

Evaluation of the Oxidation Degradation Process of Biodiesel via ¹H NMR Spectroscopy

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Biodiesel is a suitable alternative to replace the petro-diesel. The biodiesel is formed by unsaturated esters easily degraded by interferences of oxygen, temperature, contact with metals or contaminants. The aim of this research was to investigate the biodiesel degradation process via ¹H nuclear magnetic resonance (NMR) spectroscopy, observing the olefinic, bis-allylic and allylic protons signals of the chemical bonds, and by the induction period of the Rancimat. Biodiesel samples with metallic ions (Fe and Cu) and with rosemary natural extract were analyzed. The metal compounds showed a catalytic effect in the samples and the rosemary natural extract showed to be efficient by retarding the degradation process. The extract was ineffective in the presence of iron. Through the ¹H NMR spectra was possible to observe changes in the signal intensities of the olefinic, bis-allylic and allylic protons as well as the formation of oxidation products in the biodiesel in the degradation process.

Keywords: NMR, biodiesel, degradation, oxidation, spectroscopy

Introduction

Petroleum and its derivatives are used as the main energy source, present in many products as gasoline, diesel oil, LPG (liquefied petroleum gas), coal, etc. The massive use of these products causes several environmental problems such as the intensification of the greenhouse effect. Thus, these factors created the concern about finding different energy sources, in order to be cleaner and less polluting. In this context the biodiesel appeared, a biofuel said as renewable.¹

The biodiesel can be produced from oil plants as soybean and corn, from animal fats, or even from oil recycling (cooking oil). In the world, most of the biodiesel are obtained from vegetable oils.² The amount of unsaturated free fatty acids in its composition is related to the raw material used, directly associated in its susceptibility to degradative oxidative processes. There is also the possibility of the formation of decomposition products as: acids, aldehydes, esters, ketones, peroxides and alcohols.³

In the degradation can occur the formation of gums that can clog the injection systems. Also, the hydroperoxides presence with high levels of acids from the oxidation can generate corrosion in the fuel system.⁴ When the biodiesel is oxidized its performance can be increased in the engine, but its consumption also increases due to an increase in the viscosity, oxygen content as well as cetane numbers leading to an increase in the emission of NO_x compounds. In addition, the acid value of the biodiesel increases due to the formation of react aldehydes causing absorption of water, causing hydrolysis and consequently to an increase in the acidity. Furthermore, the biodiesel viscosity can increase during oxidation leading the formation of long chain saturated compounds, gums, polymers, etc., directly related to problems in the operation engines.^{1,4-8}

Several factors can influence in the biodiesel stability and degradation. Degradation of biodiesel during long-term storage can occur by oxidation in contact with air, thermal or thermal-oxidative decomposition, ultraviolet radiation, by hydrolysis in contact with water, microbiological contamination by migration of dust particles or contamination by ions metallic. Metallic

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contaminants can be derived from various sources, such as the storage or transport container, where contamination occurs by direct contact with the surface of the container, or by the presence of sediment.^{4,7-11}

The contact with the air and oxygen causes the formation of coproducts. Besides that, the presence of metallic ions can also act as catalysts of the oxidation. The fuel storage tanks are one of the main sources of contamination with these metals. Some studies already reported this influence of metals in the biodiesel degradation.¹²⁻¹⁴ Jain *et al.*¹⁵ found that the Cu has a stronger catalytic effect in biodiesel, followed by Co, Mn, Ni and Fe. Chendynski *et al.*¹⁶ studied different alloys as silver steel, carbon steel, copper, reporting that the presence of copper has a stronger degradation influence in biodiesel when compared to others metallic ions.

Due to the great difficulty in avoiding the oxidation of biodiesel, several studies have been carried out to prevent it, aiming to minimize factors that can initiate the degradation reaction by delaying the process. The most used antioxidants in the industrial environment are the synthetic such as: *tert*-butylhydroquinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), propylgallate (PG), and pyrogallol (PY).¹⁷ Besides to synthetic antioxidants, there are antioxidants from organic sources as plants. These natural antioxidants have the advantage of being inexpensive and non-toxic.¹⁸ In the literature there are different papers reporting the antioxidant properties and efficiency of different plants as rosemary,¹⁹⁻²¹ blackberry,^{5,22} senna leaves,²³ hibiscus,^{23,24} oregano,²⁵ basil,²⁵ curcumin,²⁶ β-carotene,²⁶⁻²⁸ etc.

¹H NMR (proton nuclear magnetic resonance) spectroscopy has been used along with standard analysis to analyze oils and its compositions regarded to acylglycerols, fatty acid alkyl esters (FAAEs), its byproducts.²⁹ Martínez-Yusta *et al.*³ studied the sunflower oil degradation process with accelerated storage. Howell *et al.*³⁰ investigated the steps of the castor oil degradation. Recently, the technique was applied to study the transesterification process of the biodiesel production, monitoring the reaction products as fatty acid methyl esters (FAME), triglycerides (TG), monoglycerides (MG) and diglycerides (DG),³¹ but researches using the NMR to study biodiesel degradation are not common.

The presence of olefinic, allylic and bis-allylic compounds in a sample can be related to its degradation process. It is known that the allylic compounds are primary oxidation products, unstable and form a variety of secondary oxidation products in an easy way.³² The rate of the oxidation process of unsaturated fatty acids can be related to the number of bis-allylic carbons present in

the biofuel.³² Also, olefinic compounds are related to the amount of unsaturated esters present in the raw material.³³

The aim of the present research was to investigate the presence of olefinic, allylic, bis-allylic protons in commercial biodiesel, with metallic ions-iron and copper and rosemary natural extract, via ¹H NMR spectroscopy and by the oxidative stability method (Rancimat), during the biodiesel oxidation process.

Experimental

Samples

For the analysis, it was used a commercial biodiesel (B100) provided by a local company in Brazil. The biodiesel was within the specifications established by the international legislation EN 14112.³⁴

Preparation of the rosemary (*Rosmarinus officinalis*) alcoholic extract

The alcoholic extract of rosemary (*Rosmarinus officinalis*) was produced using 10 g of dry rosemary leaves, according to the methodology established by Romagnoli *et al.*²³ The use of this extract was determined based on previous results and literature.^{19,20,35} Ten grams of rosemary leaves were added to 250 mL of ethanol (99.5%, Anidrol PA, Diadema, Brazil) and mixed with a glass stick. The mixture was kept for 48 h and the extracts were filtered. The filtrate was evaporated with a heating plate at 60 °C to obtain about 50 mL. The aliquot was transferred to a 50 mL volumetric flask and completed with absolute ethanol.

Samples preparation

Six different samples were prepared: control (B100) (B.C), B100 + extract (B.E), B100 + Cu (B.Cu), B100 + Cu + extract (B.Cu.E), B100 + Fe (B.Fe), B100 + Fe + extract (B.Fe.E). The metallic ions, Fe (FeCl₃·6H₂O, Synth, Diadema, Brazil, 99.5%) and Cu (CuCl₂·2H₂O, Vetec, Rio de Janeiro, Brazil, 99.0%), were added in a concentration of 1 × 10⁻⁴ mol L⁻¹ (27.3 and 17.0 mg L⁻¹, respectively). The rosemary extract was added in a concentration of 2% (v/v), and mixed until homogenized, according to Romagnoli *et al.*²³ The metallic ions amount was determined by preliminary assays so the concentrations do not imply in a too fast or too long degradation, since even in small amounts (ca. 1 mg L⁻¹) the metallic ions can already catalyze the reaction.³⁶ In addition, copper ions have a stronger catalytic effect than iron ions.³⁶ The samples were prepared 24 h before the assays.

Determination of the induction period and rate constants

It was performed the accelerated heating method in each sample, at 110 °C, using the Rancimat equipment (Metrohm, model: 873), with air flow of 10 dm³ h⁻¹, following the methodology described in the international standard EN 14122.³⁴ The induction periods were provided by the inflection point of the electric conductivity and time curve generated in the software.

The rate constants (k) for each sample were calculated through the linear fit of the natural logarithm as a function of time of the data obtained in the Rancimat.³⁷

Sample oxidation

Prior to the ¹H NMR experiments, the samples were degraded through the accelerated heating method. In the Rancimat equipment were placed 8 replicates of the same 6 samples. These samples were then subjected to the accelerated heating at 110 °C and withdrew at 8 different time intervals. The last replicate was maintained until the inflexion point of the curve was achieved. Then the samples were put in glass tubes for further NMR analysis. The time intervals for each sample were determined by preliminary tests.

¹H NMR spectroscopy

For the spectra acquisition it was used a high-resolution NMR spectrometer operating at 9.4 T, 400 MHz (Bruker, Karlsruhe, Germany). The samples were prepared by dissolving 50 µL of biodiesel in 600 µL of deuterated chloroform (CDCl₃, 99.8% with 0.05% (v/v) of tetramethylsilane (TMS), Sigma Aldrich, Saint Louis, USA). The parameters applied were: single pulse, spectral width of 8012 Hz, 16 scans, relaxation delay of 1 s, pulse width of 90° and acquisition time of 4.089 s. The chemical shifts are expressed in ppm using as internal standard the TMS.

All spectra were aligned in a zero-order phase and baseline corrections were made for the spectral range from δ -2.00 to 10.00 ppm, using the software TopSpin (3.6.1). The regions integration of the spectra signals corresponding of methylenes α to the carbonyl (2.2-2.4 ppm), olefinic (5.0-5.7 ppm), allylic (1.8-2.2), bis-allylic (2.6-3.0 ppm) protons, was performed using a MATLAB³⁸ routine. The area of methylenes α to the carbonyl (6 protons) present originally in TG molecules was used to normalize the results. The interval values of integration were previous described in literature²⁹ and were used with adaptations in this work.

Results and Discussion

In Table 1 are shown the induction periods (IP) and the rate constants (k) of the samples. It can be observed that the rosemary extract acted as a good natural antioxidant, showing a high IP of 9.61 h and a small k of 0.30, slowing down the radical reaction, when compared to the control. In the other hand, the presence of copper in the biodiesel helped in accelerating the reaction, acting as a catalyst, presenting a small IP of 1.15 h and a high k value of 2.01. The presence of the rosemary extract with Cu showed a little improvement in the IP and k values. However, when analyzing the presence of iron in the biodiesel, with and without the rosemary extract, the degradation reaction had a slight change, indicating that the rosemary extract is not efficient when there is iron in the sample.

Table 1. Values of induction period (IP) and rate constant (k) of the samples analyzed

Sample	IP / h	k / h ⁻¹
B.C	7.01	0.44
B.E	9.61	0.30
B.Cu	1.15	2.01
B.Cu.E	1.38	1.85
B.Fe	1.60	1.71
B.Fe.E	1.68	1.58

B.C: control (B100); B.E: B100 + extract; B.Cu: B100 + Cu; B.Cu.E: B100 + Cu + extract; B.Fe: B100 + Fe; B.Fe.E: B100 + Fe + extract.

It is known that several NMR signals can provide different information about functional groups in fatty acids components, representing good points to analyze the oxidation processes in oils, because these compounds can cause changes in the spectra, modifying some of the functional groups. This way, we focused in this research by analyzing the olefinic, bis-allylic and allylic protons intensities during the oxidation of biodiesel samples. The characteristics chemical shifts are: 5.30-5.43 ppm for the olefinic protons ($-\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}-$), 2.74-2.79 ppm for the bis-allylic protons ($=\text{C}\text{H}-\underline{\text{C}}\text{H}_2-\text{C}\text{H}=\text{C}$) and 1.98-2.04 ppm for the allylic protons ($-\underline{\text{C}}\text{H}_2-\text{C}\text{H}=\text{C}\text{H}-$).^{29,39} The ¹H NMR spectrum of the biodiesel, before being degraded, with the olefinic, bis-allylic and allylic chemical shifts is shown in Figure 1.

The ¹H NMR regions of olefinic, bis-allylic and allylic protons of the spectra obtained for the biodiesel samples with metallic ions and natural rosemary extract are shown in Figure 2. The *i* represents the initial time and *f* the final time for each sample analyzed.

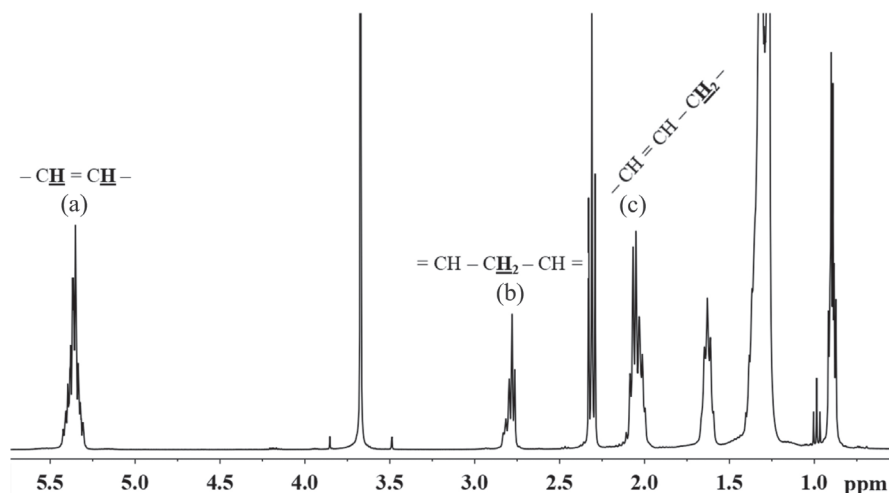


Figure 1. Biodiesel ^1H NMR spectrum (400 MHz, CDCl_3 , room temperature) of the chemical shifts of the olefinic (a), bis-allylic (b) and allylic (c) protons.

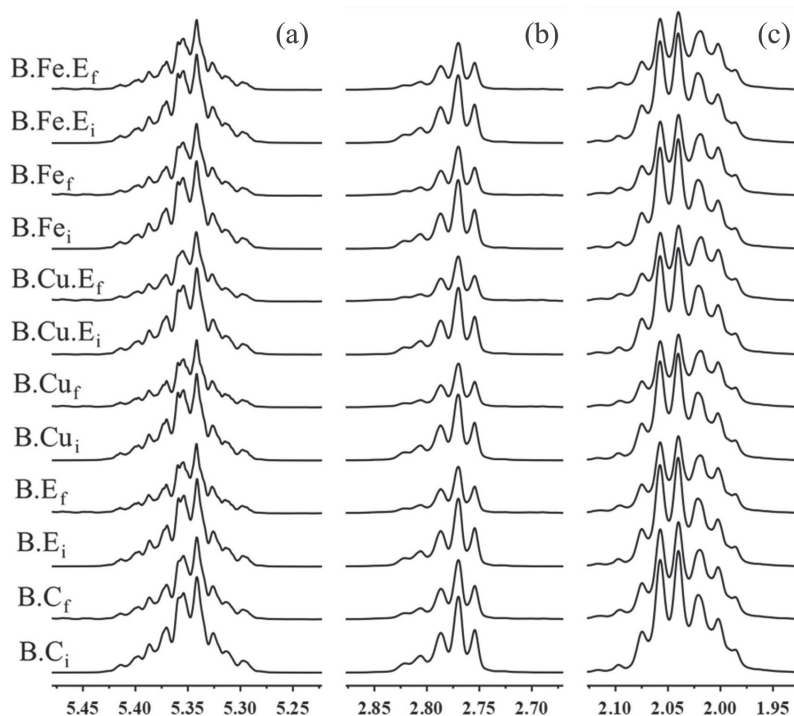


Figure 2. Initial and final signals of the olefinic (a), bis-allylic (b) and allylic (c) protons detected by ^1H NMR (400 MHz, CDCl_3 , room temperature) for B.C (control biodiesel); B.E (biodiesel + extract); B.Cu (biodiesel + Cu); B.Cu.E (biodiesel + Cu + extract); B.Fe (biodiesel + Fe); B.Fe.E (biodiesel + Fe + extract) samples.

Visually the integration regions in Figure 2 did not show a wide variation in the spectral signals for the evaluated assays. For this reason, the integration regions were presented in graphs through the signal intensity as a function of time.

Figure 3 shows the signal intensities variation from the olefinic, bis-allylic and allylic protons of the samples analyzed, throughout the degradation process over time.

It is observed in Figure 3 that the olefinic proton intensity for the B.C sample remains approximately constant until 6 h of analysis, falling from the time close to its induction

period of 7.01 h. For the B.E sample, containing rosemary antioxidant extract, the olefinic intensity signal remained approximately constant until 8 h of analysis, decreasing close to its induction period 9.61 h.

The intensity of olefinic for the copper sample remained constant until approximately 1.5 h, decaying after that. However, the B.Cu.E sample, with higher IP, showed a decrease in its intensity signal since the beginning of the analysis, presenting a higher intensity variation. The B.Fe and B.Fe.E samples showed similar behaviors besides very close IP. Both remained at

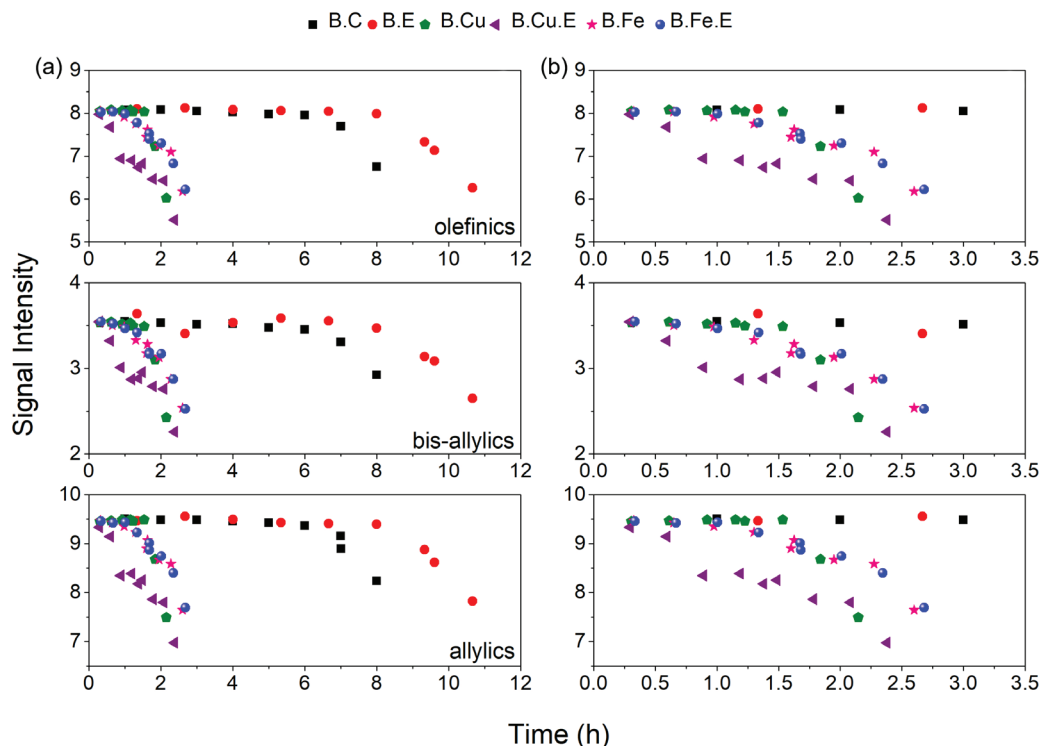


Figure 3. Change in the signal intensities from olefinic, bis-allylic and allylic protons for the samples of B.C, B.E, B.Cu, B.Cu.E, B.Fe and B.Fe.E. Figures 3a show all the data for the 6 samples, and in the right-hand side, Figures 3b show the data with a scale cut at 3.5 h in order to improve the visual graph analysis.

approximately constant intensities up to 1 h of analysis with a subsequently decay, presenting almost the same intensity variation.

Regarding the bis-allylic and allylic intensities (Figure 3), the behavior of all 6 samples are similar to those previously mentioned concerning the olefinic protons, presenting only some differences in the variation of the intensities. In general, it was observed that the samples containing rosemary extract showed greater variations in their intensities. These intensities variation in the 3 groups analyzed indicate that they have a preference in being attacked in the oxidation process.⁴⁰

Tyl *et al.*⁴⁰ studied the change in the fatty acids of fish oils by ¹H NMR spectroscopy. They showed that the signal intensities of the olefinic and bis-allylic protons had a decrease during the oxidation of the samples, and the allylic protons intensity remained constant, without changes. In general, it is known that the probability of lipid oxidation increases with the number of bis-allylic protons present in the oil.⁴¹ However, in the biodiesel samples analyzed in the present work, it was observed a decrease in all olefinic, bis-allylic and allylic proton intensities (Figures 2 and 3). Tyl *et al.*⁴⁰ studied the degradation at 40 °C and in the present work the degradation of the samples was carried out at 110 °C. Thus, in the biodiesel may be occurring the breaking of the three chemical bonding analyzed, forming more secondary products, implying in the intensities decrease.

The olefinic protons are related to the amount of unsaturated esters present in the samples.³³ In all samples the intensity signals of these protons had a decay, showing that the unsaturated esters decreased during the biodiesel degradation. Also, the olefinic fatty acid chains reacts in a preferable way with the molecule of oxygen,¹⁰ confirming the samples degradation. The bis-allylic groups are susceptible to hydrogen abstraction, also have a high probability to peroxidation initiation reaction.⁴² The variation in its intensity also corroborates the biodiesel degradation. The dissociation of C–H bonds at allylic positions is higher than the bis-allylic, being 322 and 272 kJ mol⁻¹, respectively. Thus, the fatty methyl esters with methylene-interrupted double bonds are more susceptible to oxidation than the mono-saturated methyl esters.⁴³

The presence of antioxidant should prevent the oxidation and maintain the fatty acid composition in the samples constant.⁴⁰ This behavior was observed in the sample of B.E (Figure 3), in which the olefinic, bis-allylic and allylic protons intensities remained approximately constant until the 8 h of degradation, indicating the efficiency of the rosemary extract as a natural antioxidant for the biodiesel, agreeing with the data obtained by the Rancimat. As given in the literature, the action of the natural rosemary extract as an antioxidant, retarding the oxidation process, can be due to the presence of phenolic compounds, carnosol, rosmanol, ursolic acid, etc.⁴⁴ The extract compounds can donate

electrons to reactive radicals, becoming less reactive and more stable, preventing them from reaching the molecules, thus retarding the degradation process.⁴⁴

The samples B.Fe and B.Fe.E (Figure 3) did not show substantial changes, indicating the ineffectiveness of the extract in the presence of iron. Chendynski *et al.*⁵ observed a similar behavior when investigated the biodiesel degradation in the presence of natural blackberry extract and silver steel.

The extract did not maintain the methyl ester composition constant, although the Rancimat data indicates a better oxidative stability in this sample. It can be observed that the extract was interfering in the sample at approximately 1 h of degradation by trying to stabilize the decay of the intensities. Thereby is possible to say that in the beginning of the reaction the copper interference in the sample stability was stronger than the extract, and after that the extract started competing by retarding the reaction of the copper.

The formation of the major secondary compounds in the oxidation reaction was also investigated by NMR. Tyl *et al.*⁴⁰ observed the formation of oxidation products propanal and 2-propenal of capelin oil after 30 days of degradation. The propanal has chemical shifts at approximately 9.8 ppm, and the 2-propenal has chemical shifts at 9.5-9.6 ppm and between 6.2 and 6.5 ppm. Martínez-Yusta *et al.*⁴⁵ studied deep-frying food in extra virgin olive oil in order to observe the changes in the concentration of acyl groups, the evolution of the concentration of some compounds formed as the aldehydes, epoxyethyl groups, primary and secondary alcohols. It can be observed that in the beginning of the experiments the samples did not present oxidation products signals, but during the degradation process the signals of $-\text{CHO}((E)\text{-}2\text{-alkenals})$ at 9.49 ppm, $-\text{CHO}((E,E)\text{-}2,4\text{-alkadienals})$ at 9.52 ppm and $-\text{CHO}(\textit{n}\text{-alkanals})$ at 9.75 ppm showed up, indicating the formation of aldehydes, products of the oxidation.

Figure 4 shows the signals of the oxidation products formed in the biodiesel samples during the degradation process. The i represents the initial time and f the final time for each sample analyzed.

In Figure 4 is shown the same oxidation products regions mentioned by Tyl *et al.*⁴⁰ and Martínez-Yusta *et al.*⁴⁵ It can be observed that for all samples in the initial time (i index) no signal is present, except the sample B.Cu.E. When analyzing the final times (f index), i.e., when the samples are degraded, for all the 6 samples, the chemical shifts of the oxidation products are present. This fact confirms the biodiesel degradation.

Thus, there is a correlation between the IP, k and the olefinic, bis-allylic and allylic protons intensities, showing that the IP of each sample is obtained nearby the decay of the samples intensities compounds, and the variation in the

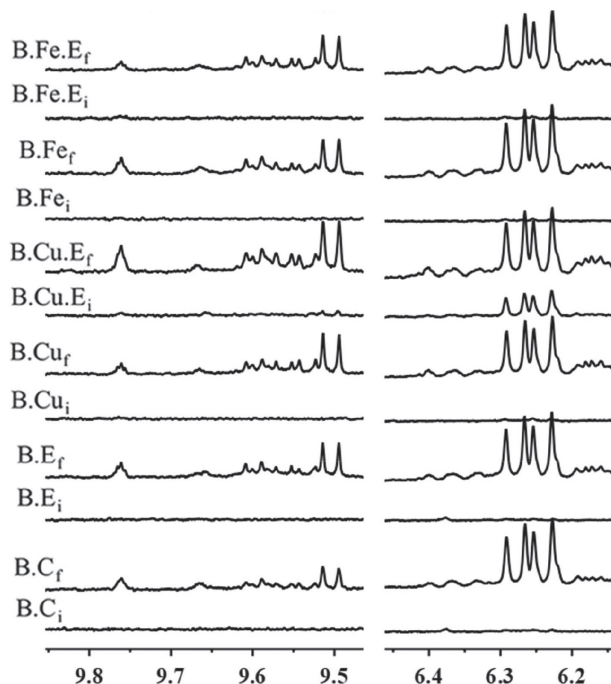


Figure 4. ^1H NMR (400 MHz, CDCl_3 , room temperature) signals of the oxidation products formed in the biodiesel samples with metallic ions and rosemary natural extract during the degradation process.

intensities can indicate the stage of the oxidation process in the samples as well as the formation of oxidation products. Furthermore, the NMR spectroscopy analysis can add relevant information in the understanding of the oxidative reactions in the biodiesel.

Conclusions

The biodiesel samples presented a decrease in the olefinic, bis-allylic and allylic proton intensities as the oxidation reaction progresses. The metallic ions, iron and copper acted as catalysts in the degradation of the samples and the natural rosemary extract showed to be a good natural antioxidant by retarding the degradation of the biodiesel, inhibiting the radical propagation. Rosemary extract was inefficient in improving the oxidative stability of biodiesel in the concentrations of metals used. At lower concentrations, close to 1 mg L^{-1} the extract could have shown more satisfactory results. Furthermore, it was possible to find a correlation between the IP and the intensities decay of the olefinic, bis-allylic and allylic protons. The NMR spectroscopy showed to be efficient by providing relevant information regardless the biodiesel oxidation reaction as the oxidation products formation.

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