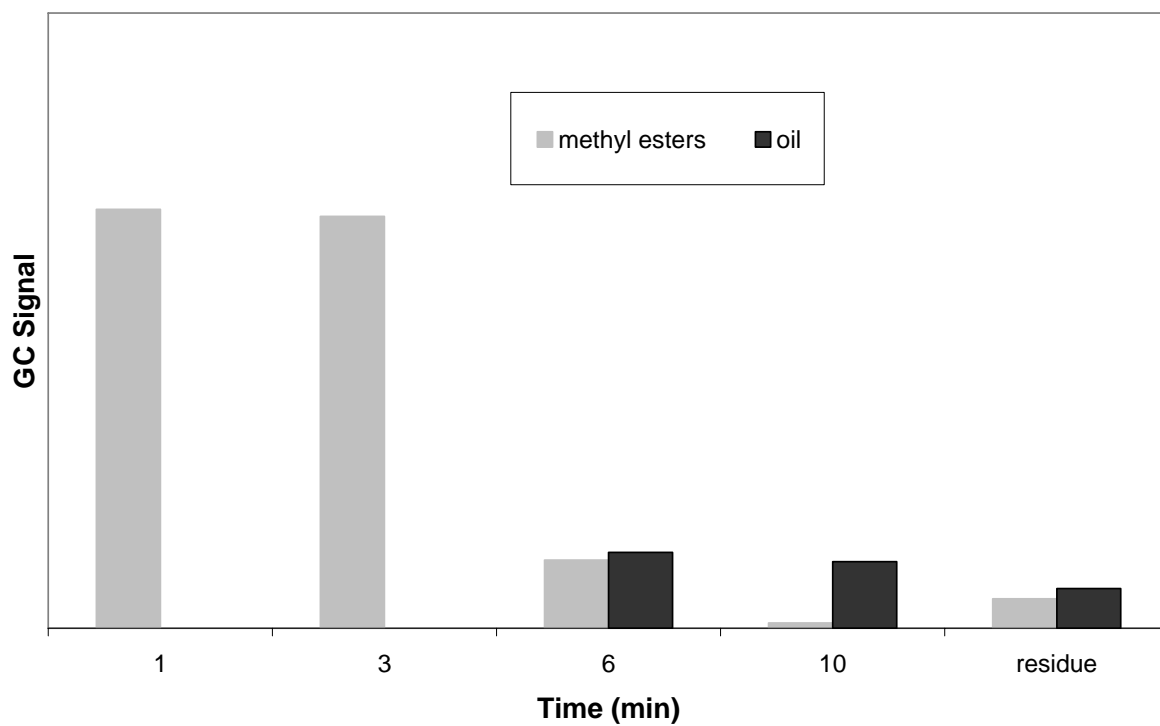Figure 3: Continuous production of biodiesel showing less-dense flow from the reactor.

Figure 4: Continuous production of biodiesel showing more-dense flow from the reactor.

Figure 5 shows superimposed gas chromatograms for unreacted oil and the methyl ester product. The oil chromatogram, with a peak at 3.7 minutes, is from direct injection of the reagent oil before processing. Glycerol, expected to be seen at 8.4 minutes from injection through measurement of a calibration standard, was not observed in the chromatogram for the biodiesel product. Partially reacted mono- and diglycerides were also not observed. Although the system is complex, with a reaction involving two immiscible phases of reagents and two separate immiscible phases of products, these data indicate that the combination of reaction and separation is an effective means to synthesize biodiesel in a continuous manner.
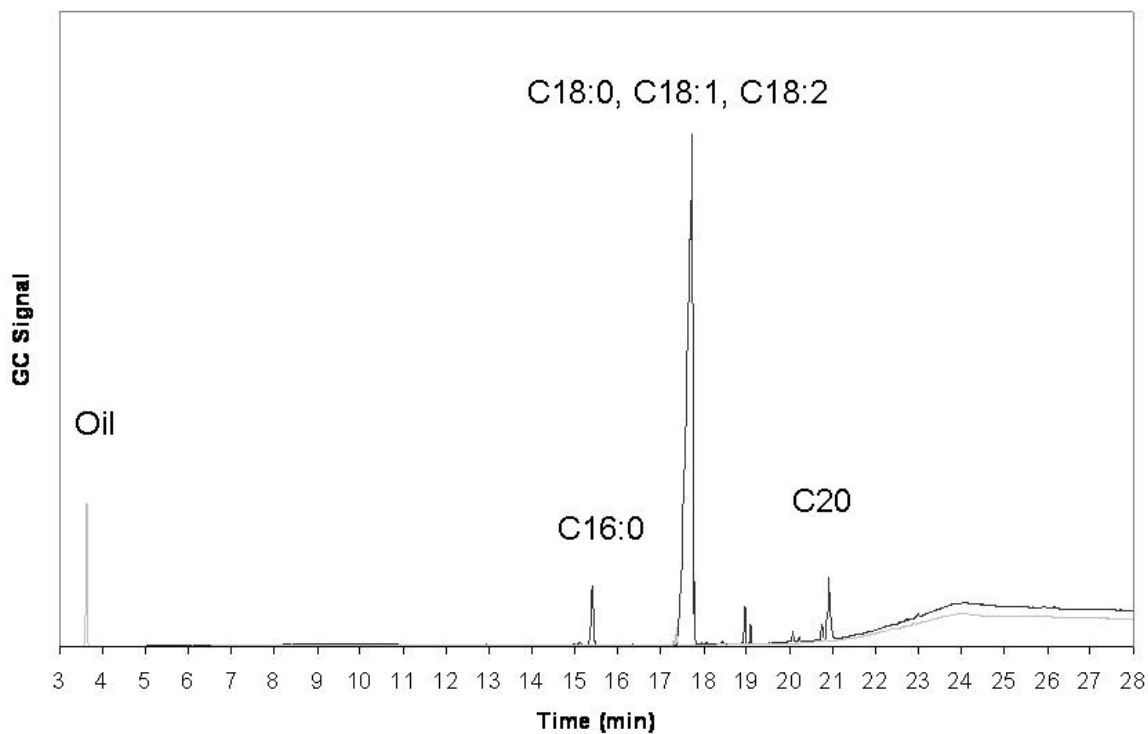

Figure 5: Gas Chromatogram of "light" side product from reactor/separator showing methyl ester peaks (black), superimposed with a chromatogram of unreacted oil (grey) taken at a separate time.

Conclusions

Simultaneous reaction/separation for the production of methyl esters from soy oil has been demonstrated in a centrifugal contactor, modified to achieve a residence time sufficient for the reaction

to go to completion. Our approach is to operate the contactor under normal conditions, at several thousand rpm, but to engineer the hold up so that a high throughput can be obtained. Oak Ridge National Laboratory is now collaborating with a biodiesel manufacturer, Nu-Energie to scale-up the apparatus so that a pilot scale test can be done at the Nu-Energie facilities with feedstocks used in commercial production. It is anticipated that success with the pilot scale may lead to further applications in pre-and post-treatment in the biodiesel production process, allowing biodiesel production with less-than-optimal, but much less expensive, feedstocks.

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