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Enhancing Biodiesel Production from Soybean Oil using Ultrasonics

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Abstract. *The objective of the study was to determine the effect of high-powered ultrasonics on enhancing biodiesel production from soybean oil. In this study, soybean oil was mixed with methanol and sodium hydroxide and was sonicated at 3 amplitude levels of the ultrasonic ($60\mu\text{m}_{pp}$, $120\mu\text{m}_{pp}$ and $180\mu\text{m}_{pp}$) in a pulse mode (5 seconds on/25 seconds off). The results were compared to a control group where the same reactant composition was allowed to react at 60°C for intervals ranging from 5 minutes to 1 hour with no ultrasonic treatment. It was observed that ultrasonic treatment resulted in a 96% yield (percent conversion to biodiesel) in less than approximately 90 s; compared to 5 to 10 minutes for the control sample. The highest yield was obtained from sonicating the mixture at $120\mu\text{m}_{pp}$ amplitude.*

Keywords. Soybean oil, ultrasound, sonication, biodiesel, methanol, transesterification, thermogravimetric analysis.

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Introduction

Vegetable oils such as soybean oil have been considered as fuel for diesel engines (Knothe et al., 2005). However, such oils cannot be used directly in standard diesel engines because of their high molecular mass, kinematic viscosity, poor atomization, lubrication problems, and carbon deposits due to incomplete combustion (Hanna and Ma, 1999). These issues can be resolved by: dilution, microemulsification, and pyrolysis (Toda et al., 2005) and transesterification with methanol; the latter approach being used most commonly in industry (Srivastava and Prasad, 2000). Biodiesel, a fatty acid methyl ester (FAMES) is produced by the transesterification of vegetable oils and an alcohol in presence of a suitable catalyst. The triglyceride reacts with three molecules of methanol, to produce three molecules of a fatty acid methyl ester (biodiesel) and a molecule of glycerin (Freedman et al., 1984). The byproducts of this reaction are glycerol and a relatively small amount of soap.

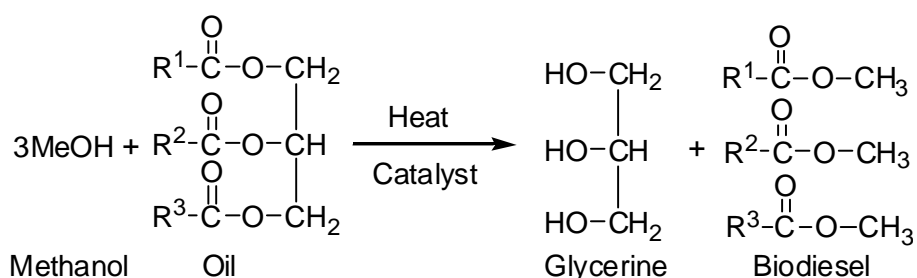


Figure 1. Transesterification reaction of soybean oil with methanol in presence of sodium hydroxide as catalyst produces biodiesel and glycerine.

As mentioned earlier, biodiesel is produced by reacting vegetable oil and an alcohol in the presence of a suitable catalyst. This process also requires continuous mechanical mixing and relatively high temperatures (+60°C). Therefore, biodiesel production plants employ continuous mechanical mixing and heating of reactants, which represents a significant part of the energy consumption by the facilities.

It was observed by Colucci et al. (2005) that the transesterification reaction time can be significantly reduced by irradiating the reactants with ultrasonic sound waves at room temperature. Ultrasonic waves are sound waves that are above normal human hearing range (i.e., above 18-20 kHz). Ultrasonic waves ranging from 20 kHz to 100 kHz are used for industrial purposes, such as welding, cleaning and chemical reactions (Mason and Lorimer 1988).

The effect of ultrasonic waves on liquids has been explained by Suslick (1985). When ultrasonic waves are passed through a mixture of immiscible liquids, such as vegetable oil and alcohol, extremely fine emulsions can be generated. These emulsions have large interfacial contact areas, which provide more reaction sites for the catalytic action and thus increase the rate of reaction. For example, in this work, ultrasonic energy increased the reaction rate several fold, reducing the reaction time from approximately 15 to 30 minutes to few minutes. In addition, ultrasonic treatment of liquids produces streaming (Faraday, M., 1831), which further promotes mixture.

In this work, a novel characterization technique, Thermogravimetric Analysis (TGA), was used to study the reaction rate of biodiesel production based on work by Grewell et al. (2008). TGA is an experimental method for characterizing a system (element, compound or mixture) by measuring the changes in its physico-chemical properties as a function of increasing

temperature. A study of thermal degradation of biodiesel and soybean oil mixtures using TGA shows that weight percentage of biodiesel in a mixture consisting of soybean oil and biodiesel can be easily determined by TGA.

The goal of this work was to obtain a high biodiesel conversion percentage in less time from transesterification of soybean oil with the ultrasonic treatment. Biodiesel was produced by two methods:

- a) By mechanical stirring of the reactants, and
- b) By applying ultrasonics to the reactants.

The biodiesel conversion percentage at various times was recorded for both methods and compared to determine the effect of the ultrasonic energy.

Experimental Procedures

Materials

The materials used in this study were commercially refined soybean oil obtained from Watkins E. Inc. Sodium hydroxide (NaOH), methanol, anhydrous magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and hexanes were all obtained from Fisher Scientific. A Branson 2000 Series bench scale ultrasonics unit with a maximum power output of 2.2 kW and a frequency of 20 kHz was used. The ultrasonic horn used was a 20 kHz catinodial titanium horn with a flat 13 mm diameter face and a gain of 1:8.

Preparation of biodiesel/soybean mixtures from transesterification through mechanical stirring:

Mixtures were prepared by collecting samples from a transesterification reaction mixture at specific times. In the experiments that characterized conventional mixing techniques for biodiesel production, 5 mL of methanol was added to 0.2 g of sodium hydroxide (0.74 M). This mixture was continuously stirred at a temperature of 40 °C for 5 min to form a sodium methoxide/sodium hydroxide equilibrium mixture. This mixture was then added to 20 mL of soybean oil, which requires approximately 3 ml methanol to undergo 100% conversion to biodiesel (1:3 molar ratios); however, excess methanol was supplied to drive the reaction equilibrium to completion and to account for losses during the reaction. The mixture was allowed to react at 60 °C in a shaker water bath with continuous stirring. The reaction was stopped at predetermined times by adding water (50 mL) and hexanes (50 mL) to the reaction mixture. Water stops the reaction and the biodiesel and residual soybean oil are extracted with the hexanes. Additional hexanes (200 mL) were added to dissolve biodiesel and soybean oil. This mixture is allowed to settle for ten minutes in a separatory funnel for clear separation of the two layers. The top layer contains biodiesel, soybean oil and hexanes, while the bottom layer contains glycerol, water, catalyst and soap. The top layer was then separated and anhydrous magnesium sulfate was added to remove trace amounts of water. This mixture was then passed through filter paper to remove the magnesium sulfate and the filtrate was subjected to rotary evaporation to remove the solvent. The remaining sample was then analyzed by TGA for the degree of conversion to biodiesel.

Preparation of biodiesel/soybean mixtures from transesterification through ultrasonics:

For the experiments that characterized ultrasonic treatment of biodiesel production, 10 ml soybean oil was added to sodium methoxide solution prepared by reacting 2.5 ml methanol and 0.1 gm sodium hydroxide. The same method of preparation of sodium methoxide as explained

in the previous section was used. The sample size was scaled to match the available reaction chamber size for the ultrasonic horn (~30 mL). Ultrasonic energy was applied in a pulse mode (5 s on and 25 s off). Thus, the samples were collected at the end of every 30, 60, 90, 120 and 150 second interval. Three amplitude levels of ultrasonic energy were studied: $60\mu\text{m}_{\text{pp}}$, $120\mu\text{m}_{\text{pp}}$ and $180\mu\text{m}_{\text{pp}}$. The reaction was stopped by adding water (50 mL) and hexane (50 mL) immediately after ultrasonic treatment. Mixtures of oil and biodiesel were separated in a similar manner as detailed in the previous section. For accuracy of results, all the experiments in this paragraph were replicated five times.

Analytical methods:

TGA was used to measure the biodiesel and oil contents in the samples. In this experiment, 10 μL samples of biodiesel and oil mixture were heated at a constant heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in an atmosphere of nitrogen. The temperature range was maintained at $25\text{ }^\circ\text{C}$ to $400\text{--}500\text{ }^\circ\text{C}$. The weight loss occurred for biodiesel at approx. $150\text{ }^\circ\text{C}$. The weight loss provides the weight percentage of biodiesel present in the sample. Similarly, weight loss associated with soybean oil occurred at approx. $350\text{ }^\circ\text{C}$ providing the weight percentage of soybean oil in the sample (Grewell et al., 2008). For example, Figure 2 shows the analysis of a sample of biodiesel and soybean oil mixture produced by applying ultrasonics to the reactants at an amplitude of $180\mu\text{m}_{\text{pp}}$ for three pulses where the reaction was stopped at the end of 90 s for biodiesel characterization. From this plot, the weight percentage of biodiesel in the mixture is 90.7%. Similarly, weight percentage of biodiesel is measured for all samples prepared at different conditions of amplitude and time.

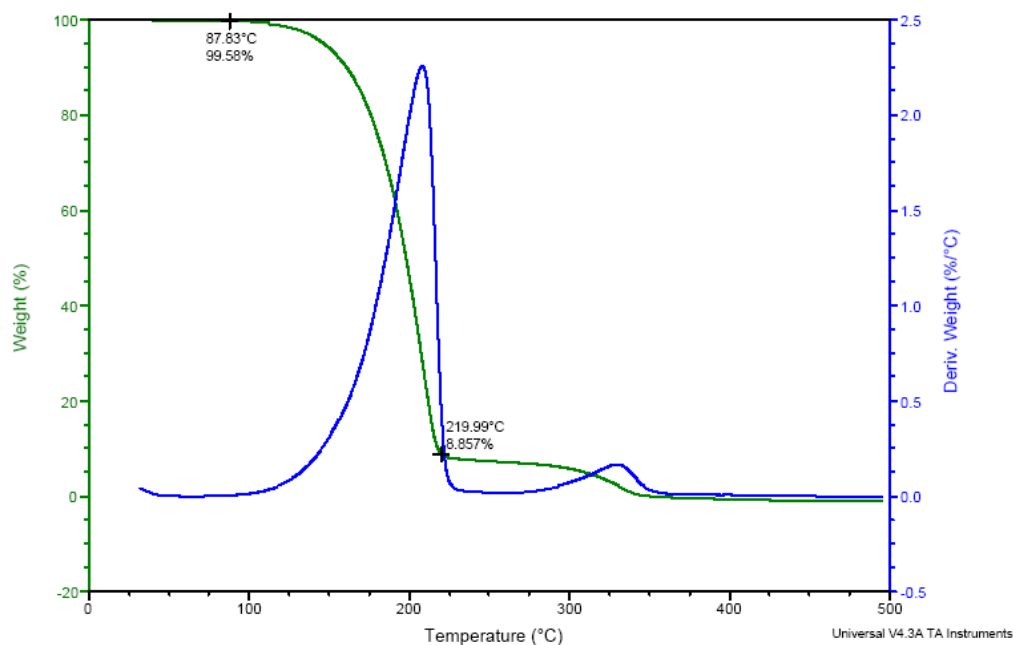


Figure 2. Thermogravimetric curve for a mixture containing biodiesel and soybean oil. This mixture is produced by applying ultrasonics to the reactants in pulse mode and the reaction is stopped at 90 s.

Results and Discussion

As previously mentioned, conventional mixing was used to convert vegetable oil to biodiesel and the recorded rate of conversion was used as a control group. In more detail, transesterification of soybean oil was carried out through a conventional method where the temperature of reactants was maintained at 60 °C and the reaction mixture was continuously stirred throughout the reaction. The results are seen in Figure 3. It is seen that the highest percentage of conversion to biodiesel obtained was 97% and the reaction time was 30 minutes. It is also seen that that a relative high yield (+95%) is achieved in a relatively short time, 5 minutes. The time required to achieve this relatively high yield is shorter (5 minutes) than expected (45 to 60 minutes). This shortened time is believed to be related to the relatively small chamber size and good mixing in the experimental setup.

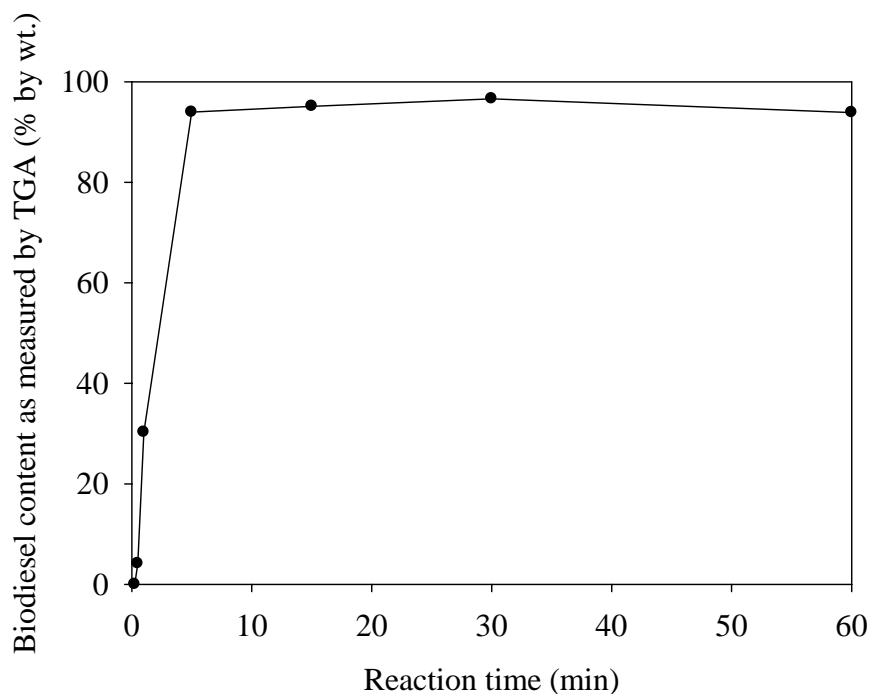


Figure 3. Biodiesel (%) conversion from transesterification of soybean oil through mechanical stirring and determined by TGA analysis.

Figure 4 shows the biodiesel production as a function of esterification time with the ultrasonic treatment. It is seen that relatively high yields (+85%) are achieved within 90 s and yields as high as 96% are produced within 120 s. Compared to the control group (Figure 3), this suggests that the time required to achieve a yield above 95% is reduced from 5 minutes to 1.5 minutes by using ultrasonic treatment. This enhanced reaction kinetic is believed to be related to the emulsions that are generated by the ultrasonic treatment as well as the streaming effects of the ultrasonics. The highest biodiesel conversion yield was obtained when the reactants were sonicated for 150 s in the pulse mode as detailed in Table 1. It is seen that the highest yield was generated with the 120 μm_{pp} amplitude. It is believed that the higher amplitude 180 μm_{pp} (109 W, average power during sonication) promoted degradation of the chemistries and the lower amplitude 60 μm_{pp} (44 W) required longer times than those studied to achieve a higher yield. Thus, the medium amplitude was the optimum value of the amplitudes that were studied. This

observation is also seen in Figure 5 where biodiesel conversion percentage is highest at $120\mu\text{m}_{\text{pp}}$ for all reaction times.

Table 1. Highest biodiesel production for various sonication treatments

| Amplitude (μm) | 60 | 120 | 180 |
|---|----|-----|-----|
| Biodiesel content in the product (% by wt.) | 87 | 96 | 92 |

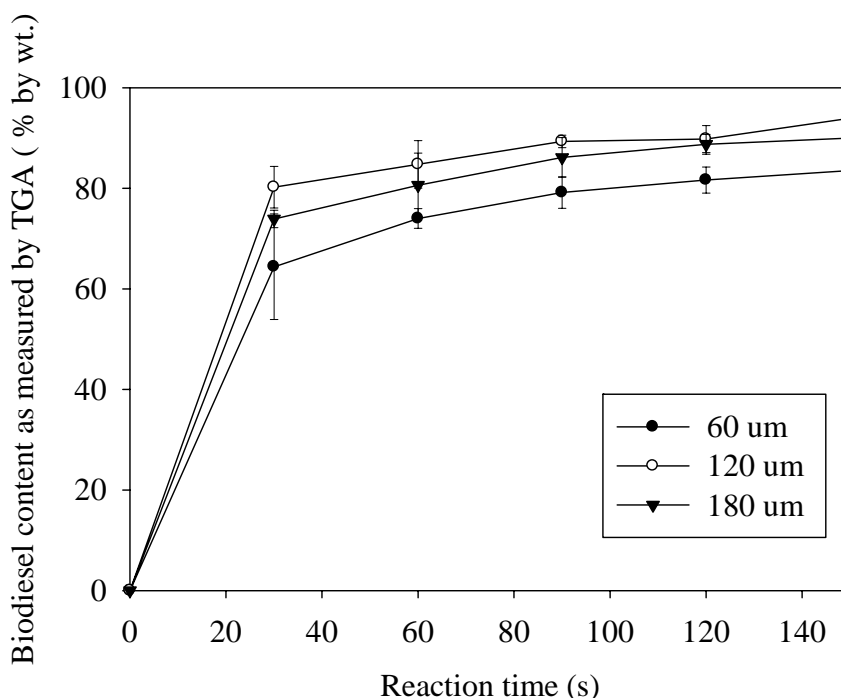


Figure 4. Biodiesel (%) weight conversion from transesterification of soybean oil by applying ultrasonics at three amplitude levels

Conclusion

The time required to achieve a 95% yield was reduced by several fold by ultrasonic treatment in a pulse mode. In more detail, by using standard mixing systems, the time required to achieve 95% biodiesel yield was 5 minutes, while in contrast, this time was reduced to 1.5 minutes when ultrasonic treatment was used.

Further experiments are required to find out the optimum amplitude for highest biodiesel conversion percentage as well as characterize the quality of the biodiesel in terms of consistency, energy content and gel temperature.

Acknowledgements

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