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Monitoring the Transesterification Reaction of Vegetable Oil to Biodiesel by Fluorescence Spectroscopy with UV Excitation: Correlation with Viscosity

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Abstract: The transesterification reaction is the most widely used process for biodiesel production. Monitoring it in real time enables optimization of the operational parameters, hence providing better yields and lowering the costs of biodiesel production. Techniques that have been used for this purpose include chromatography and spectroscopic methodologies. In this work, transesterification reactions were monitored on line, in situ, by fluorescence spectroscopy with ultraviolet excitation at ~360 nm. The temporal behavior of the fluorescence intensity was similar to that of the viscosity of the oil/alcohol/catalyst solution, as reported in the literature. The results indicated that UV-Vis fluorescence spectroscopy could be used on-line, in situ, for the efficient monitoring of biodiesel production, providing a valuable indication of the degree of success of the transesterification reaction.

Keywords: biodiesel; fluorescence spectroscopy; transesterification reaction; viscosity

1. INTRODUCTION

Biodiesel is a promising substitute for mineral diesel. It is comparable to petroleum diesel in terms of practically all its properties and offers several additional advantages over the fossil fuel: It is derived from renewable raw materials (vegetable oils and animal fats); it is biodegradable; its use reduces the emission of exhaust gases; it has a high flash point, which provides safer handling and storage; it has excellent lubricity and a high cetane number, which increases both the lifespan of diesel engines and the power delivered by self-ignition and combustion [1, 2].

It is well known that biodiesel can be produced from a variety of raw materials, usually by means of a transesterification process in which a vegetable oil or an animal fat (a triglyceride, TG) reacts with methyl or ethyl alcohol. This reaction occurs in the presence of a catalyst, which is generally basic, and mainly forms biodiesel (ester) and crude glycerol as a byproduct. Real-time monitoring of the transesterification reaction can assist in optimizing the experimental parameters, improving yields, and lowering the costs of biodiesel production [3-5].

Different chemical and physical analytical techniques can be used to monitor the transesterification of triglycerides, notably near-infrared spectroscopy (NIR) [6, 7], Raman spectroscopy [8], gas chromatography [9], high performance liquid chromatography (HPLC) [10], and viscosimetry [11]. Despite the recognized efficiency of these techniques, a drawback is that they require preparation of the sample for the analysis. Recently, fluorescence spectroscopy with UV excitation was used to monitor biodiesel production [12, 13]. This methodology was also used for on-line and in situ monitoring of the transesterification reaction of soybean oil and ethanol, with excitation at 532 nm [14]. This last study showed the potential of fluorescence spectroscopy as a rapid methodology for monitoring the transesterification reaction, which could be easily coupled to the reactor for control of industrial biodiesel production.

In this work, transesterification reactions were monitored on-line, in situ, using ultraviolet fluorescence spectroscopy, and the results were

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correlated to the temporal variability of the viscosity of the solution during the chemical reaction. The aim of this study was to evaluate the potential of ultraviolet fluorescence spectroscopy for monitoring the industrial process that is currently most widely employed for biodiesel production.

2. MATERIAL AND METHODS

The transesterification reaction was carried out using the ethylic route, with potassium hydroxide (KOH) as the catalyst. KOH (85%, Vetec) was dissolved in absolute ethanol (99.8%, Vetec) and then added to refined soybean oil (Sadia®). The soybean oil used contained linoleic (52.7%), oleic (24.9%), and linolenic (6.1%) acids as the main unsaturated fatty acids. The saturated fatty acids present at highest concentrations were palmitic (10.8%) and stearic (3.6%) acids. The soybean oil had a low water content (~0.05%) and low acid number (0.05%).

The reactions were performed using the same ethanol:oil molar ratio (20:1), at room temperature or with heating the mixture at 60 ºC. The solution was agitated during 20 min, using a magnetic stirrer at 600 rpm. After the transesterification, the mixture was distilled in a rotary evaporator at low pressure to remove the excess ethanol, followed by transferring it to a funnel and keeping it at room temperature for phase separation of the biodiesel and the crude glycerol.

In order to monitor the transesterification reaction, the solution (oil + ethanol with KOH) was excited at approximately 360 nm for 20 min, using an Innova 308C argon laser. A bifurcated optical fiber (Ø = 600 µm) conducted the laser beam to the solution. The power density was < 260 W/m^2 at the tip immersed in the sample solution. The fluorescence signal returned to the optical fiber and was transmitted to a spectrometer (Model HR4000, Ocean Optics) coupled to a computer for signal processing. During the reaction, emission spectra were collected and recorded every 2 s using SpectraSuite software (Ocean Optics), for subsequent analysis. A total of two reactions were monitored at room temperature and six reactions were followed at 60 °C. Further details of the experimental setup can be found elsewhere [14].

3. RESULTS AND DISCUSSION

Fluorescence spectra of the soybean oil, biodiesel, and crude glycerol were first collected in order to identify the shape and intensity of the emissions for the fractions present in the reaction mixture. The fluorescence spectra obtained with excitation at 360 nm are plotted in Figure 1. The spectral curves for soybean oil and biodiesel were similar and broad, covering the visible spectral region and with maximum at 500 nm. Acids, β-carotenes, and α-tocopherols present in the oil were responsible for these emissions [15-17]. The difference between the emission intensities for soybean oil and biodiesel was mainly due to their different viscosities [14], since the absorption coefficients at around 360 nm were similar for the two samples [18, 19]. Thin lines at around 360 nm corresponded to the elastic laser light scattering, and the emission at approximately 670 nm was due to chlorophyll [15]. The fluorescence signal for the crude glycerol was very small, compared to the signals for soybean oil and biodiesel, indicating that with UV excitation, the emission of the byproduct could be ignored. This finding was exactly opposite to results reported recently by our group, where the fluorescence signal for crude glycerol excited with visible irradiation (at 532 nm) was very intense and exceeded the intensities of the soybean oil and biodiesel emissions [18]. In that case, the crude glycerol emission signal was used for monitoring the biodiesel production.

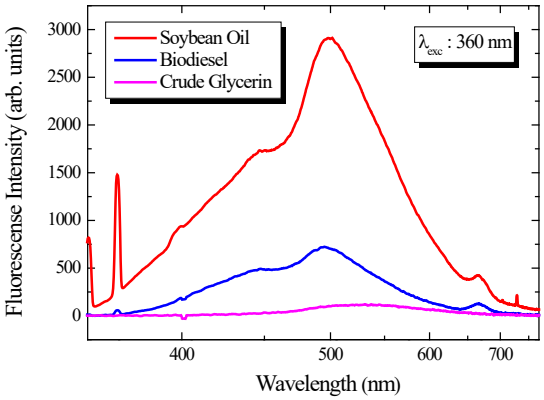

Figure 1. Fluorescence spectra for soybean oil, biodiesel, and crude glycerol, obtained with excitation at 360 nm.

An important phenomenon observed during the experimental procedure for the determination shown in Figure 1 was a temperature dependence of the fluorescence intensity. Although the spectra were collected at room temperature, the absorbed energy converted into heat by the samples caused the signal intensity to decrease within a short time interval, exactly corresponding to the time required for thermal

stabilization. This effect was recently reported by Michels et al. [20]. In order to avoid this phenomenon during the transesterification reaction, the laser power was reduced substantially.

Figure 2 shows the fluorescence spectra obtained during reaction at 60 °C, as a function of time, for the first 1.5 min. The fluorescence intensity decreased rapidly during this period, which was indicative of changes in the physical, chemical, and optical parameters, including viscosity.

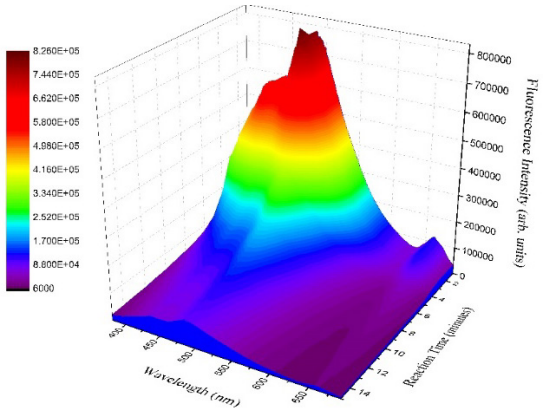

Figure 2. Evolution of the transesterification reaction during the first 1.5 min, as monitored by fluorescence spectroscopy with excitation at 360 nm.

The soybean oil and biodiesel spectra showed two positions of maximum emission intensity, at 439 and 490 nm. Several factors could have influenced the intensity of fluorescence of the solution during the reaction, including the temperature. Thermal equilibrium was difficult to observe during the transesterification reaction, with the emission intensities oscillating during the procedure. In order to evaluate the variation of the intensities at 439 and 490 nm (I_{439nm} and I_{490nm}, respectively) during the reaction, and to minimize or exclude the contribution of temperature variation to the observed fluorescence signals, the following relative intensity was used:

(1)

Two transesterification reactions were monitored at room temperature. The relative intensity profile for one of them, obtained using Equation 1, is shown in Figure 3. The behavior was very similar for the second reaction. A very fast decrease in the signal was observed during the first few minutes, as discussed above, followed by a slight increase up to 10 min of reaction. After this time, the relative intensity signal became almost constant, indicating that there were no more significant changes in the reaction. The apparent gap in the data that can be seen in Figure 3 during the first minutes of the reaction was an indication that the reaction was slowly reaching thermodynamic equilibrium.

Figure 4 shows the relative intensity curves obtained when the mixtures were heated at 60 ºC. Biodiesel production, with phase separation of the biodiesel and the crude glycerol, was only observed in one of the reactions. The behavior observed for the reaction without ester formation was unexpected, with a continuous increase of the signal, as a function of time, following an initial rapid decrease. In contrast, the reaction with ester formation showed an almost constant signal, following the rapid decrease during the first few minutes. The difference between this curve and the curve shown in Figure 3 could be explained by the greater ester production at higher temperature. A further four reactions were performed under the same conditions, with results very similar to those shown in Figure 4 for the process with biodiesel production.

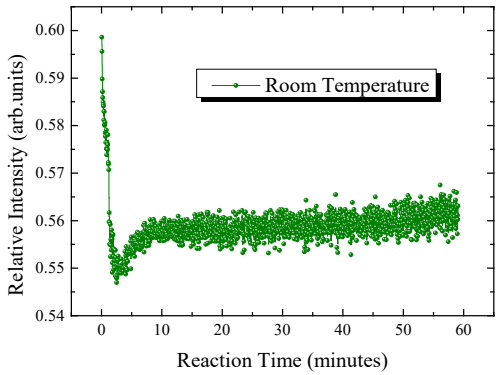

Figure 3. Normalized fluorescence signal (obtained using Equation 1), as a function of transesterification time, for reaction at room temperature.

A possible explanation for an absence of biodiesel production is that the ultraviolet radiation could have affected the properties of the compounds in the mixture. Michels et al. recently reported that UV radiation is a highly critical parameter for monitoring the biodiesel fluorescence signal [20], with the potential to cause thermal degradation (due to the temperature) and photodegradation (due to the excitation beam). This could result in oxidation of the oil and biodiesel, following conversion of the energy absorbed in the solution into heat, hence increasing the temperature of the mixture [21]. The results indicated that if low UV intensity is used during the reaction, ultraviolet fluorescence spectroscopy can be used to evaluate the success of the transesterification,

mainly because the spectra obtained in the cases with or without ester production were markedly different.

It is important to note that continuous monitoring of the viscosity, as it decreased to a plateau in the viscosity curve, revealed the progress of the reaction as it reached its end-point [14]. In the same way as the fluorescence signal, the experimental viscosity data indicated that an unsuccessful transesterification reaction would also show a different trend.

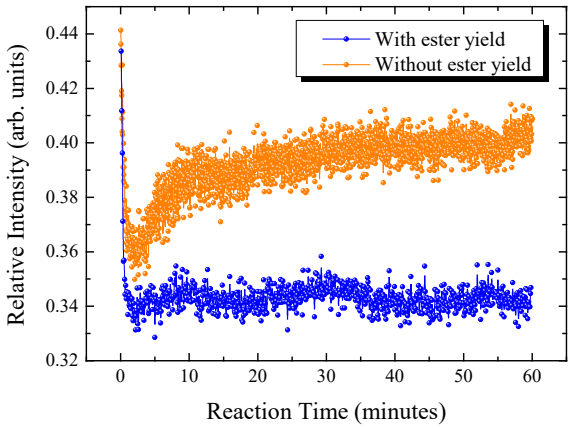

Figure 4. Normalized fluorescence signal of the solution (obtained using Equation 1), as a function of the transesterification time. The reactions with and without ester production were performed at 60 °C.

4. CONCLUSIONS

The findings of this work demonstrate that visible fluorescence spectroscopy with UV excitation can be useful for on-line, in situ, monitoring of the transesterification reaction. This methodology can indicate the point at which the reaction is completed, although the radiation intensity needs to be as low as possible, in order to avoid degradation of the oil and biodiesel.

5. ACKNOWLEDGMENTS

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