

Cashel Nut Shell Liquid (CNSL)-based antioxidant synthesis through electrolysis of hydroquinone

Síntese antioxidante à base de Cashel Nut Shell Liquid (CNSL) através da eletrólise de hidroquinona

Síntesis de antioxidantes a base de Cashel Nut Shell Liquid (CNSL) a través de la electrólisis de hidroquinona

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Abstract

Energy is considered a strategic issue for a country and the proportion of its use has always been directly associated with industrial development. With the discovery of oil at the beginning of the 19th century, the industrialization process was intensified even more, causing an intense modification of the space occupied by man. But the impending shortage, the generation of energy through fossil fuels such as oil, cannot indefinitely supply the energy required by the world's population. In this context, biodiesel emerges as a promising biofuel substitute for fossil fuels derived from oilseeds or animal fats composed of alkyl esters that can totally or partially replace diesel. However, it contains a significant amount of unsaturated fatty acid and is susceptible to heat-mediated oxidative degradation, especially in the presence of oxygen, which can negatively affect the stability of biodiesel. Phenolic compounds submitted to the electrochemical reaction of biodiesel obtained from soybean oil, through the electrolytic reaction, structural changes were sought to improve the technical antioxidant activity of LCN, using methanol and hydroquinone as solvent and as electrolyte. The LCCHQ was the product of this reaction whose antioxidant efficiency as an additive for biodiesel was measured by the "Schaal Oven Storage Stability Test" - accelerated oxidation method and later analyzed by molecular absorption spectroscopy in the UV region (240 to 300 nm) and rancimat. The antioxidant activity results of LCCHQ were satisfactory in retarding the progress of oxidation when compared to CNSL in all technical tests.

Keywords: Antioxidants; Biodiesel; Electrolytic reaction; Hydroquinone.

Resumo

A energia é considerada questão estratégica de um país e a proporção de seu uso sempre esteve diretamente associada ao desenvolvimento industrial. Com a descoberta do petróleo no início do século XIX, foi intensificado ainda mais o processo de industrialização, provocando uma intensa modificação do espaço ocupado pelo homem. Mas a escassez iminente, a geração de energia por meio de combustíveis fósseis, como o petróleo, não pode fornecer indefinidamente a energia exigida pela população mundial. Nesse contexto, o biodiesel surge como um promissor biocombustível substituto para combustíveis fósseis derivados de oleaginosas ou gorduras animais compostas por ésteres alquílicos que podem substituir total ou parcialmente o diesel. No entanto, contém uma quantidade significativa de ácido graxo insaturado, é suscetível à degradação oxidativa mediada pelo calor, principalmente na presença de oxigênio, o que pode afetar negativamente a estabilidade do biodiesel. compostos fenólicos submetidos à reação eletroquímica do biodiesel obtido a partir do óleo de soja, através da reação eletrolítica buscou-se realizar alterações estruturais para melhorar a atividade antioxidante técnica do LCN, utilizando metanol e hidroquinona como solvente e como eletrólito. O LCCHQ foi o produto dessa reação cuja eficiência antioxidante como aditivo para biodiesel foi medida pelo "Schaal Oven Storage Stability Test" - método de oxidação acelerada e posteriormente, analisado por espectroscopia de absorção molecular na região do UV (240 a 300 nm) e método Rancimat. O antioxidante os resultados de atividade do LCCHQ foram satisfatórios em retardar o progresso da oxidação quando comparados ao CNSL em todos os testes técnicos.

Palavras-chave: Antioxidantes; Biodiesel; Reação eletrolítica; Hidroquinona.

Resumen

La energía es considerada un tema estratégico para un país y la proporción de su uso siempre ha estado directamente asociada al desarrollo industrial. Con el descubrimiento del petróleo a principios del siglo XIX, se intensificó aún más el proceso de industrialización, provocando una intensa modificación del espacio ocupado por el hombre. Pero la escasez inminente, la generación de energía a través de combustibles fósiles como el petróleo, no puede suplir indefinidamente la energía requerida por la población mundial. En este contexto, el biodiésel surge como un prometedor biocombustible sustituto de los combustibles fósiles derivados de semillas oleaginosas o grasas animales compuestas por ésteres alquílicos que pueden sustituir total o parcialmente al diésel. Sin embargo, contiene una cantidad significativa de ácidos grasos insaturados y es susceptible a la degradación oxidativa mediada por calor, especialmente en presencia de oxígeno, lo que puede afectar negativamente la estabilidad del biodiesel. compuestos fenólicos sometidos a la reacción electroquímica del biodiesel obtenido a partir del aceite de soja, mediante la reacción electrolítica se buscaron cambios estructurales para mejorar la actividad antioxidante técnica del LCN, utilizando metanol e hidroquinona como solvente y como electrolito. El LCCHQ fue el producto de esta reacción cuya eficiencia antioxidante como aditivo para biodiesel fue medida por el "Schaal Oven Storage Stability Test" - método de oxidación acelerada y posteriormente analizado por espectroscopía de absorción molecular en la región UV (240 a 300 nm) y rancimat. Los resultados de la actividad antioxidante de LCCHQ fueron satisfactorios para retardar el progreso de la oxidación en comparación con CNSL en todas las pruebas técnicas.

Palabras clave: Antioxidantes; Biodiésel; Reacción electrolítica; Hidroquinona.

1. Introduction

Energy is considered a strategic question for the global community and the proportion of its use is directly associated with the development of the peoples. The discovery of energy resources and the development of processes and technologies for employ them are recorded since the early eighteenth century. Initially, the firewood was the source of energy and later, because of the shortage of this product due to the population increase at the time and the growing demand for coal, which resulted in the development of the industry (de Oliveira *et al.*, 2008; Dabdoub *et al.*, 2009). The discovery of petroleum, that happened in beginning of the nineteenth century, combined with the invention of internal combustion engine, and in low cost and high availability of petroleum at that time it became a widely used fuel. A new revolution was introduced in the industrial world and the energy matrix is now based on this non-renewable energy source (Meher *et al.*, 2006).

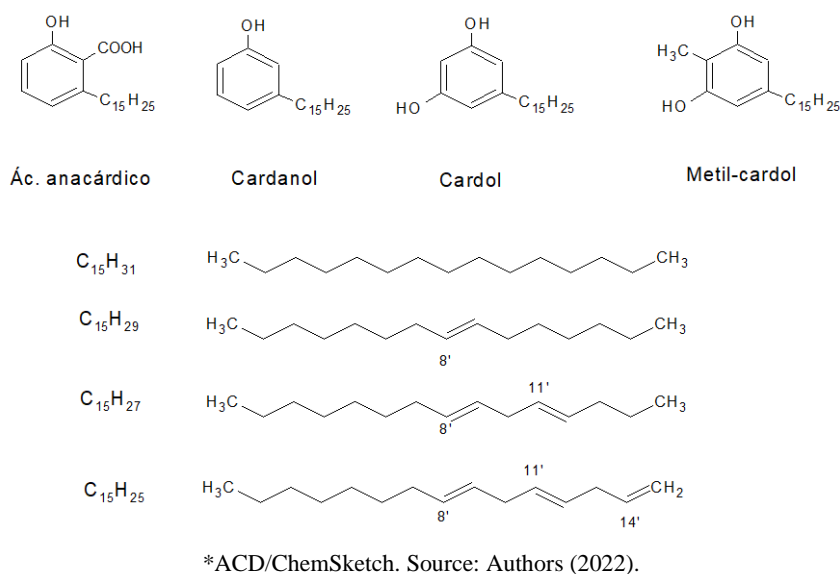
The imminent shortage of mineral oil foreseen for the coming decades, terrorist threats, political instability in the Middle East, rising demand have pushed up petroleum prices in recent years. Thus, the generation of energy based on fossil fuels can not indefinitely provide the energy required by the world's population (Lima *et al.*, 2007; Corma *et al.*, 2005). Moreover, the growing concern about the environment and, in particular, global climate change raises questions about the sustainability of the current pattern of energy consumption (Sharma & Singh, 2009). In recent decades, research on renewable and clean energy source, has been intensified because of rising levels of air pollution caused by improper use of too much

fossil fuels and derivatives (Corma *et al.*, 2005; Sharma & Singh, 2009, Lam *et al.*, 2010). In this context, biodiesel presents itself as an alternative to replace diesel. Biodiesel is the name given to alkyl esters of fatty acids since they meet certain quality standards (Vasudevan & Briggs, 2008; MME, 2008). Traditionally, biodiesel is produced through the transesterification reactions of triglycerides, usually using alkaline catalysts, (Dabdoub *et al.*, 2009; Corma *et al.*, 2005) or the esterification of free fatty acids (FFAs), whereas in the latter case, free fatty acids are submitted to direct reaction with an alcohol of 4 carbons or less, in the presence of acid catalysts. In addition, more recently the use of various heterogeneous catalysts also has been described in the literature (Dabdoub *et al.*, 2009). The use of biodiesel as a fuel is growing rapidly worldwide as the production chain of this fuel has a promising potential in various sectors such as social, environmental and technological (Vasudevan & Briggs, 2008; Vichi & Mansor, 2009; MME, 2008). Environmentally, there will be a significant and quantitative reduction of levels of environmental pollution, considering that the biodiesel is free of sulfur and aromatics, which emits a lower rate of particulates, as HC, CO and CO₂, is not toxic, is biodegradable, and it comes from renewable sources (Mello *et al.*, 2007; Fukuda *et al.*, 2001). Including, in Europe the main reason for the use of biodiesel is linked to environmental issues (de Carvalho *et al.*, 2013).

Nowadays, a major problem associated with the use of soy biodiesel is its susceptibility to oxidative processes, such as self-oxidation. The chain grease oil has hydrogens allylic and bis-allylic, more reactive sites in the initial stage of autoxidation (Pinto *et al.*, 2005, Albuquerque, 2010). Oxidation of the biodiesel producing various compounds such as aldehydes, ketones, acids, peroxides, polymers which modify the properties of the fuel thus compromising engine operation. That way, the oxidative stability must be considered as a key parameter in controlling the property of the biodiesel (Dunn, 2005; Dantas *et al.*, 2011; Ferrari & Souza, 2009). An important method to prevent oxidation is the use of specific additives that inhibit oxidation. Such inhibitors represent a class of substances widely varying chemical structures, and have different reaction mechanisms (Castro, 2008). The literature reports that phenolic compounds are effective antioxidants against the oxidative deterioration of polyunsaturated fatty acids (Castro, 2008, Jain & Sharma, 2010).

Several studies have been conducted in order to evaluate the oxidation stability of biodiesel additive with antioxidants (Rodrigues *et al.*, 2006; Santos *et al.*, 2011). Oxidation of fatty materials is promoted by factors such as elevated temperature, presence of light or extraneous materials such as metals or initiators. The nature of the radicals also influences the products observed and double bond geometry can also play a role (Ferrari & Souza, 2009; Castro, 2008). In order to slow the oxidation process, several additives are added to these fuels with the aim of inhibiting or retarding such undesirable reactions. Among them, the phenolic antioxidants are especially considered because they are able to directly seize peroxy radicals formed during oxidative degradation, thus breaking the auto-oxidation chain reaction (Castro, 2008, Jain & Sharma, 2010). Synthetic antioxidants like, Tert-Butylhydroquinone (TBHQ), Butylated Hydroxytoluene (BHT), Butylated Hydroxyanisole (BHA) and Propyl Gallate (PG) has been reported in many studies as important examples of phenolic antioxidants (Rodrigues *et al.*, 2006; Santos *et al.*, 2011; Figueiredo, 2009). Another class of compounds that have been reported is the phosphorylated compounds; in general, they are used in several chemical products, such as lubricants, fuels, synthetic diesels, biodiesel, and others. The oxidation stability and performance of these products are dependent upon the chemical structure of the molecule and formation of soluble compounds of decomposition during usage (Dunn, 2005; Goodrum, 2002). Recent studies (Rios *et al.*, 2010; Tuner & Korkmaz, 2007; Luo *et al.*, 2012) have reported the antioxidant capacity of the cashew nut shell liquid (CNSL) constituents (Fig. 1).

Figure 1. Cashew nut shell liquid (CNSL) constituents.



A typically solvent-extracted CNSL is composed mainly by: anacardic acid (60-70 %), cardol (15-20 %), cardanol (10 %), and traces of 2-methylcardol. When obtained as a residue from the industrial roasting shell process, which employs elevated temperatures, anacardic acid suffers a decarboxylation reaction and CNSL is then considered as technical CNSL, which contains mainly cardanol (60-70 %), cardol (15-20 %), polymeric material (10 %), and traces of 2-methylcardol.

In order to obtain an antioxidant derived from CNSL the technique of organic electrochemistry was employed (Tuner & Korkmaz, 2007; Luo *et al.*, 2012). The electrochemical synthesis of organic compounds has been the subject of laboratory investigations since the mid-nineteenth century. In recent years, primarily due to the economic feasibility, a large number of reagents used in synthetic chemistry are prepared by electrochemical methods (Ticianelli, 1998; Carrijo & Romero, 2000). Electrochemistry in organic synthesis offers other important advantages over conventional methods: mild reaction conditions, which often guarantee a high selectivity using the electron as redox reagent, leading to drastic reduction of environmental problems, greater efficiency in the process of feedstock transformation; ease the process of separation and isolation of products (Carrijo & Romero, 2000; Torii, 1985). An electrochemical system must comprise at least two electrodes (electrical conductors) immersed in an electrolyte that carries ions. Electrochemical oxidation processes usually can be divided into two main categories: direct oxidation at the anode and at the cathode indirect (Torii, 1985, Araújo *et al.*, 2009), where the middle step combines heterogeneous and homogeneous redox reaction of the substrate with the active mediator (Ticianelli, 1998). Generally, the direct electrochemical method offers several advantages therefore, it does not require stoichiometric amounts of expensive or dangerous reagents, and avoids corrosion of the electrode reactions develop in potential lower than that required for the corresponding direct conversion.

Therefore, the main objective of this work is to produce an antioxidant additive for biodiesel polyunsaturated based on cashew nut shell liquid obtained by processing it along hydroquinone using electrolysis method in alcoholic medium.

2. Methodology

For the synthesis of the antioxidant via electrolysis, the following features were used: The cashew nut shell liquid (CNSL - technical) obtained from EUROPE nut factory - (Altos - PI). Electrodes 304 stainless steel. As materials for electrolyte synthesis was used: electrolytic tub, energy source and magnetic stirrer. Soy bean oil was acquired in local market in Teresina city, Piauí state. As reagents: methyl alcohol, hydroquinone and sodium hydroxide applied without further

purification.

2.1 Antioxidant synthesis

Antioxidants were prepared by electrolytic reaction of technical CNSL dissolved in methyl alcohol in the presence of electrolytes according to the reference (Figueiredo, 2009). The reaction was performed in an electrolytic tank electrolyte with two stainless steel electrodes 304, which has a current of 5.0 A through the solution over two hours with constant stirring. It was used the ratio 10:100:10 (w/w) of technical CNSL, methyl alcohol and hydroquinone as electrolyte, respectively. At the end of the electrolytic reaction, the product was put on a glycerin and water bath, in order to completely evaporate the methanol at 70 °C, dried and stored.

2.2 Antioxidant characterization

2.2.1 Infrared spectroscopy

The reflectance analysis of absorption in the infrared region was performed on a Shimadzu FT-IR-8300 spectrometer scanning from 4000 to 400 cm^{-1} . Antioxidant sample has been analyzed as film.

2.2.2 Thermogravimetric analysis (TGA)

The thermogravimetric curves of the samples were obtained using a Shimadzu TGA-50 equipment, using a platinum crucible and synthetic air atmosphere with a flow of 50 mL/min in the temperature range of 25 to 600 °C at a heating rate of 10 °C/min. The mass of the samples was 10 mg. The parameters studied were: the onset of decomposition temperature (T_i), peak temperature (T_p), residual mass at 600 °C.

2.2.3 X-ray diffraction (XRD) analysis

XRD analyzes were performed on an equipment of the mark-ROTAFLEX Rigaku rotating anode with, using monochromatic $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) and graphite monochromator. The assays were done with voltage of 40 KV and a filament current of 150 mA, which used a 2θ range of 5-75°. The XRD patterns of the samples were analyzed and compared with JCPDS and ICDD cards ("Joint Committee on Powder Diffraction Standards and International Centre for Diffraction Data").

2.2.4 Nuclear magnetic resonance spectroscopy of hydrogen (^1H NMR)

Antioxidants samples were analyzed by ^1H NMR in order to evaluate the interactions between the electrolyte and CNSL. Analyses were performed on a Bruker Advance DRX equipment-500, operating at 500 MHz in CDCl_3 .

2.2.5 Determination of antioxidant activity by DPPH method

Antioxidant activity determination was studied by a classical method which is based on the measurement of the DPPH trap-radical (1,1-diphenyl-1, 2-picrylhydrazyl) activity (Rios, 2008). At first, it was prepared a stock solution of DPPH at 40 $\text{mg}\cdot\text{mL}^{-1}$ in methanol. Six antioxidant samples (CNSLQ and LCCHQ) were prepared in methanol at the levels: 25, 50, 100, 150, 200 and 250 $\text{mg}\cdot\text{mL}^{-1}$. Aliquot of 300 μL was taken to a test tube where 2700 μL of DPPH stock solution was added. After 30 minutes, absorbance was measured at 517 nm in reaction mixtures (Jain & Sharma, 2010; Knothe & Steidley, 2005). The absorbance values so were converted to percentage of antioxidant activity (% AA) determined by the following equation: $\text{AA} (\%) = 100 (A_{\text{DPPH}} - A_{\text{DPPH}+\text{sample}}) / A_{\text{DPPH}} \rightarrow A_{\text{DPPH}}$: initial absorbance of DPPH solution (40 $\text{mg}\cdot\text{mL}^{-1}$) $A_{\text{DPPH}+\text{sample}}$: absorbance of each sample concentration DPPH +.

2.3 Biodiesel synthesis

The transesterification reaction was performed using 100 g of soy bean oil, 20 g of methanol and 0.7 g of NaOH, which corresponds to the molar ratio of 1:6 (oil: MeOH) with 0.7 % of catalyst. The mixture was stirred at room temperature over 50 min. and after that it was transferred to a separatory funnel of 250 mL where the ester in the upper phase were separated from the glycerin (lower phase). The upper phase was washed with distilled water in order to remove impurities and then it has been heated at 110 °C as a way of to eliminate the water excess. Yield conversion was calculated using the expression described in the literature (Phani *et al.*, 2002).

2.4 Physicochemical characterization of the soy bean biodiesel.

The physicochemical properties analysis of the biodiesel were performed according to the standards of the American Society of Testing and Materials (ASTM) and the Comité Européen de Normalisation (CEN) indicated by the Resolution N° 14/2012 of the National Agency of Petroleum, Natural Gas and Biofuels (ANP) (Lam *et al.*, 2010). Specific density, acidity value and the rate of saponification of the raw oil and biodiesel were determined in accordance with analytical standards of the renamed Adolfo Lutz Institute and the American Oil Chemists' Society (AOCS) (de Oliveira *et al.*, 2008; Phani *et al.*, 2002; de Oliveira *et al.*, 2012).

2.5 Study of the biodiesel stability

2.5.1 Preparation of the samples

The antioxidant additives: CNSL and LCCHQ were incorporated into the soybean biodiesel in the proportions 1000-5000 ppm, through simple mixtures.

2.5.2 Evaluation of acid value

Acidity index analyses were performed using methods described in the literature (Lôbo *et al.*, 2009) using sodium hydroxide as titrant agent and phenolphthalein as indicator.

2.5.3 Accelerated oxidation test

The accelerated oxidation test was performed based on the accelerated oxidation test into an oven ("Schaal Oven Storage Stability Test") over 90 days at 60 °C (± 1 °C). The samples were analyzed by Molecular Absorption Spectroscopy in the Ultraviolet Region (Manahan, 2017), with spectral scans in the range 240-300 nm, performed using spectrophotometer Varian model Cary 300 double beam UV/Vis with quartz cuvette 1 m. The samples were diluted arrays in hexane at a concentration of 1:1000.

2.5.4 Oxidative stability at 110 °C (Rancimat method)

Analyzes were performed on Rancimat equipment, model 617 at the temperature of 110 °C and air blow rate of 10 L/h. Samples of 3 grams were weighed in appropriated vials used for Rancimat run. For determination of biodiesel oxidative stability five samples of biodiesel were prepared with different concentrations of antioxidant that ranged between 1000 and 5000 ppm (CNSL and LCCHQ). One control sample containing no antioxidant was kept.

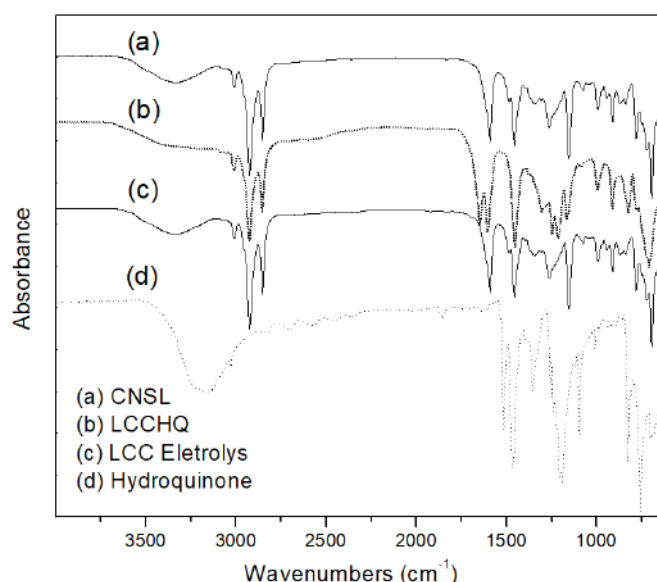
3. Results and Discussion

3.1 Infrared spectroscopy (FTIR)

The infrared spectroscopy is a widely accepted technique for polymer characterization. However, it is limited to identify just characteristic bands of functional groups and is not efficient for elucidating structures.

The infrared spectra of the samples HQ pure, CNSL and antioxidant LCCHQ are showed in the Figure 2. The infrared spectra showed very similar bands. The main bands observed for all samples were at 3500 cm^{-1} as consequence of the HO-groups (phenol) and strong signals between $2850\text{-}3052\text{ cm}^{-1}$ assigned to axial deformations of CH, CH₂, CH₃ and CH axial deformation of aromatics. However, two points should be taken into account first and decreasing the intensity of the absorption band in the region $3000\text{-}3400\text{ cm}^{-1}$ in the spectrum of LCCHQ which may be consequence of the dimerization reaction between hydroquinone and technical CNSL. Another band that appears in the region between the bands 1370 and 1450 cm^{-1} that may be result of the methoxylation processes.

Figure 2. Infrared spectra of the samples HQ pure, CNSL and antioxidant LCCHQ.

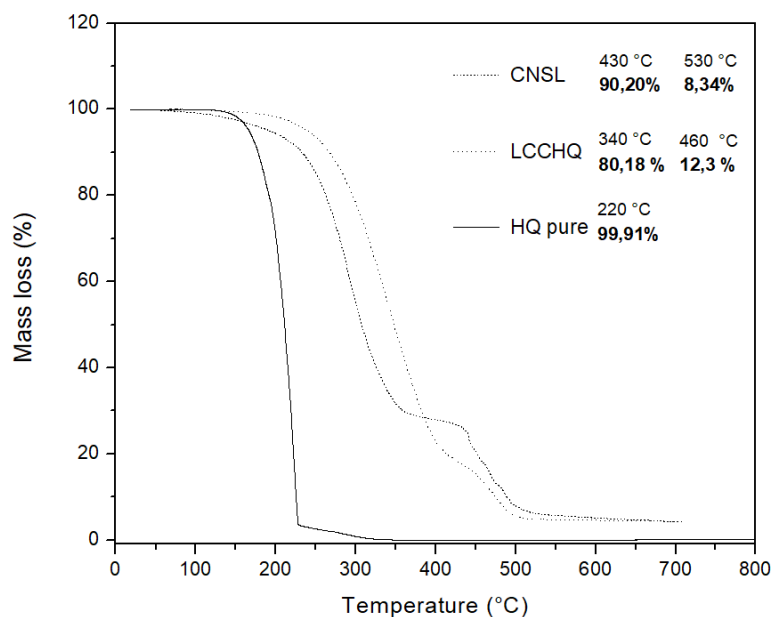


*FT-IR-8300. Source: Authors (2022).

3.2 Thermogravimetric analysis (TGA)

The TGA curve of HQ, pure CNSL and LCCHQ (Figure 3) shows a thermal decomposition behavior quite different from HQ and the others. Pure HQ showed just one mass loss range from 168 to $220\text{ }^{\circ}\text{C}$, which corresponds to 99.91% of mass. This low thermal stability can be explained considering that the HQ is mainly constituted by one component, 1-4,benzylidihydroxide, that is weakly stable.

Figure 3. TGA curve of HQ, pure CNSL and LCCHQ.



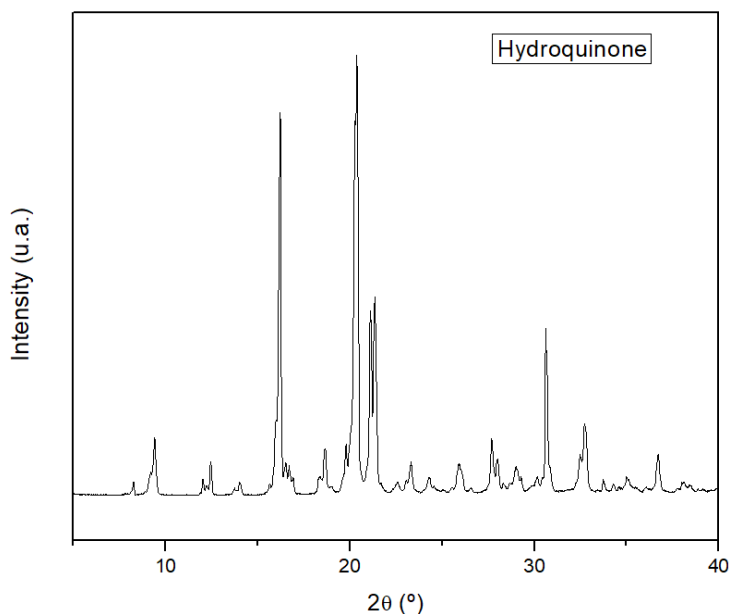
*Shimadzu TGA-50. Source: Authors (2022).

Pure CNSL TGA curve exhibited two major events in ranges between 168-282 °C (72 %) and 400-490 °C (17 %). The first event is related to mass loss of volatiles substance present in the sample and the second one is related to the properly decomposition. LCCHQ TG curve presented a mass loss corresponding to more than 99 % around 420 °C. This behavior is similar to that observed for pure CNSL and may be assigned to the interaction between both CNSL and HQ in the reaction environment.

3.3 X-ray diffraction (XRD) analysis

The X-ray diffraction is used mainly as a tool for identifying crystalline materials structures. Each crystalline compound is structured as a differently, therefore its X-ray diffraction analysis patterns are unique and characteristic of each material. This characteristic allows to know the internal structure of a given solid and to identify which are the comprised compounds in the bulk (Mazzetto *et al.*, 2009). The analysis diffractogram for the HQ used, showed that it has a well-defined crystal structure as can be seen in Figure 4. According with Frizon, (Parente, 2003), HQ present three crystal forms, which are quite stable agreeing with analyzed material.

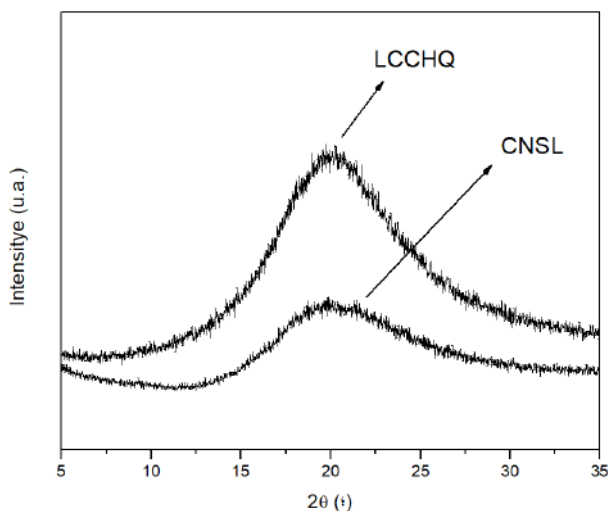
Figure 4. Diffractogram for the HQ.



*Mark-ROTAFLEX Rigaku. Source: Authors (2022).

The spectrum of x-ray diffraction of CNSL and LCCHQ, Figure 5, presents different behavior when compared with pure HQ. It was observed that the crystalline peaks present in pure HQ do not appear in the sample electrolyzed. This fact can be explained by the disruption of the crystalline structure caused after the reaction. In this aspect, the polymer has formed favorable feature because of its low crystallinity degree.

Figure 5. The spectrum of x-ray diffraction of CNSL and LCCHQ.



* Mark-ROTAFLEX Rigaku. Source: Authors (2022).

3.4 Hydrogen nuclear magnetic resonance (^1H NMR)

The nuclear magnetic resonance spectra of hydrogen CNSL coach, Table 1, shows values in accordance with what is predicted by the literature (Ramos *et al.*, 2003). Presence of four signals assigned to aromatic hydrogen in ^1H NMR spectrum suggested the presence of a phenolic derivative. Those signals are: a triplet (7.12 δ) integrated to hydrogen, two doublets at 6.62 and 6.74 δ respectively and one broad singlet at 6.64 δ . This set of signals suggested phenols in the meta position (Manahan, 2017; Meher *et al.*, 2006).

Table 1. Values in accordance the nuclear magnetic resonance spectra of hydrogen CNSL.

¹ H	RMN ¹ H		Integral
	LCC δ (ppm)	LCCHQ δ (ppm)	
-CH=	5,84-5,83	5, 86-5,9	0,43
-CH=CH-	5,50-5,30	5,5-5,30	4,18
=CH ₂	5,10-5,00	5,30- 510	1,12
(CH)Ar	7,22-7,12	7,3 -7,12	0,70
(CH)Ar	6,84-6,82	6,89- 6,54	1,10
(CH)Ar	6,75-6,72	6,75-6,72	2,28
CH ₂ CH=CH-	2,85-2,80	2,78 -2,85	2,98
-OCH ₃	-	3,6-3,0	2,14*
Ar-CH ₂	2,80-2,55	2,80-2,55	2,45
CH ₂ CH=CH-	2,03-1,99	2,03-1,99	4,53
ArCH ₂ CH ₂	1,69-1,61	1,69-1,62	3,54
(CH ₂)n	1,42-1,28	1,45-1,29	10,40
CH ₃	0,94-0,88	0,94-0,88	2,17

*Microsoft Excel (2007). Source: Authors (2022).

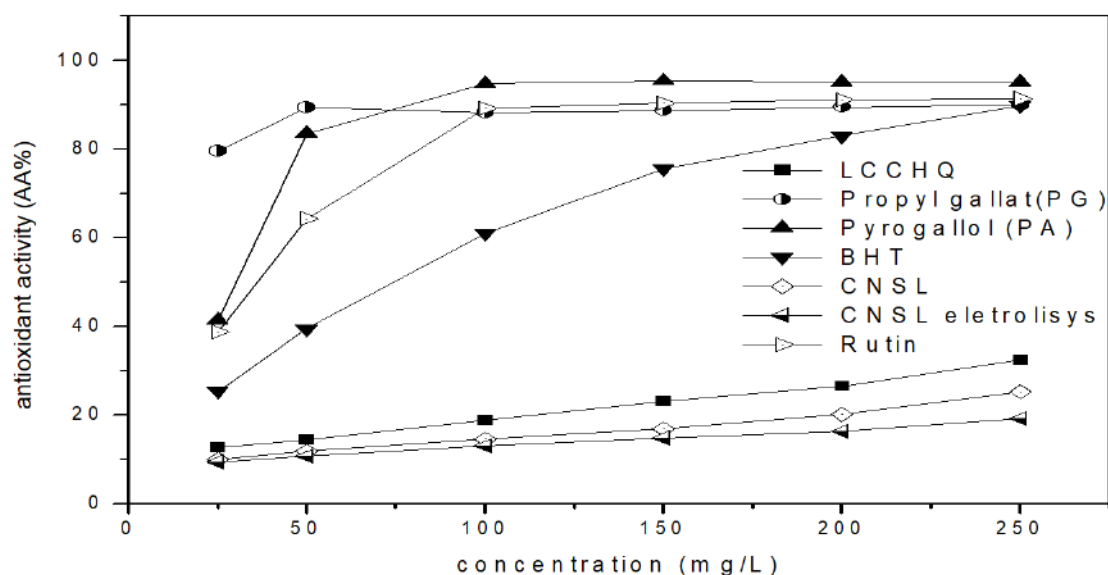
The presence of a triplet 2.54δ can be assigned to the benzylic hydrogen. A triplet between 0.84 δ regarding the hydrogen belonging to methyl group; between 1.24 and 1.6 δ regarding the methylene hydrogen of the side chain; between 2.0 and 2.5 δ that hold allylic methylene hydrogen of the group of chain aliphatic methylene protons and referring to the aromatic ring linked.

Analysis of the CNSL base in alcoholic medium in the presence Hydroquinone (LCCHQ) ¹H NMR spectrum, Figure 9, shows the appearance of a single signal between 3.5 to 4.0δ, probably methoxyl hydrogen. Another point observed was the appearance of a single sign on 6.62 δ for the aromatic hydrogen characteristic of symmetric molecules (Rios *et al.*, 2010; Rodrigues *et al.*, 2006; Santos *et al.*, 2006).

3.5 Determination of antioxidant activity by DPPH method

The reduction assay of DPPH free radical is a method commonly used to investigate the antioxidant potential and allows variation in the mode of presentation of the results concerning the antioxidant activity investigated. Thus, the present results were expressed as the ability to sequester/reduce DPPH in percentage as can be seen in Figure 6.

Figure 6. Results were expressed as the ability to sequester/reduce DPPH.



*Origin Pro 2020. Source: Authors (2022).

The CNSL technical and LCCHQ at all concentrations tested has showed antioxidant activity values below 50%, making it impossible to determine the EC₅₀ (effective concentration able to reduce DPPH at 50 %). To be compared with the standard BHT, gallic acid and rutin, CNSL showed a weak antioxidant activity, because at the highest concentration tested (250 mg/mL) the percentage of activity was 32.19 %, comparable to that obtained for BHT (30.41 %) at the lowest concentration (25/ml).

3.6 Characterization of soybean biodiesel

Due to the growing importance of biodiesel as an alternative fuel in many countries, it is absolutely necessary to establish standards for quality control worldwide (Su-Waterhouse *et al.*, 2011). All physiochemical parameters of methyl soybean biodiesel stood within the limits established by Resolution 14/2012 of ANP (Table 2). All characteristics of that biodiesel has presented are in accordance with the limits established by Brazilian previously mentioned. This results shows that the conditions for synthesis and purification were quite efficient. This fact was expected since these conditions and procedures have proven effective for the synthesis of conventional biodiesel.

Table 2. Results for the physicochemical parameters of soybean biodiesel.

Characteristics	Test Metod	Result	Limit ANP
Aspect	-	LII	LII
Density a 20 °C (Kg/m ³)	ASTM D 4052	876	880
Kinematic Viscosity at 40 °C (mm ² /s)	ASTM D 445	4,5	6,0
Water Content (mg/Kg)	EN 12937	350	500
Flashpoint, min (°C)	ASTM D 93	136	100
Acid value, máx. (mg KOH/g)	IAL	0,03	0,80
Free Glycerine, máx. (% mass)	ASTM D 6584	0,01	0,02
Total Glycerine , máx. (% mass)	ASTM D 6584	0,20	0,38
Monoacylglycerol (% mass)	ASTM D 6584	0,0495	Anotate
Diacylglycerol (% mass)	ASTM D 6584	0,0158	Anotate
Triacylglycerol (% mass)	ASTM D 6584	0,0302	Anotate
Methanol, máx. (% mass)	EN 41110	0,01	0,50
Ester content, mín. (% mass)	EN 14103	98,8	96,5

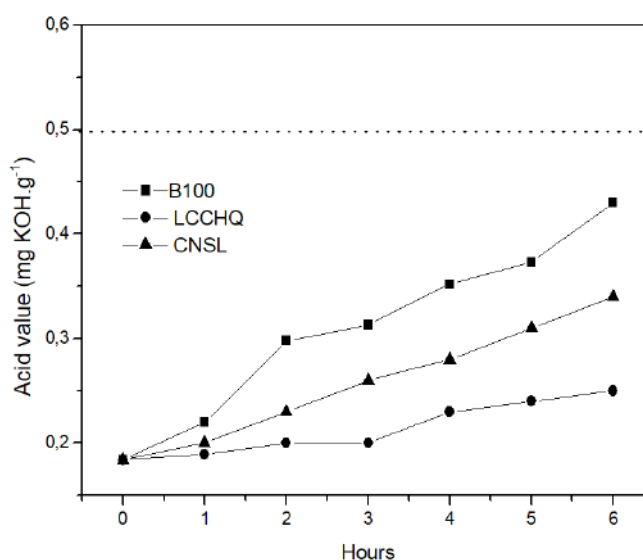
*Microsoft Excel (2007). Source: Authors (2022).

3.7 Evaluation of acid value

According to Knothe (Phani *et al.*, 2002), acid value measures the amount of free fatty acids and influences the aging process of biodiesel. Hence, it is a very important determination since it serves both to provide data to assess the biodiesel conservation status and to inform about the quality of the product. High levels of acidity can cause corrosion in the storage tank and the engine. ANP has set the biodiesel business maximum acidity limit as 0.5 mg.KOH/g.

The results of the study about acidity variation in pure biodiesel and in biodiesel added of 5000 ppm of LCCHQ or CNSL being submitted to different heating times at 120 °C are showed in Figure 7. The results showed that there was an increase in acidity function of heating time in all sample, however pure biodiesel showed a greater variation in acidity compared to biodiesel additives were 5000 ppm of CNSL with pure LCCHQ. This behavior can be elucidated by the presence of phenolic antioxidant that provides oxidation inhibitor characteristics.

Figure 7. Acidity variation in pure biodiesel and in biodiesel added of 5000 ppm of LCCHQ or CNSL being submitted to different heating times at 120 °C.



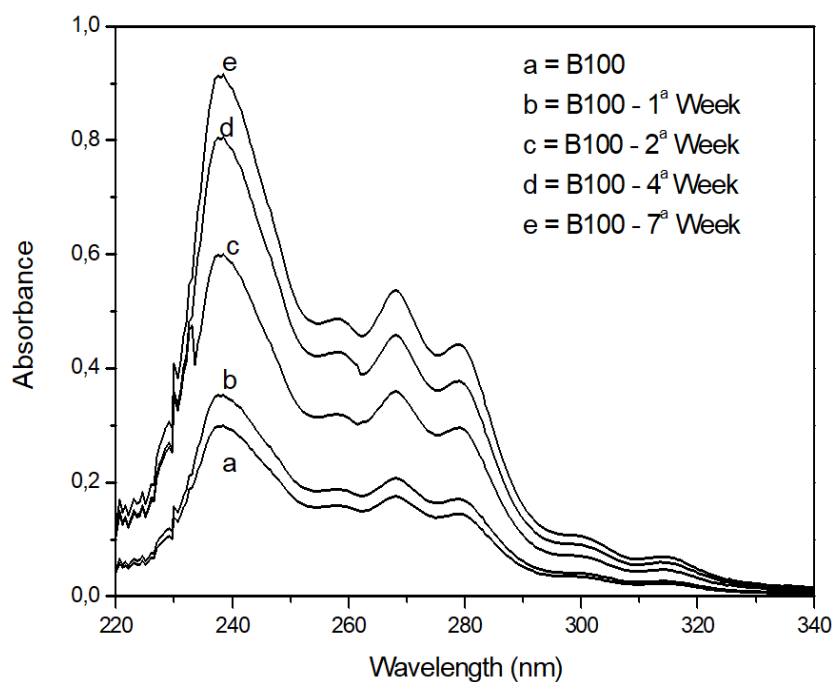
*Origem Pro (2020). Source: Authors (2022).

3.8 Accelerated oxidation test

Spectrophotometric examination at the ultraviolet region can provide information on the quality of a lipid substance as well as its state of preservation and changes caused by technological processes, since the products generated by auto-oxidation of biodiesel exhibit characteristic spectra in this region (Rios *et al.*, 2010; Santos *et al.*, 2011).

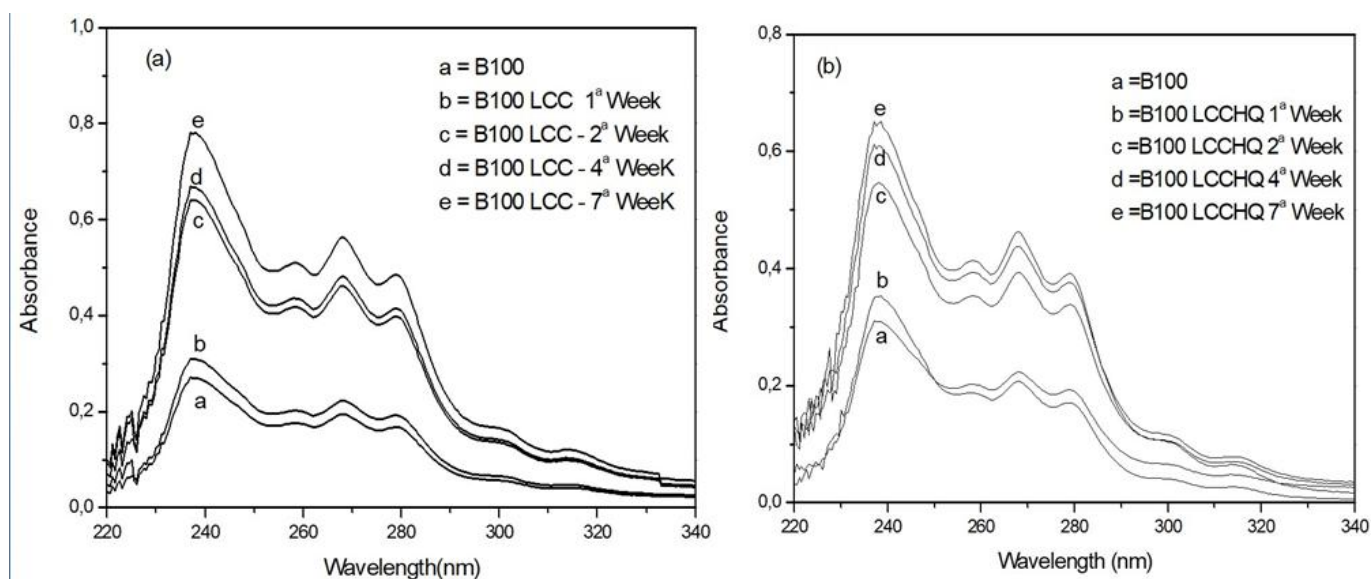
The results for the spectrophotometric analysis of soybean in the UV region are disposed in Figures 8 and 9. In the initial phase, also known as induction of oxidative process, the first free radicals are formed as result of the light action on the allyl group and the attack to the singlet oxygen (¹O₂) directly to the double bond (Rios *et al.*, 2010; Sun-Waterhouse *et al.*, 2011).

Figure 8. Results for the spectrophotometric analysis of soybean in the UV region.



*Spectrophotometer Varian model Cary 300 double beam UV / Vis. Source: Authors (2022).

Figure 9. Results for the spectrophotometric analysis of soybean in the UV region.



* Spectrophotometer Varian model Cary 300 double beam UV / Vis. Source: Authors (2022).

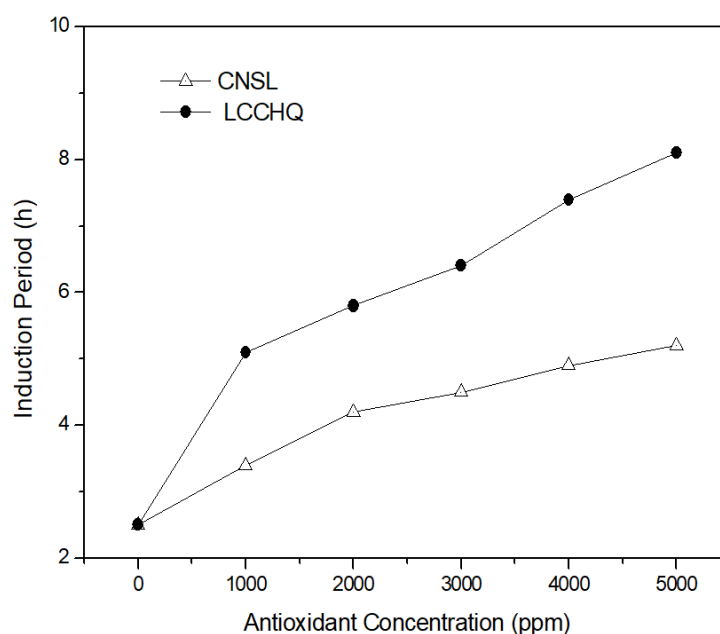
In this step, the chemical changes can be analyzed by the increased absorptivity in the ultraviolet spectrum, since lipids containing double bonds present in the string resonance, resulting in isomerization and conjugation (Tepe & Sokmen, 2007). Figure 9 presents the soybean biodiesel no additive tested for greenhouse and observed that it presents an increased absorbance in the spectral range from UV to visible indicating the formation of conjugated dienes around 245 nm. In Figure 9 (a) and (b) present the soybean biodiesel doped with CNSL and LCCHQ at 5000 ppm. According to the results, it can be inferred that the insertion of the compounds slowed increased specific absorption in the UV at 243 nm, which monitors the increasing the concentration of secondary products of oxidation of the samples, in particular suggesting the presence of ketonic aldehydes α , β ethylenically. These results are in agreement with a study reported in the literature (Rodrigues *et al.*, 2006).

3.9 Oxidation stability at 110 °C (Rancimat method)

Evaluation of stability, theoretically, means the ability of a material to maintain its integrity as long as possible (Rodrigues *et al.*, 2006). The Rancimat method is the standard oxidative stability, EN 14 112, which has parameters as aeration, temperature of 110 °C and atmospheric pressure only. This method analyzes the variation of the deionized water conductivity by collecting volatile compounds from the final stages of the biodiesel oxidation process (Tepe & Sokmen, 2007; Ticianelli, 1998). Figure 10 show the results of induction period for pure soybean biodiesel and with CNSL pure and LCCHQ as additive in concentration varying from 1000 to 5000 ppm.

It was found that the soybean biodiesel additive showed an increase in the induction time when increasing antioxidant concentration added to biodiesel. On other hand, the LCCHQ showed better results than the CNSL pure at the same concentrations. What is in agreement with is reported in the literature (Sun-Waterhouse *et al.*, 2011; Ticianelli, 1998).

Figure 10. Study of the stability of biodiesel CNSL pure and LCCHQ as additive in concentration varying from 1000 to 5000 ppm.



*743-Rancimat. Source: Authors (2022).

The addition of 5000 mg.kg⁻¹ of LCC into pure soybean biodiesel provided an increase in the induction period from 3.01 to 5.60 h, whereas the same amount of LCCHQ increased to 8.12 h. The addition of additive to biodiesel improved oxidative stability observed through the induction period increase. This improvement was proportional to additive concentration grow up. Oxidative stability minimum limit of 6 hours, as established by resolution of ANP, was achieved when using LCCHQ at a concentration of 2000 mg.kg⁻¹, i.e., 0.2 % antioxidant, obtaining a value of 6.02 h.

The special insight of CNSL use as antioxidant is that it has not demanded further treatment or isolation of specific molecules. It was just electrolyzed. The results show that the LCCHQ appears as an interesting alternative for improve the oxidative stability of biodiesel. It can be economically feasible, especially in countries with large cashew production.

4. Conclusion

Since Brazilian biodiesel is majority produced from soybean, due to technical and industrial causes, the use of antioxidants is very much necessary. The electrolytic reaction is efficient for being innovative, not to require deep purification

by increasing the antioxidant activity of technical CNSL in the presence of hydroquinone (LCCHQ) to modify the chemical composition of the technic degree CNSL. The antioxidant LCCHQ proved be ineffective against the DPPH radical concentrations, however efficient when tested by rancimat method. According to the accelerated technics, LCCHQ was able to interfere in the process of soybean biodiesel oxidation at the initial time of storage. It was observed that the induction period increased as the concentration of the antioxidant increased as well in a way of to reach highest values that the minimum established by the laws EN 142 112 and 14/2014 of ANP. In order to confirm the efficiency of CNSL-based antioxidant, a quick check at the quality parameters of soybean biodiesel are enough to show that no change occurred with the addition of LCCHQ, being them according to the allowed limits.

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