In Situ Monitoring of Biodiesel During Transesterification Using Ultrasonic Transducers

Abstract

Biodiesel is produced by transesterification, a process in which oil is reacted with an alcohol in the presence of a catalyst. Generally, the optimum reaction time can vary dramatically with reaction conditions and starting materials. In this investigation, an on-line biodiesel transesterification monitoring system was developed. The system utilizes ultrasonic transducers equipped with an Arduino UNO board for data collection. The proposed method was applied to the transesterification of fresh vegetable and waste oil with methanol catalyzed by KOH at 65℃. Our system provides a reliable and sensitive means for monitoring a biodiesel reaction mixture. The ultrasonic sensors were able to distinguish each reaction step, and indicated the optimum endpoint of the reaction.

Introduction

Since the major expansion of the oil drilling industry, the majority of the world's energy usage has comprised of non renewable petroleum sources [1], which is associated with irreversible environmental damage. The primary pollutants emitted from the burning of standard diesel fuel include carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxide (NO), particulates, etc. [2]. They pose health risks and environmental risks. With such negative trade-offs, nations have started to accept biodiesel as a more environmentally friendly source of fuel. Brazil and Germany have become major biodiesel producers [3].

The emission of particulates, carbon monoxide, and total unburned hydrocarbons are reduced with biodiesel by 47%, 48% and 67%, respectively, compared with that of petroleum diesel. Having a comparable viscosity and heat of combustion, biodiesel can replace petroleum diesel in many applications. Biodiesel is the only alternative to petroleum fuel that has passed the health effects testing requirements under the Clean Air Act in the United States [2]. It can be produced from renewable sources, such as vegetable oil, and non-edible sources, such as algae and waste cooking oil. Biodiesel may soon constitute the majority of the energy sources in various applications.

There are four primary methods to prepare biodiesel: direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification. Our investigation focuses on the transesterification method. Biodiesel, a mixture of fatty acid methyl esters (FAMEs), can be obtained by the transesterification reaction of triglycerides with an alcohol and a catalyst [5].

The time to complete the transesterification process varies depending on different

parameters, such as reaction temperature, type of oil used, and stir rate. Having a prolonged or shortened reaction time can lead to excessive contaminant byproducts, such as free fatty acids, mono- and diglycerides [6]. These final products can lower biodiesel yield by up to 20% and lead to lengthy purification processes lasting several days [7]. Obtaining the endpoint can prevent the creation of excessive waste products that prolong the purification process and reduce the conversion to biodiesel [4]. During transesterification, it is, therefore, important to monitor the progress of the reaction by measuring certain physical or chemical properties of the fluid to determine the endpoint of the reaction. Although this is achievable by pausing the reaction at certain intervals and directly measuring the chosen property, it is very time-consuming and may affect the progress of the reaction.

Previous studies have demonstrated methods for monitoring biodiesel reactions. The use of the Fourier Transform Infrared spectroscopy (FTIR) technique [8] and the use of gas chromatography for biodiesel monitoring [9] have been developed. However, such methods require expensive analytical devices, have long processing times, or are not suitable for immediate online measurement, because they require interruption during the reaction. Monitoring the reaction with interruptions leads to temperature changes during transesterification and thus affects the biodiesel yield [6]. Recent results have shown that the biodiesel reaction could be monitored without interruption by monitoring changes in refractive index of the fluid media [5]. Electrical impedance, which is correlated with viscosity, has also been shown to enable online monitoring of biodiesel reaction [4].

During the reaction, the density could change due to several factors. Initially, the density

will experience a significant decrease due to the dispersion of low density methanol (0.79g/mL) in vegetable oil (0.93g/mL). The methanol, or polar component is likely to become more dense as it interacts with tri-, di-, monoglycerides, and glycerol, and as methanol is consumed. Eventually, the production of biodiesel in place of glycerides should cause the nonpolar component to have a lower density. When biodiesel is present as a major component, it is likely that the formation of fatty acids from biodiesel occurs simultaneously with the ongoing conversion of triglycerides to biodiesel and glycerol [6]. After exhaustive reaction, the formation of fatty acids is likely to be the dominant reaction. Thus, the optimal conversion of vegetable oil to biodiesel may occur before all glycerides are converted, since both fatty acids and mono- and diglycerides can lead to emulsion formation in the subsequent water washes.

Previous studies have demonstrated that viscosity is indirectly related to biodiesel yield, [10] and that density has a direct correlation with viscosity [11]. Therefore, we hypothesized that the density may have a relationship with biodiesel yield and the free fatty acid content. In our hands, monitoring density by sampling and measuring volume and mass proved too insensitive when distinguishing between stages of the reaction.

Acoustic impedance has been shown to have a relationship with the density of a heterogenous fluid [12]. Ultrasonic sensors can be used to measure the reflection of an ultrasonic signal off of the solid-fluid interface. The amount of acoustical signal reflected off of the fluid varies depending on the properties of the fluid. We carried out a study on the transesterification process by inferring its density changes during the reaction from amplitude

changes in an ultrasonic wave reflected through a solid block of nylon in contact with the reaction fluid. Since this ultrasonic technique is insensitive to opacity, it is suitable for both opaque and transparent liquids.

Material and Methods

Materials. The oil was Wesson oil, and waste oil was vegetable oil from a local restaurant. Reagent grade methanol is obtained from Scholar's Chemistry. Potassium hydroxide pellets are from Ward's Science. Ultrasonic sensors were obtained online from a Chinese robotics manufacture. 1 inch 6/6 natural color Nylon was obtained from McMaster-Carr. A 500ml Polypropylene flask was obtained from Fisher.

Biodiesel Reaction: Standard transesterification procedure was followed using a KOH methanol catalyst solution with a 1:6 molar ratio. Once the oil reached a stabilized temperature of 65°C, the catalyst solution was poured into the oil and the resulting solution stirred with a magnetic stir bar. After the reaction was complete, the product was stored in a separatory funnel to isolate the glycerol from the solution and a standard water washing technique was applied.

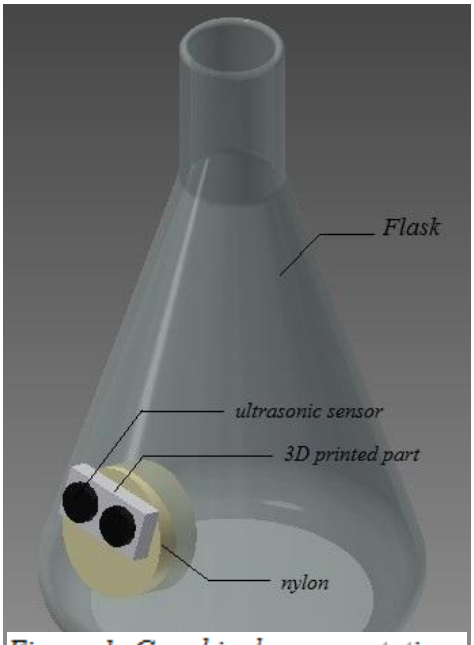


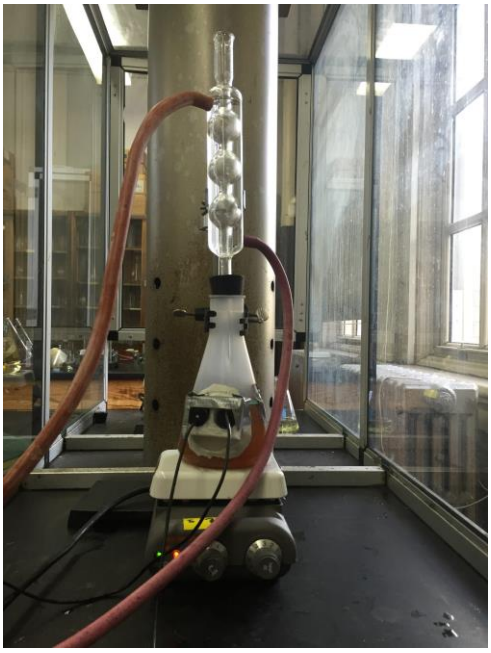
Figure 1: Graphical representation of experimental apparatus

Biodiesel yield measurement: The mass of the oil used was measured before reaction. The solution is then washed until crude biodiesel was obtained. The

ratio of the mass of the crude biodiesel to the mass of the oil used was considered the fractional yield.

Total density measurement: The total mass of the reaction mixture was divided by its total volume in order to calculate its total density.

Reactor design: A diagram of the experimental is depicted in Fig. 1b. The transesterification process was performed in the erlenmeyer polyethylene flask, with a cylindrical piece of 6/6 nylon (diameter of 2½") mounted in a hole drilled on the side of the flask, with the center roughly 3 inches from the base. The nylon piece was sealed into place with epoxy. Two ultrasonic transducers were placed on the nylon. The head of both sensors were coupled to the nylon with pressure sensitive adhesive putty. 3D printed parts were made to hold the transducers in place.



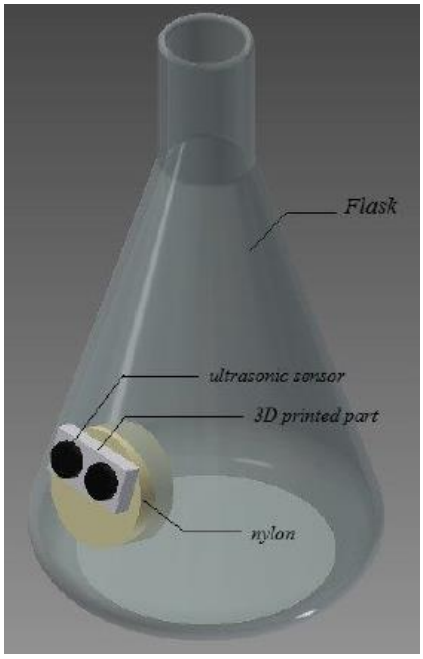


Figure 1a. Experimental setup *Figure 1b. Apparatus setup*

Data Collection: The transducers were connected to two separate Arduinos, in which one transmitted periodic acoustical signals while the other received the reflected acoustical signal. The voltage reading relayed to a computer for data analysis and noise reduction [12]. The sensors were activated before methanol was added to the oil. Data were sampled 160 times per second. The voltage output reading was recorded and graphed using code written in the Python language [13].

One of the ultrasonic transducers was used to relay a tone burst pulse that was reflected at the solid-liquid interface. The reflected pulse was received by a second ultrasonic transducer which t converted the received ultrasound into an electrical signal. The electrical signal was processed by an Arduino UNO board and a specific voltage value was displayed on a computer.

The amount of signal reflected was dependent upon the difference in acoustic impedance at the solid-fluid boundary. As the reaction proceeded, the variations in the fluid composition caused a corresponding change in the acoustic impedance. Since the acoustic impedance is directly proportional to liquid density, as shown in equation 2, any change in the reflected signal will signify a change in the fluid density. As the fluid's density increases, the intensity of the reflected sound wave decreases. Consequently, the plot of density over time implied an inverse relationship between voltage recorded and fluid density.

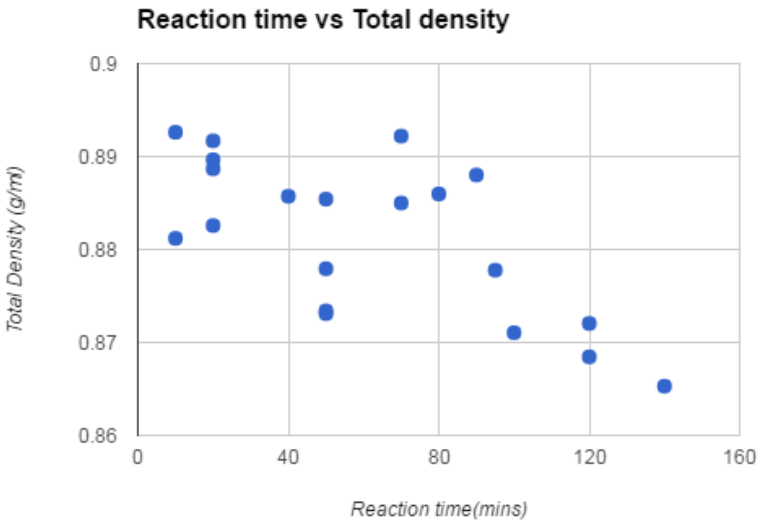
$$R = \frac{Zs - Zliq}{Zs + Zliq} \qquad (1)$$

$$\frac{\square\square\square\square}{c} = \rho \qquad (2)$$

Where Z_{liq} is the acoustic impedance of the fluid, Z_s is the acoustic impedance of the solid (nylon), which was known, c is the speed of sound, ρ is the fluid density, and R is the measured reflection coefficient [8].

Results & Discussion

Biodiesel yield vs Reaction time: Our goal was the development of a sensor that reliably predicted the optimal production of biodiesel. In this investigation, we have measured the biodiesel yield and the fluid density vs reaction time, and we have monitored the reaction with ultrasonic technology. Fig. 2 shows the relationship between reaction time and biodiesel yield.



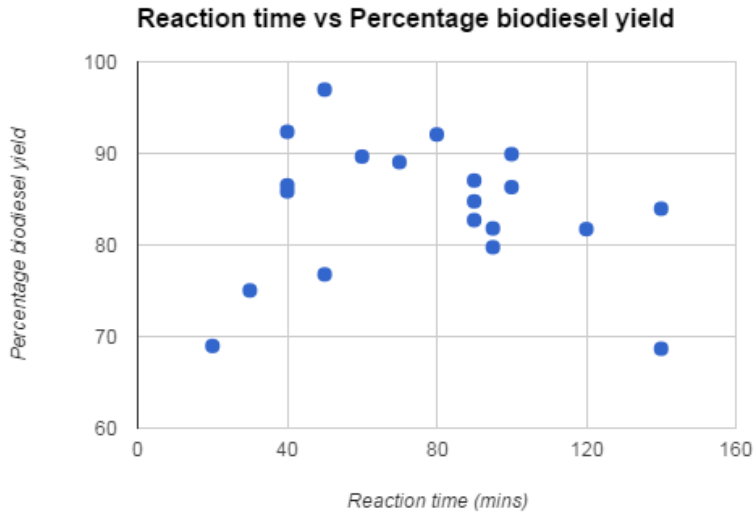


Figure 2. Data plot of Reaction time vs percentage biodiesel yield

The trend then stayed nearly a constant during the interval of minutes 50 to 80 and then proceeded in a downward trend during minutes 90 to 140. This trend was summarized as a bell curve relationship between reaction time and biodiesel yield, which was consistent with previous studies [6]. This trend was consistent with previous studies in which it was demonstrated that most of the oil to biodiesel conversion occurred during this time, causing a sharp increase in biodiesel yield [5].

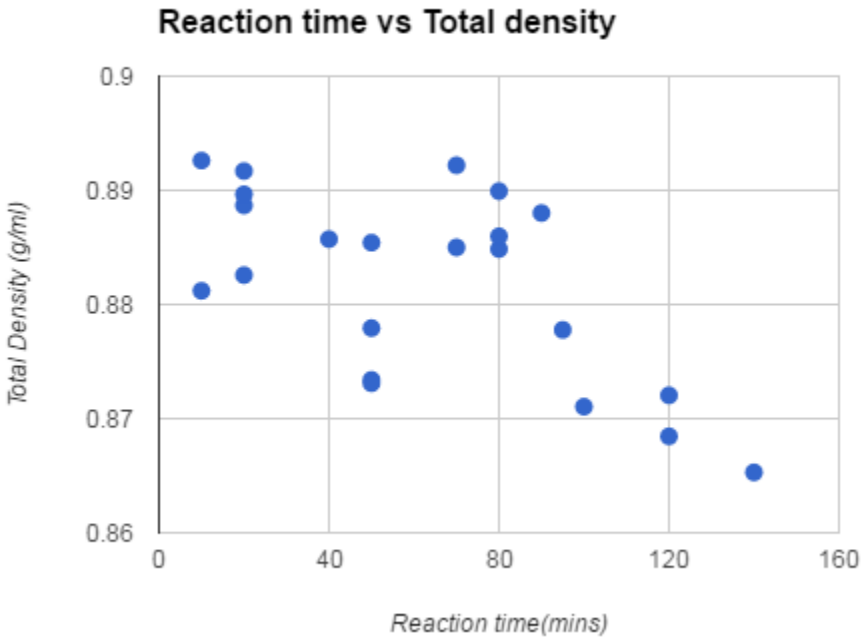


Figure 3. Data plot of Reaction time vs total density

By the end of 50 minutes, most triglycerides have been converted to diglycerides and monoglycerides. The maximum biodiesel yield is obtained at this time. During interval minute 50 to 80, a plateau in biodiesel yield is observed. During this time, mono- and diglycerides are still reacting with methanol, but the biodiesel produced is also reacting with potassium hydroxide at the same time to create free fatty acids. However, as the rate of biodiesel production slows, reverse transesterification occurs during this stage, in which the rate of biodiesel conversion into free fatty acids and glycerol becomes faster.

Total density vs time: Reaction was stopped at different times and the density of the entire solution is measured by mass/volume. From 10 to 80 minutes, the density remained

constant, but dropped at times greater than 90 minutes. The long reaction times also produced the greatest conversion of oil to glycerol. at this point, the non polar component should be entirely biodiesel and fatty acid. This period of constant density overlaps with the plateau were observed in the percentage biodiesel yield trend. It was consistent with the data from previous studies [6] showing a high concentration of fatty acids at later reaction times. It was also repeatedly observed in our washing process that reaction time had a direct relationship with separation time between fatty acids and biodiesel.

Correlation of total density with biodiesel yield: Figure.2 and Figure.3 demonstrated a relationship between biodiesel yield and overall density. In Figure.2, Biodiesel yield appeared to reach a maximum between 50 to 80 minutes of reaction. Since this maximum in Figure 2 overlapped with the constant density observed in Figure.3, we concluded that density could be used as monitoring indicator for optimization of biodiesel yield.

Measuring density by ultrasound: In our work, ultrasonic sensors were utilized to collect density. Reaction trials were started in the constructed vessel as previously discussed and reflected signal is collected via the ultrasonic transducers and processed by Arduino UNO hardware. The Arduino output of voltage is processed and presented using Python programming. Two reaction trials were selected with the setup illustrated in Figure 1a. & Figure.1b. The received signal voltage with respect to the reaction time are shown in Figure 4, where blue and green represent the first and second trials respectively.

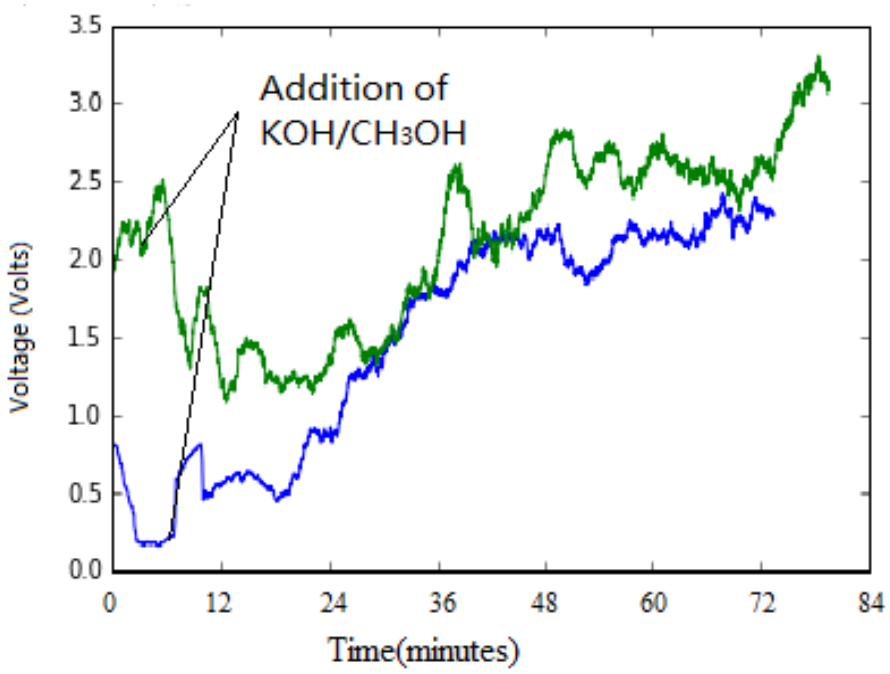
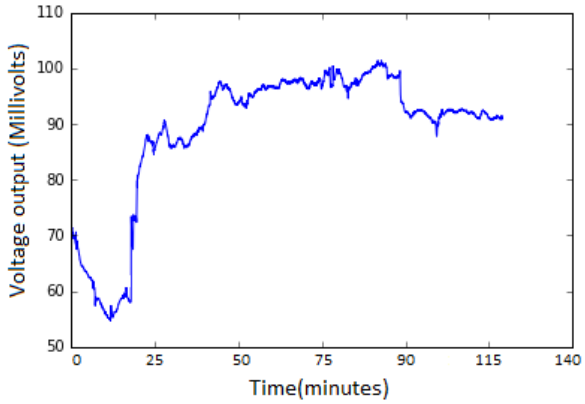


Figure 4. The green line represents voltage readings for a 80-minute reaction, and the blue line represents voltage readings for a 75-minute reaction

In both trials, it is observable that the voltage output increased immediately after the addition of KOH/CH_3OH, which symbolized an immediate drop in density. Then, the voltage output decreased to a value, signifying an increase in density, which can be explained by the emulsion forms and the formation of di- and monoglycerides. Mono- and diglycerides have both long chains and OH groups with hydrogen bond. This could possibly lead to large molecules more tightly bonded together, and therefore greater density. The output voltage then gradually increased, representing a decrease in density as a result of triglycerides conversion into biodiesel. It then attained a plateau from minute 42 to 72. The rate of conversion of mono- and

di-glycerides into biodiesel during this plateau may be offset by the production of free fatty acid. The reaction could be stopped anytime during the plateau region.which was immediately before the voltage curve peaks at minute 72 to 80, to obtain maximum biodiesel yield. The percentage biodiesel yield at its optimum reaction time and and any time during which its density plateaus, were very similar. This data suggested that once a plateau trend was detected, the reaction should be stopped to obtain optimum biodiesel yield with minimal washing time.



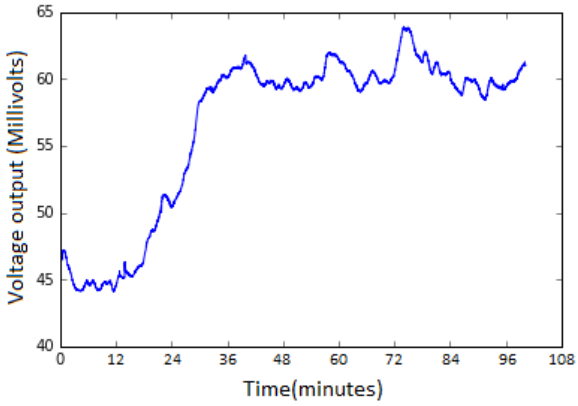


Figure 5a. 100 minute reaction

Figure 5b. 120 minute reaction

Ultrasonic sensing during longer reaction time: Figures 5a. and 5b. showed the voltage during longer reaction times. The same pattern appeared in the first 50 minutes of the reactions as seen in the earlier reactions. In Figure 5a, the features required a shorter time to appear suggesting that this reaction was accelerated compared to the other reactions. Both Figures 5a and Fig. 5b displayed a decrease in voltage associated with an increase in density at times greater than about 80 minutes. This trend resulted in a the bell curve observed earlier in Figure 3. At that point, percentage biodiesel yield started to decrease near the same time that density was detected to be increasing. Additionally, glycerol volume was found to be higher than usual and slow purification time was observed.

Conclusion

We discovered that ultrasonic technology could be used to monitor the biodiesel reaction using the relationship between the density of fluids and amplitude of the ultrasonic signal reflected at the solid-liquid interface. We have learned that this ultrasound technique is extremely sensitive at detecting small physical changes in a reaction fluid. Using this technique, the yield of biodiesel can be optimized under a variety of reaction conditions.

We believe that our trials support our conclusions. However, they are based on laboratory scale reactions using fresh, or lightly used vegetable oil. We have not explored the range of biodiesel processes. Our results are consistent with previously reported work both in the biodiesel field and the monitoring of nuclear waste stream [3].

Possible future investigations could include an extension to other chemical reactions, other biodiesel processes, including other biodiesel reaction vessels, better sensing systems for noise reduction, and scaling the sensor for commercial use.

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