Monitoring biodiesel reactions of soybean oil and sunflower oil using ultrasonic parameters

MK K Figueiredo¹, CE R Silva¹, AV Alvarenga¹, RP B Costa-Félix¹
¹Laboratory of Ultrasound (Labus), Directory of Scientific and Industrial Metrology (Dimci), National Institute of Metrology, Quality and Technology (Inmetro), Av. Nossa Sra. das Graças 50, Duque de Caxias, RJ, Brazil, ZIP 25250-020
E-mail: mkfigueiredo@inmetro.gov.br

Abstract. Biodiesel is an innovation that attempts to substitute diesel oil with biomass. The aim of this paper is to show the development of a real-time method to monitor transesterification reactions by using low-power ultrasound and pulse/echo techniques. The results showed that it is possible to identify different events during the transesterification process by using the proposed parameters, showing that the proposed method is a feasible way to monitor the reactions of biodiesel during its fabrication, in real time, and with relatively low-cost equipment.

1. Introduction
Meeting current energy demand is a challenging issue. Environmental concerns associated with fossil fuel burning have brought in focus the necessity of renewable energy resources [1]. Biodiesel is an example of the employment of (renewable) biomass to produce energy. Biomass is an alternative to diesel that is biodegradable, nontoxic, and has a low-emission profile [2].

It is important ensure the quality of the fuel and to understand the stages of the transesterification reaction. Monitoring reaction kinetics is of extreme importance for the optimization of industrial processes. A robust method that performs accurate non-destructive monitoring and ensures the quality of biofuel is in demand. In this direction, ultrasound has emerged as a feasible tool. Koc in 2009, for example, has shown the feasibility of using ultrasound to monitor the deposition of glycerol during the transesterification reaction [3].

This paper presents a study that evaluates the usefulness of ultrasound parameters as tools for real-time monitoring of transesterification reactions by using low-power ultrasound and pulse/echo techniques. Time of flight and amplitude of ultrasonic signals were the parameters used in the study.

2. Method
The materials used in this study were soybean and sunflower oil, methanol and ethanol (purity > 95 %), and potassium hydroxide (KOH) (purity > 95 %). The alcohol to oil proportion was 6:1 and 1 % (m/m) of catalyst.

The ultrasonic measurement system consisted of a Beaker (vessel) in which the reactions were carried out, a 1 MHz ultrasonic transducer with a diameter of 12.7 mm (A303-S, Panametrics-NDT Olympus Corporation, Japan), a waveform generator (33250A, Agilent Technologies, CA, USA), an oscilloscope (TDS3012B, Tektronix, Beaverton, OR, USA), a data acquisition unit (34970A, Agilent Technologies, CA, USA) and a computer with a program developed in LabView 11, (National Instruments, Austin, TX, USA). It is noteworthy that the ultrasonic power delivered to this system was...
low, i.e., less than 100 mW. Typically, ultrasonic power delivered in an ultrasonic-assisted process is in the range of hundreds of watts [4, 5], much greater than that delivered in this work.

A waveform generator was used to excite the transducer by driving a 4-cycle sine wave burst at 20 Vpp of amplitude. The echo signal was acquired and digitalized by using the oscilloscope. Temperature measurement was carried out by using a thermocouple and a data acquisition system. All signals and acquired data were recorded every 30 seconds and analysed by using the software developed in LabView. In Figure 1, a scheme of the experimental setup is presented. It allows identifying the variation that occurs during the reaction through the ultrasonic time of flight and amplitude of signal. Amplitude, time of flight of the ultrasonic waveform, and temperature of the reaction are displayed in real time and recorded in all the experiments.

![Figure 1](image.png)

**Figure 1.** Experimental setup that uses ultrasound for monitoring the transesterification reaction.

3. Results

The results of the transesterification reaction of soybean oil with methanol are presented in Figure 2. In Figure 2a, one can observe the ultrasonic waveform, where the signal with the highest amplitude represents the echo signal from the beaker bottom (the particular waveform disclosed is a sample picked up after the stirring was finished).

The temperature variation during the transesterification process is shown in Figure 3b. The amplitude (Figure 2c) and time of flight (Figure 2d) calculated from the echo signal also vary correspondently. After the end of the stirring, the glycerol deposition starts, and a two-phase sample (biodiesel/glycerol) is formed. The ultrasound reflection on that interface appears as an echo signal before the beaker bottom reflection (arrow in Figure 2a). As the layer of glycerol increases, the distance between the glycerol/biodiesel interface and the beaker bottom increases. Figure 2a was obtained when total glycerol deposition has already occurred.

Once the stirring starts, temperature, time of flight, and amplitude decrease quickly, and after approximately one minute, all the parameters start to increase. The time of flight achieves its maximum in 30 seconds and immediately starts to decrease presenting three stages of decay: till the 5th minute, the time of flight decays very fast (negative steepest part of the curve); between the 5th and 30th minutes, the rate of decay reduces; and finally, after the stirring is turned off, the rate of decay reduces a little bit more. The temperature keeps increasing until approximately the 10th minute, and then it starts to decrease until the 30th minute, when the stirring is turned off. After that, the
temperature increases until the 50th minute and then it decreases rapidly. Contrarily, the amplitude stays increasing fast until the 10th minute, and after that, it presents a lower rate of increase.

Figure 2. Monitoring of the transesterification reaction of soybean oil with methanol. One can observe (a) the ultrasonic waveform at the end of the experiment, (b) the temperature variation during the transesterification process, (c) the time of flight, and (d) the amplitude calculated from the echo signal.

An example of the parameters obtained during the transesterification reaction of soybean oil with ethanol is presented in Figure 3. Figure 3a shows the waveform at the end of the transesterification, where the signal with the highest amplitude represents the echo signal from the beaker bottom. Glycerol deposition was not observed immediately after the end of the reaction. Correspondingly, no echo signal concerning glycerol deposition was observed in the waveform. Similarly, that reaction using methanol, once the stirring starts, temperature, time of flight, and amplitude decrease quickly. After approximately one minute, temperature and time of flight quickly increase in the 10 first minutes and tend to stabilize after reaching the maximum temperature, while the amplitude decreases until the stirring is turned off. Thereafter, the amplitude increased.
Figure 3. Monitoring of the transesterification reaction of soybean oil with ethanol. One can observe (a) the ultrasonic waveform at the end of the experiment, (b) the temperature variation during the transesterification process, (c) the time of flight, and (d) the amplitude calculated from the echo signal.

An example of the parameters obtained during the transesterification reaction of sunflower oil with methanol is presented in Figure 4. Figure 4a shows the waveform at the end of the transesterification. Similarly, that reaction using soybean oil with methanol, after the end of the stirring, the glycerol deposition starts, and a two-phase sample (biodiesel/glycerol) is formed. The ultrasound reflection on that interface appears as an echo signal before the beaker bottom reflection (Figure 4a).

The same way, that using the soybean oil, once the stirring starts, temperature, time of flight and amplitude decrease quickly. Then, the temperature keeps increasing until approximately the 7th minute, and then it starts to decrease until the 30th minute, when the stirring is turned off. The time of flight increase quickly in one minute and after increasing slow until 15 th minute and hereafter tend to stabilize. The amplitude stays increasing fast until the 4th minute, and after that, it presents a lower rate of decrease and after 6th minute tend to stabilize.
Figure 4. Monitoring of the transesterification reaction of sunflower oil with methanol. One can observe (a) the ultrasonic waveform at the end of the experiment, (b) the temperature variation during the transesterification process, (c) the time of flight, and (d) the amplitude calculated from the echo signal.

Analysing the transesterification reaction of sunflower oil with ethanol. It is observed that glycerol deposition was not observed immediately after the end of the reaction. Furthermore once the stirring starts, temperature and amplitude decrease quickly, however the time of flight increase speedily and after approximately one minute decrease for one minute and then increase until the 5th minute, and after that, it presents a lower rate of decrease.

The temperature increases until approximately the 8th minute, and then it starts to decrease until the 30th minute, when the stirring is turned off. The amplitude increases for one minute, remains stable for two minutes, and after that, it presents decrease and after 5th minute tend to stabilize, when the stirring is turned off.
While assessing the methanol biodiesel reactions, in all cases, glycerol deposition was observed after turning off the stirring. Consequently, all ultrasonic waveforms presented the echo signal from the interface of glycerol and biodiesel. On the contrary, none of the ethanol biodiesel reactions presented glycerol deposition after turning off the stirring presented the same only sometime later when the sample was placed to rest in the funnel. According to literature, separation of glycerol is not spontaneous when ethanol is employed to obtain biodiesel owing to the higher water presence in its composition [1].

In this study, three parameters were studied during the transesterification reactions: the time of flight and amplitude, both calculated from the ultrasonic waveform, and temperature. With the graphics shows in this work, it note that the behaviour of all the parameters studied were sensitive to the type of alcohol and the type of feedstock used, which proves to be a selective method. Observing the same feedstock (soybean oil) and different alcohols, note that the parameters have different behaviours, temperature and time of flight for example, when the reaction occurred via methanolic, had a tendency to increase up to a certain point and then decreased until the moment that the stirring is turned off. However, when the reaction occurred via ethanolic, these same parameters had only a tendency to increase.

Analysing the graphs of the same alcohol, such as ethanol, and different feedstock is also observed significant differences, thus showing the efficiency of the method developed.

5. Conclusion
With the proposed procedure, it was possible to identify different events during the transesterification process by using the proposed parameters. Through the method developed was also possible to
identify differences between the feedstock and alcohols used, showing to be a selective method. The preliminary results suggest that the proposed method may be feasible for monitoring the reactions of biodiesel during its fabrication, in real time, and with relatively low-cost equipment.

Acknowledgement

The authors thank the CNPq and FAPERJ for the financial support.

References

[1] Lôbo, I. P., Ferreira, S.L.C., Cruz, R.S., 2009, Biodiesel: Quality parameters and analytical methods, *Quim. Nova*, v. 32, nº 6, 1596-1608 [in Portuguese].
[2] Corrêa, S. M., Arbilla, G.; 2006, Aromatic hydrocarbons emissions in diesel and biodiesel exhaust, *Atmos. Environ.*, 40, 6821-6826.
[3] Koc, A. B., 2009, Ultrasonic monitoring of glycerol settling during transesterification of soybean oil, *Bioresource Technology*, v.100, 19-24.
[4] Ji, J.; Wang, J.; Li, Y.; Yu, Y.; Xu, Z.; 2006, Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation, *Ultrasonics*, 44, e411-e414.
[5] Badday, A. S.; Abdullah, A. Z.; Lee, K. T.; Khayoon, M. S.; 2012, Intensification of biodiesel production via ultrasonic-assisted process: A critical review on fundamentals and recent development, *Renewable and Sustainable*, 16, pp. 4574-4587.