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THE PRODUCTION OF BIODIESEL MONITORED WITH REAL-TIME LASER SPECTROSCOPY . CONFIRMATION OF THE TECHNIQUE WITH PROTON NUCLEAR MAGNETIC RESONANCE.

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ABSTRACT

Biodiesel is a synthetic fuel usually produced by the transesterification reaction. This study was undertaken in order to monitor the kinetics of the transesterification reaction between soybean oil and methanol catalyzed by KOH and determine when the reaction reached chemical equilibrium. A series of reactions was monitored with a laser spectrometer used to analyze the absorption and scattering of light in real time. The monitoring system combined the information received thorough multiple sensors. The correlation of the present technique with ^1H NMR spectra confirmed that the reaction was approaching chemical equilibrium when the monitoring curve showed asymptotic behavior.

KEY WORDS: Biodiesel, Laser Measurements, ^{1}H NMR, Chemical Kinetics, Optical Activity of Chemical Reaction, Multiple Sensors

RESUMO

O biodiesel é um combustível sintético, geralmente produzido através da reação de transesterificção, Este trabalho foi desenvolvido para monitorar a cinética da reação de transesterficação entre oléo de soja e metanol, catalisada por KOH e determinar quando a reação atingiu equilíbrio químico. Uma série de reações foi monitorada com um espectrômetro laser utilizado para analisar a absorção e espalhamento da luz em tempo-real O sistema de monitoramento combinou a informação recebida através de vários sensores. A correlação desta técnica com espetroscopia de RMN de ^1H confirmou que a reação estava se aproximando do equilíbrio químico quando a curva de monitoramento exibia comportamento assintótico.

PALAVRAS CHAVE: Biodiesel, Medidas com Laser, RMN de 1H, Cinética Química, Atividade Ótica de Reações, Vários Sensores

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INTRODUCTION

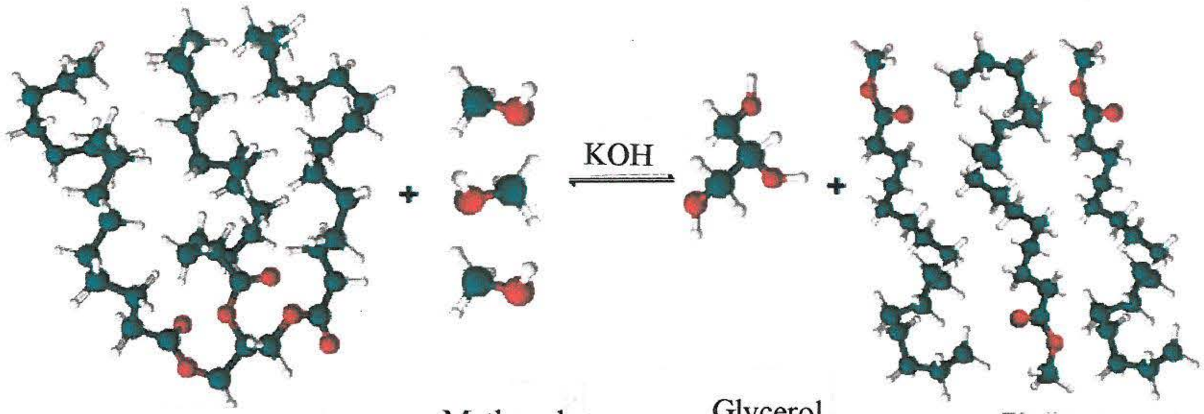
The production of synthetic combustion fuels from biomass is the focus of a large number of research groups in Brazil and the world. Biodiesel is usually produced by the esterification reaction of free fatty acids or the transesterification reaction of triglycerides (1-15).

. This study was undertaken to monitor the kinetics of the transesterification reaction between soybean oil and methanol catalyzed by KOH and determine when the reaction reached equilibrium. The reaction under consideration is given in Figure 1. A triglyceride (TG) reacts with methanol in the presence of KOH to give the corresponding esters (biodiesel,BD) and glycerol. The detailed mechanism of the transesterification reaction is given in Figure 2.

The improvement and the efficient use of energy for the production of biofuels is of paramount importance since it avoids unnecessary energy input in the reaction and consequently contributes to reduce a nation's dependence on external sources of energy.

The principal aim of this study was to monitor the transesterification reaction by laser spectroscopy, determine when it reached equilibrium and avoid unnecessary energy use for the reaction, improve reaction time, reduce energy intake, reduce the generation of secondary products and residues and increase the profitability of the process.

A series of reactions was monitored with a laser spectrometer used to analyze the absorption and scattering of light in real time. The monitoring system combined the information received through multiple sensors. A correlation was performed between the experimental results obtained by laser spectroscopy and proton nuclear magnetic resonance (6-10).



$$TG + 3CH_3OH \leftrightarrows C_3H_8O_3 + BD$$

Figure 1. The Transesterification Reaction Leading to Biodiesel.

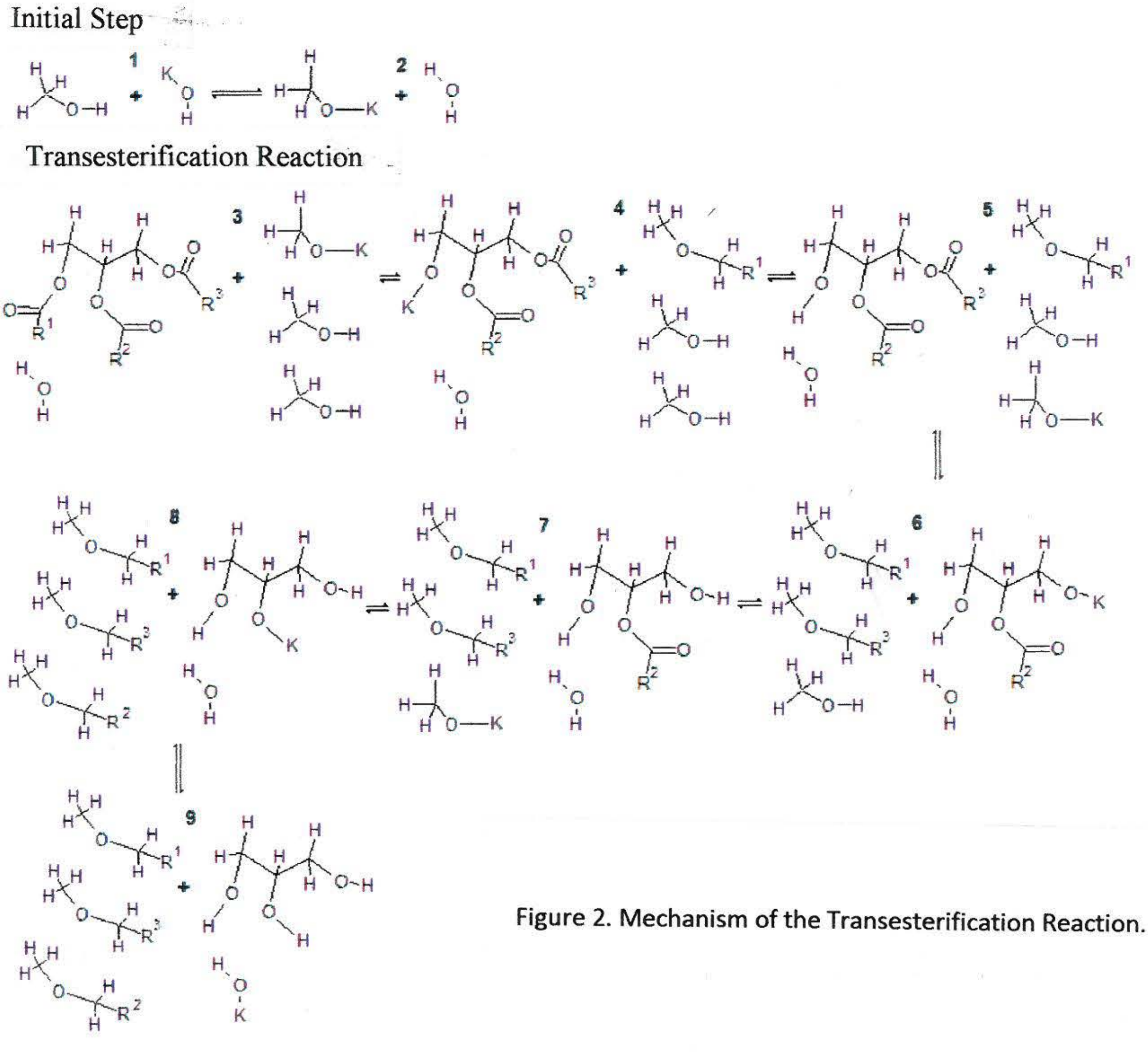


Figure 2. Mechanism of the Transesterification Reaction.

MATERIALS AND METHODS

The experimental technique has been described in detail in the literature (1-15).

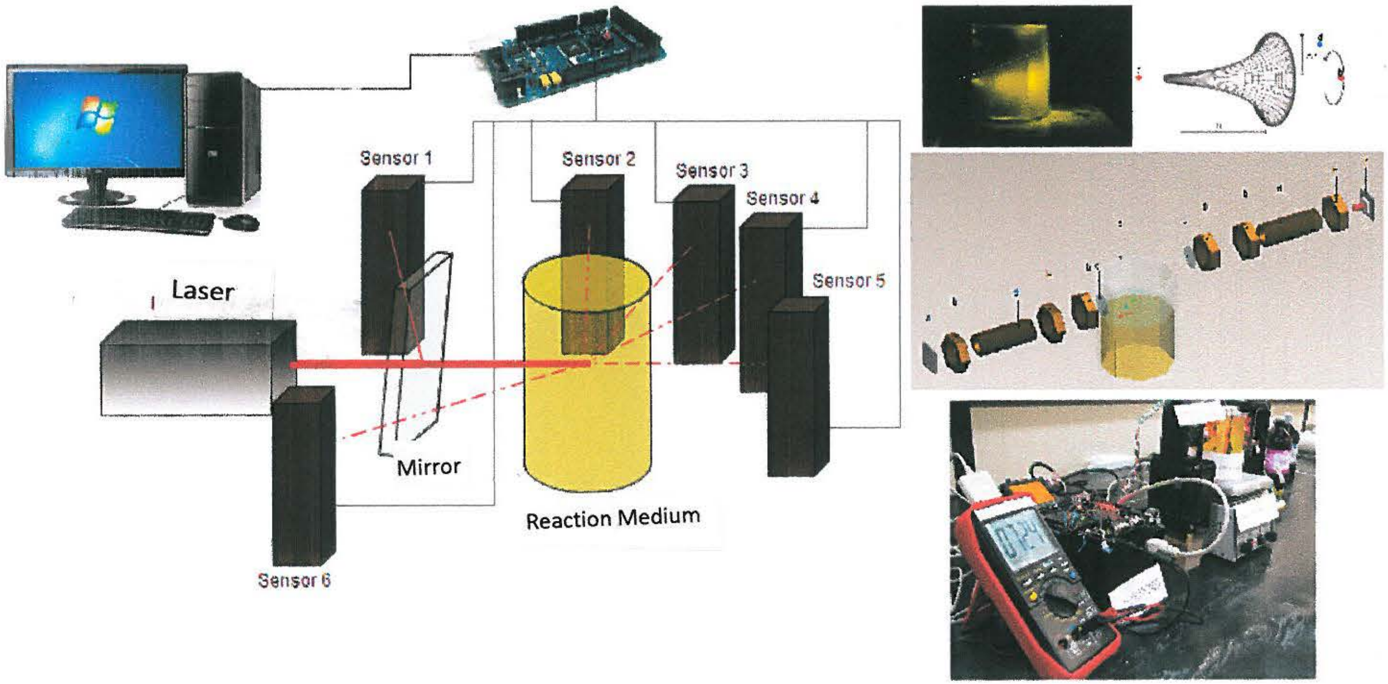
The transesterification reaction was performed at 60 C using a stoichiometric molar ratio of soybean oil/methanol of 3:1 and 1% KOH was used as catalyst. The methanol (pure commercial grade) and potassium hydroxide of 85% purity were obtained from Nuclear. The soybean oil was purchased from a local supermarket. The reaction was monitored for 2 hours and samples were taken every second.

The monitoring technique was computer assisted. An illustration of the experimental equipment is shown in Figure 3. It consisted of an optronic sensor that was inserted into the reaction medium and was able to measure the change of light as a function of the reaction development. As the reaction tended to chemical equilibrium, the change in the light captured by the sensors became nearly constant. At this time interval it was possible to arbitrate that the reaction reached chemical equilibrium. This made possible the separation of glycerin from the biodiesel and the continuation of the fuel refining operations(1-5).

The results obtained by laser spectroscopy at 650 nm in real time were correlated directly to data obtained by 1H nuclear magnetic resonance using a method similar to that described by Knothe (10). Specifically, the results obtained by laser spectroscopy were correlated and compared to results of samples collected during the reaction and analyzed by nuclear magnetic resonance, NMR.

RESULTS AND DISCUSSION

Typical experimental results obtained for the transesterification reaction by laser spectroscopy and 1H nuclear magnetic resonance are summarized and illustrated in Figures 4-10.



The prototype includes or shows

- Real-time monitoring of the reaction.
- Easy interpretation of the graphical interface.
- Improves of the reaction time.
- Reduction of the energy intake.
- Reduction of the generation of co-products and waste .
- Raises the profitability of the process.

Figure 3. Illustration of the Experimental Equipment.

Figure 4 shows the transesterification reaction being monitored by laser spectroscopy and points of extraction of samples for NMR studies. Time is given in seconds.

Figure 5 illustrates a correlation of the transesterification reaction with 1H nuclear magnetic resonance.

Figures 6-10 show 1H NMR spectra obtained by monitoring the system before, during and after the transesterification reaction.

Figure 6 illustrates a typical NMR spectrum obtained for soybean oil before the reaction begins.

Figure 7 shows the progress of the transesterification reaction for a sample collected at the peak of the curve monitored by laser spectroscopy.

Figure 8 illustrates the NMR spectrum at a point that is near the equilibrium of the reaction.

Figure 9 shows the 1H nuclear magnetic resonance spectrum of the system 15 minutes after decantation.

Finally, Figure 10 shows the NMR spectrum obtained for a sample of biodiesel that was refined with water.

The areas under the NMR spectral curves were calculated using MestReNova software (v.6.0.2-5475).

Subsequently, they were analyzed with Equation (I), proposed by Knothe (10) and given below.

$$C_{ME} = 100 \cdot \frac{5 \cdot I_{ME}}{5 \cdot I_{ME} + 9 \cdot I_{TAG}} \qquad \text{Equation (I)}$$

where CME= Percent (%) conversion of soybean oil into biodiesel

IME= Value of the integration of the methyl ester peak

ITAG= Value of the integration of the glyceride peaks in the triglycerides

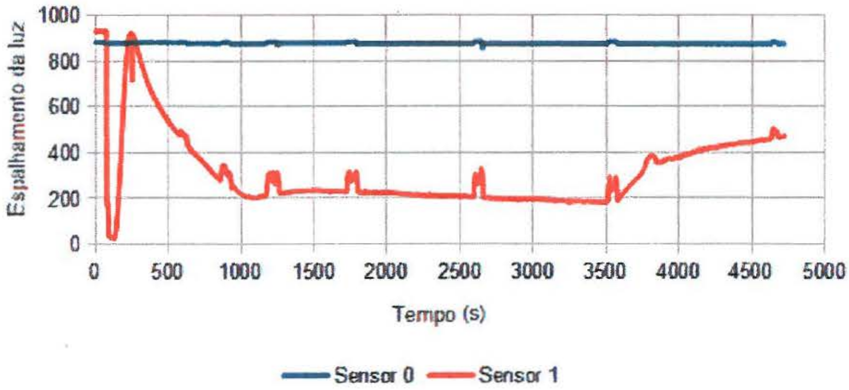


Figure 4. Transesterification Reaction Monitored by Absorption Spectroscopy and Extraction of Samples for Correlation with 1H NMR.

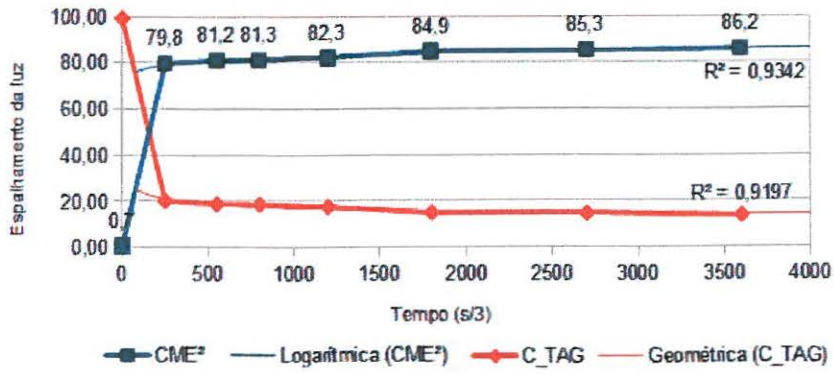


Figure 5 . Correlation of Transesterification Reaction with 1H NMR.

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SOUTH. BRAZ. J. CHEM., Vol.21, No.21, 2013

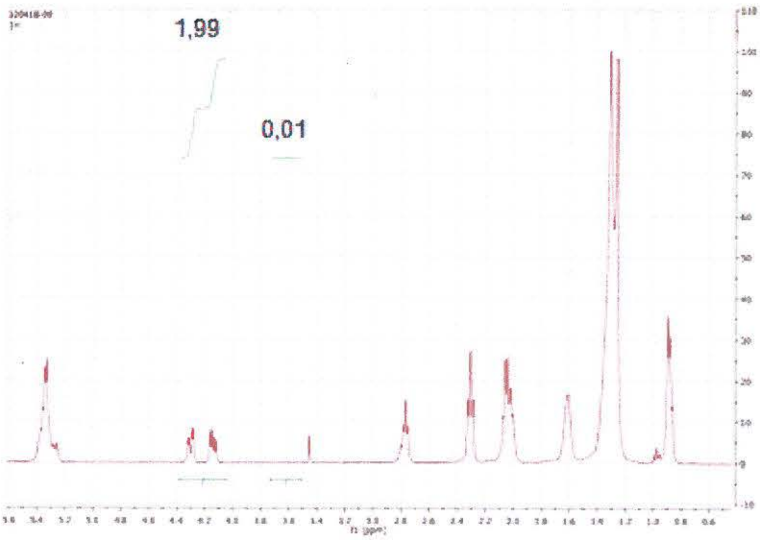

Figure 6. NMR Spectrum of Soybean Oil.

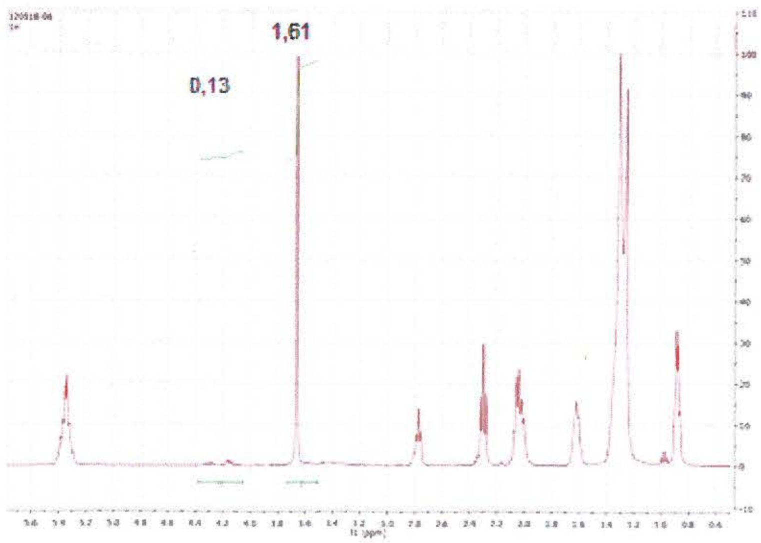

Figure 7. Normalized NMR Spectrum of Sample Collected at the Peak of the Monitoring Curve.

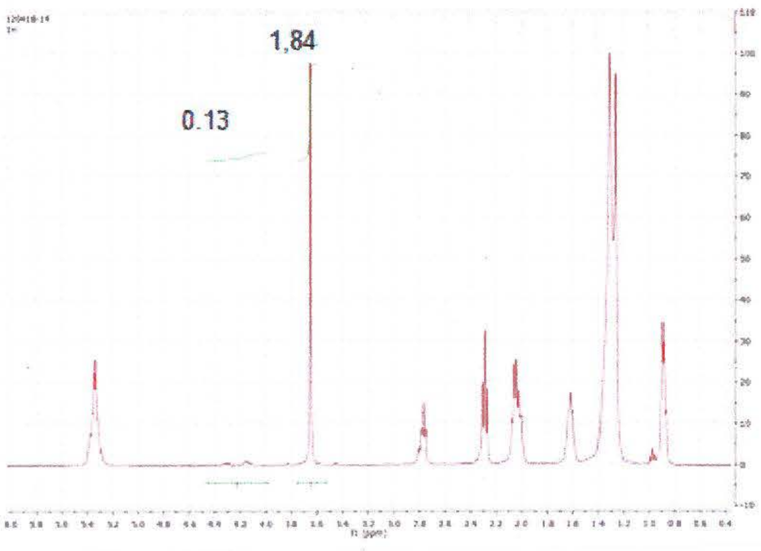

Figure 8. Normalized NMR Spectrum of a Sample Near Equilibrium.

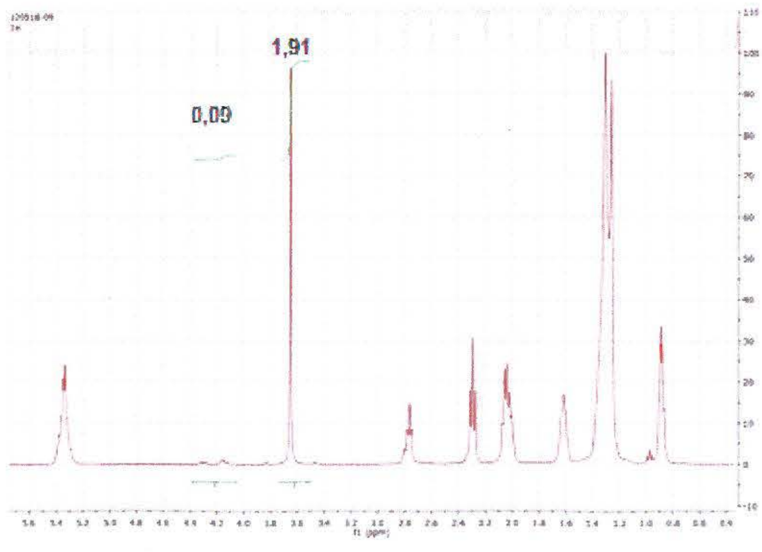

Figure 9. Normalized NMR Spectrum of Sample Collected 15 Minutes after Decantation.

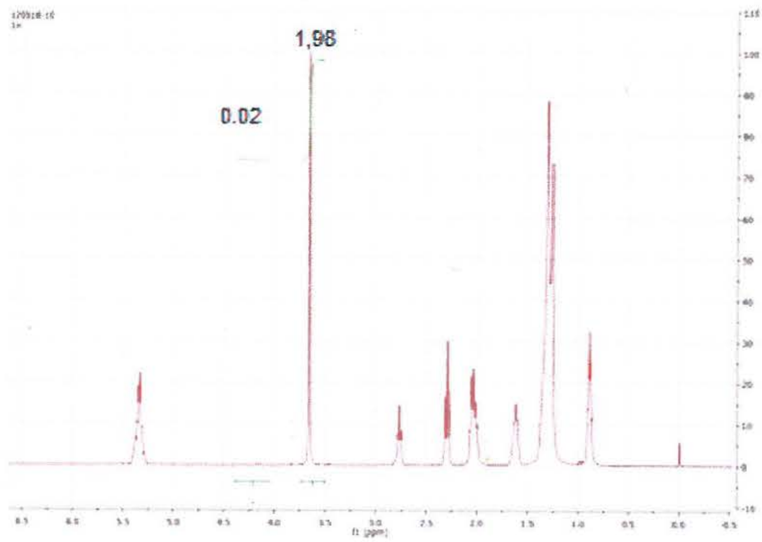

Figure 10. Normalized NMR Spectrum of a Biodiesel Sample Refined with Water.

The results correlated the conversion of monoalkyl glycerides to monoalkyl esters.

The correlation of the results obtained in real-time by laser spectroscopy with those obtained by 1H nuclear magnetic resonance provides evidence for the fact that the reaction reached equilibrium when the monitoring curve for the transesterification reaction began to exhibit asymptotic behavior. According to the data presented in Figure 5, the reaction reached 80% conversion during the initial first 10 minutes. An additional 50 minutes of reaction time increased the conversion only about 6%.

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