SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

WASTE FRYING OIL TRANSESTERIFICATION TREATED BY STEAM DRAG METHOD

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Received 12 November 2018; received in revised form 30 November 2018; accepted 14 December 2018

ABSTRACT

Demand for diversified biodiesel feedstocks is high and increasing, but few are viable for large-scale production, and many of those selected compete with other sectors of the chemical industry. To improve energy and environmental sustainability, fatty acids from waste oils that are improperly disposed of and pollute the environment can be used for transesterification reactions. However, they need treatment to achieve high conversion rates. In this context, the aim of this work was to perform and analyze the treatment of residual frying oil with the evaporation and entrainment process, aiming at its use as raw material to obtain biodiesel (methyl esters) by a transesterification reaction. The physicochemical properties of the residual oil after treatment were characterized by moisture content, pH and the acidity, saponification, iodine, and peroxide index. The conversion rate of the residual oil to methyl esters was determined by ^{1}H NMR analysis. After the treatment, the method of analysis of variance showed that the oil obtained a significant reduction of the saponification, iodine, peroxide and acidity indexes, being the acidity reduced from 9.36 to 7.85 mg KOH g^{-1}. The moisture content of 0.733 % and elevation of pH to 8.0. The conversion rate of fatty acid biodiesel of residual oil was 79.3 %, lower value of standards norms (ASTM, 2005; EN, 2008; ANP, 2014), showing that the assigned methodology for frying residual oil is inefficient in biodiesel production.

Keywords: *Fatty acid, Biodiesel, Analysis of variance, Standards norms*.

1 INTRODUCTION

The interest of alternative and renewable sources for the production of biofuels as a renewable energy resource has been intensified over the years to gradually soften the social, environmental and economical energy problems caused by fossil fuels (Marcossi e Moreno-Perez, 2017; Jain *et al*., 2018).

Biomass, considered as a renewable source of energy, is used in the production of biofuels such as biodiesel. Biodiesel is defined internationally by the American Society for Testing and Materials (ASTM) as a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel can be produced by several methods, the transesterification reaction of triglycerides with short-chain alcohol (methanol and ethanol) in the presence of a homogeneous or heterogeneous catalyst is the most used method (Tan *et al*., 2019).

Although some biofuels are already represented in the world energy matrix by some developed and underdeveloped countries, there are still recent studies that evaluate viability and sustainability with diversified production processes and raw materials (Saladini *et al*., 2016). Brazil is among the largest producers and consumers of biodiesel in the world. According to the ANP statistical yearbook (ANP, 2018a), B100 biodiesel production in 2017 in the major regions and units of the Federation was 4,291,294 m^3. As of March 2018, the Brazilian government has enacted laws requiring the addition of 10% of biodiesel superimposed on mineral diesel for commercialization (B10) (ANP, 2018b).

Some factors contribute to the production of biodiesel in Brazil, such as the broad territory and technology for the planting of oleaginous raw materials such as soybean, canola, peanut, palm,

castor bean, palm, macaúba, jatropha and others, slaughterhouses of animals that produce animal fats (Marcossi e Moreno-Perez, 2017). Soybean oil and bovine fat are the main raw materials used in Brazil.

In order to increase biodiesel production, research and technological innovations focus on the application of new methods of production involving raw materials such as microalgae and inedible and residual oils, aiming to reduce costs of current methods and avoid competition of raw material with too much products (food, cosmetics, pharmaceuticals, etc.) (Arumugam e Ponnusami, 2019; Sandouqa e Al Hamamre, 2019). One of the most important calls for biodiesel production from these new resources is that many of these crops will not displace the traditional areas of food crops, which is one of the main criticisms for the production of biodiesel from oleaginous plants (Atabani *et al*., 2012; Tan *et al*., 2019).

Residual frying oils are a problem for the environment, most of which are improperly disposed of, causing clogging in sewage pipes, river degradation, soil infertility, and in other ways contributing to increased pollution. With the evolution of environmental legislation, it is practically required that the oil be reused, for this reason, it becomes feasible to recycle residual frying oil due to the preservation of the environment. (Silva, 2013; Sabesp, 2008).

The continuous frying of food in vegetable oils leads to the formation of free fatty acids that alter the sensorial characteristics of the product and its physicochemical properties, the formation of free fatty acids causes chemical changes such as oxidation reactions, hydrolysis, and polymerization, besides physical changes such as smoke point reduction, browning, and foam and viscosity increase, rendering this matter inappropriate as an immediate reactant for transesterification reaction (Freire; Mancini-Filho; Ferreira, 2013). Neutralization processes, clarification, and drag evaporation are some methods used in oils to improve their quality as a raw material for biodiesel.

The quality control methods for waste oils and fats are complex and specific to determine each physical or chemical property. The acid index, peroxide index, and iodine index methods can be some methods that quickly and simply determine the amount of compounds formed during the oxidation. Gas chromatography, which determines which fraction of the oil has not undergone physical and chemical changes, is also highlighted, as well as determining which fractions concentrate the oxidized triglyceride degradation products, polymers, dimers, diglycerides, and free fatty acids. Other methods of quality control, such as Nuclear Magnetic Resonance (NMR), total polar compounds, fluorescence, or ultraviolet radiation, can also be used (Freire; Mancini-Filho; Ferreira, 2013).

Based on these factors, the purpose of this work is to obtain biodiesel (methyl esters) through the transesterification reaction of frying oil treated by the evaporation and entrainment method and to analyze the physicochemical properties and the conversion rate according to the norms standardization of ANP (2014), EN (2008), and ASTM (2005).

2 MATERIALS AND METHODS

2.1 Material

The municipal government of Jaguariaíva PR. provided the residual frying oil used for the treatment and for obtaining biodiesel from this study. The same was obtained from collection points of frying oil used by the population. The residual oil was filtered to remove solids and stored properly.

2.2 Oil treatment by evaporation and drag method

The treatment of the residual oil by evaporation and drag is due to adaptations of the methodology proposed by Watanabe *et al*. (2006). The evaporation and entrainment process was carried out for 15 minutes, and the treatment was carried out using a round bottom flask containing 100 mL of distilled water evaporated by a heating mantle. The flask was coupled with silicone hose in direct contact with 100 mL of frying residual oil. Subsequently, the oil was centrifuged and separated from the run-off water in a separatory funnel, and in the filtrate with anhydrous sodium sulfate (Synth).

2.3 Physicochemical characterization of residual oil

The Physicochemical characterization analyzes, such as moisture content, acidity index,

saponification, iodine, and peroxide, were performed according to the methodology of the Adolfo Lutz Institute (IAL, 2008). The data obtained were interpreted by the method of analysis of variance, the means of the indices were compared using the Tukey test with 5% of probability. The pH was determined with the aid of a universal pH strip (pH-fix0-14).

2.4 The reaction of transesterification via homogeneous basic catalysis

The transesterification reaction was performed employing 100 mL of treated frying residual oil added in approximately 0.5 grams of NaOH P.A. (Dynamic, 98% concentration) dissolved in 50 mL of methyl alcohol P.A. (Dynamic). The reaction was carried out in a flat bottom flask coupled to the reflux condenser in a water bath at a temperature of 70 °C ± 5 °C, the reaction time of one hour and constant stirring. After the reaction, the phases of the products (biodiesel and glycerin) were separated through a separating funnel, where the corresponding phase of the biodiesel was washed with 0.1 mol L^{-1} HCl solution and distilled water, respectively, and then filtered with anhydrous sodium sulfate (Synth).

2.5 Conversion rate of methyl esters by ^{1}H NMR

The conversion rate of residual oil methyl esters was determined by ^{1}H NMR analysis of the residual oil before and after transesterification reaction. The analyses were performed on Agilent NMR spectrometer, Mercury Plus 300 MHz multinuclear model (Magneto NMR 300-OXFORD) under standard conditions for ^{1}H NMR using solvent $CDCl_3$ (Deuterated Chloroform).

The rate of conversion of triglycerides to biodiesel was determined using the method of Ruschel *et al*., (2016), where the conversion rate was calculated using equation (Eq. 1) using the values of integral hydrogen spectra of the methylene group of carbon adjacent to the carbonyl (I-CH_2) and methoxy hydrogens of the O-CH_3 group.

$$C_{ME} = 100 \times \left(\frac{\frac{I_{ME}}{3}}{\frac{I_{\alpha-CH_2}}{2}} \right) \qquad \text{(Eq. 1)}$$

Where: C_{ME} = Conversion to methyl ester;

I_{ME} = Value of the methoxylic hydrogen spectrum (O-CH_3);

$I\alpha$-CH_2 = Value of the spectrum integral of the methylene hydrogens adjacent to the ester carbonyl.

3 RESULTS AND DISCUSSION:

3.1 Physicochemical properties of frying oil and biodiesel

In order to perform the transesterification reaction, it was necessary to analyze the physicochemical properties of the raw material with the purpose of informing the state of conservation of the oil before and after the treatment with evaporation and drag, and its sufficiency to obtain biodiesel by transesterification through homogeneous catalysis basic. The results obtained indicate the possibility and/or feasibility of improving the treatment method, adding other processes making the material propitious to reach higher conversion rates. (Silva, 2011; Völz, 2009). The results of the residual oil and biodiesel analyzes are shown in Tables 1 and 2.

According to Table 1, the results of the analyzes are outside the quality parameters of edible oils (ANVISA, 2006). The residual oil has a high acid value, probably predicted by the formation of free fatty acids due to oxidation and hydrolysis reactions when subjected to high temperatures. This is a detrimental factor to obtain biodiesel by transesterification through basic homogeneous catalysis, since it allows the formation of soaps, converting part of the raw material into salts of fatty acids (Ramos *et al*., 2017; Silva, 2011). The effects of the steam drag process significantly reduced the acidity, but it remains high enough to apply the transesterification reaction, and the treatment method needs to be improved.

The iodine content of the treated oil has been supposedly reduced because lower halogenation reactions occur in double bonds of acidic compounds present in the oil, such as free fatty acids and others. The peroxide index is also probably lower due to the evaporation and drag process to remove partially compounds of oxidizing agents such as peroxides and hydroperoxides or other similar products from the

raw material oxidized grease (Corsini e Jorge, 2006; Silva; Borges; Ferreira, 1999).

Pursuant to the ANP (DOU 26.8.2014), ASTM D6751 and EN 14214 standards for biodiesel standardization, the acid value for biodiesel shall be 0.50 mg KOH g^{-1} and iodine maximum 120 g I_2/100 g according to EN 14111. There are no specifications for saponification index and also for peroxides, to analyze better the biofuel was replaced peroxide analysis by oxidation stability by induction period by the Rancimat method EN 14214 (Lôbo; Ferreira; Cruz, 2009) . The acidity index of biodiesel (1.14 ± 0.04 mg KOH g^{-1}) is higher than the quality standards, indicating that the steam drag treatment is inefficient to reduce acidic components in the residual oil to obtain biodiesel.

The biodiesel iodine content (101.50 ± 0.03 g I_2/100g) is within the quality standards, claiming that they have adequate unsaturation fatty acids in the biodiesel standard. The number of unsaturations in the biodiesel chain reflects on oxidative stability, pour point, fog, and cold clogging (Ramos *et al*., 2017; Lôbo; Ferreira; Cruz, 2009).

The saponification index of treated waste oil and biodiesel is lower than the residual oil index, consistent results since, after treatment, they also have lower acidity indexes and moisture contents (Table 2) in their composition, requiring less demand for alkali needed for saponify the product in indirect titration.

The biodiesel obtained a peroxide index of 9.59 ± 0.03 mEq/kg, indicating that the initial oxidation state is relatively high and supposedly does not exceed 6 hours the induction time by the Rancimat method without addition of antioxidant. Silva *et al*. (2000) reported that both methods of analysis were based on biodiesel from frit residue residual oil (IP = 3.09 mEq/Kg and induction time of 8.19 hours) and ethanol (4.44 mEq/Kg, and induction time of 5.38 hours), concluding that the oxidative stability of biodiesel is inversely proportional to the peroxide index, that is, the higher the peroxide index the lower the oxidative stability.

Table 2. *Moisture content and pH of frying residual oil after treatment and biodiesel.*

Samples	Moisture content (%)	pH
Residual Oil	2.643[a] (±0.030)	7.0
Filtered Oil	2.413[b] (±0.015)	7.0
Treated Oil	0.733[c] (±0.011)	8.0
Biodiesel	0.480[d] (±0.003)	7.0

Table 2 shows that the treatment of the residual oil resulted in the increase of pH, favoring the production of biodiesel by transesterification through basic homogeneous catalysis and that after the transesterification reaction it became neutral (pH = 7.0). The moisture content of biodiesel of 0.480% corresponds to 480 mg/kg (0.0048 g), which is higher than the maximum amount allowed by law in biodiesel that is 200 mg/kg (0.0002 g), indicating that this method of biodiesel from waste oils reduces moisture, but in a non-effective way, being subject to microorganisms proliferation and corrosion during storage, storage and transport (Ramos *et al*., 2017).

3.2 Conversion of triglycerides to methyl esters

In order to evaluate the rate of conversion of the transesterification reaction of the residual oil treated with the steam drag method, ^{1}H NMR analysis was carried out in the residual oil (Figure 1) to report through the spectra the components that characterize the triglycerides, and subsequently the types of hydrogens belonging to the different fatty acids.

The signals of the ^{1}H NMR spectra of Figure 1 are apparently similar to ^{1}H NMR spectra of soybean oil (Glycine max L.) (Shimamoto; Bianchessi; Tubino, 2019; Martin-Rubio; Sopelana; Guillén, 2018; Li *et al*., 2018; Ruschel *et al*., 2016), The results of this study indicate that a large part of its composition has triglycerides similar to those of refined soybean oil. The results obtained are similar to those of Wako *et al*., (2018) which performed ^{1}H NMR analysis of residual oils, and determined the fatty acid profile by gas chromatography spectroscopy, stating that it had the same fatty acids found in soybean (oleic, linoleic, linolenic, palmitic, stearic, myristic, eicosanoic).

By analyzing ^{1}H NMR spectroscopy of the treated residual oil (Figure 1), the respective signals characterizing the triglycerides, the main components found in the residual frying oil, are noted: Sign "A" between 5.50-5.35 ppm represents hydrogen of the CH_2=CH_2 group, the "B" spectrum (5.35-5.25 ppm) glycerolic hydrogens of tertiary carb (H-CH), "C" groups (4.0-4.5 ppm) glycerol hydrogens of secondary carbon groups (H-CH_2), "D" (2.60-2.90 ppm) bis-allylic hydrogens (CH_2=CH-CH_2-CH=CH_2), "E" , (2.25-2.50 ppm) hydrogen of the methylene group of the carbon adjacent to carbonyl (Iα-CH2), “F” (1.80-2.20 ppm), allylic hydrogen, "G" (1.50-1.75 ppm) β-carbonyl hydrogen, “H” (1.25-1.50 ppm) hydrogens of H-CH_2 groups distant from CH_2=CH_2, groups, “I” (0.85-1.00 ppm) hydrogens of the H-CH_3 group of acids large and unsaturated fatty acids, and "J" (0.65-0.85 ppm) hydrogen peroxide from the H-CH_3 group (Martin-Rubio; Sopelana; Guillén, 2018; Popescu *et al*., 2015).

Signals "B" and "C" in the ^{1}H NMR spectrum are specific to indicate whether triglycerides have reacted in the transesterification reaction. These signals are absent in the ^{1}H NMR spectra of biodiesel samples because in the conversion of oils to biodiesel no glycerol hydrogens are found in their composition. The disappearance of the signals "B" and "C" after the transesterification reaction theoretically justifies the conversion of biodiesel through the appearance of the new signal (K), a singlet located in the displacement 3.50-3.75 ppm corresponding to methoxylic hydrogels methyl group (COOCH3), as observed in Figure 2 (Ruschel *et al*., 2016).

Figure 2 shows the 1H nuclear magnetic resonance spectrum, which corresponds to the biodiesel phase of the product of the transesterification reaction.

Observing the spectra in Figure 2, the presence of the "C" and "K" signals is noted, which proves that the triglycerides reacted with the methanol in the presence of the catalyst. However, the presence of the "C" signal shows that the product of the reaction did not reach 100% conversion, and may contain triglyceride residues such as diglycerides and/or monoglycerides, which have signals in the same spectral regions (4.10-4.30 ppm) than glycerol hydrogens (Ruschel *et al*., 2016). These compounds affect changes in the physical and chemical properties of biodiesel carried out in this study, mainly in the acidity index.

The absence of the "B" signal is a predicted result, indicating that the tertiary carbon hydrogens do not makeup part of the biodiesel but of the glycerin, another product formed in the reaction.

To evaluate the conversion to esters by the calculation of equation 1 proposed by Ruschel *et al*., (2016), the signal "K" was compared with the "E" signal (Iα-CH2), since this signal represents all the molecules and triglyceride derivatives such as diglycerides and monoglycerides, free fatty acids, and other long-chain carbon compounds, both of which may arise at the time of the reaction.

Table 3 shows the result of the conversion rate of methyl esters of biodiesel through the values of the integrals of the signals "E" and "K" applied in equation 1.

Table 3. Conversion of methyl esters and values integral’s I_{ME} and *Iα-CH_2*.

Sample	C_{ME} (%)	I_{ME}	*Iα-CH_2*
Methyl esters	79.3	1.00	0.84

The result expressed in Table 1 shows that the transesterification reaction obtained a conversion rate of 79.3%, lower than 96.5%, which is the minimum established by ANP (2014), ASTM (2005), and EN (2008) for conversion to esters. In this paper, the low value of the conversion rate clarifies why the physical properties of biodiesel (Tables 1 and 2) have highly unsatisfactory results.

In this context, the product obtained from the reaction is prevented by law from being marketed because it is declared as a mixture of methyl esters instead of biodiesel.

4 CONCLUSIONS:

Regarding the main objective of this work, it was not possible to obtain biodiesel from frying oil treated by the steam and drag method, as a result of which the conversion rate in the methyl esters obtained is lower than 96.5% established by the quality parameters for biodiesel.

The effects of treatment of frying residual oil with the evaporation and entrainment process altered the physicochemical properties of the same, reducing the acidity, saponification, iodine, peroxide and the moisture content significantly, causing pH rise.

The conversion rate in esters of 79.3% is one of the factors for which the physical properties of the methyl esters obtained have values outside the quality standards for biodiesel in the index of acidity and moisture content. The high peroxide index indicates that the initial degree of oxidation is high, and probably antioxidant should be added to the methyl esters to reach the induction period of 6 hours, according to the parameters of quality for biodiesel.

5 ACKNOWLEDGMENTS:

The authors thank the Nuclear Magnetic Resonance Laboratory of the Department of Chemistry of the State University of Maringá for the analysis of ^{1}H NMR.

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Table 1. Acidity, saponification, iodine, and peroxide indexes of frying residual oil after treatment and biodiesel.

Samples	Indexes			
	Acidity (mg KOH g^{-1})	**Saponification (mg KOH g^{-1})**	**Iodine (g I_2/100g)**	**Peroxide (mEq/kg)**
Residual Oil	9.36^{ab} (±0.04)	223.83^{a} (±0.08)	114.24^{ab} (±0.06)	19.33^{a} (±0.06)
Filtered Oil	9.35^{ab} (±0.02)	223.04^{b} (±0.10)	114.18^{ab} (±0.08)	19.17^{b} (±0.05)
Treated Oil	7.85^{c} (±0.02)	178.38^{c} (±0.04)	101.52^{c} (±0.07)	14.46^{c} (±0.03)
Biodiesel	1.14^{d} (±0.04)	163.12^{d} (±0.05)	101.50^{d} (±0.03)	9.59^{d} (±0.03)

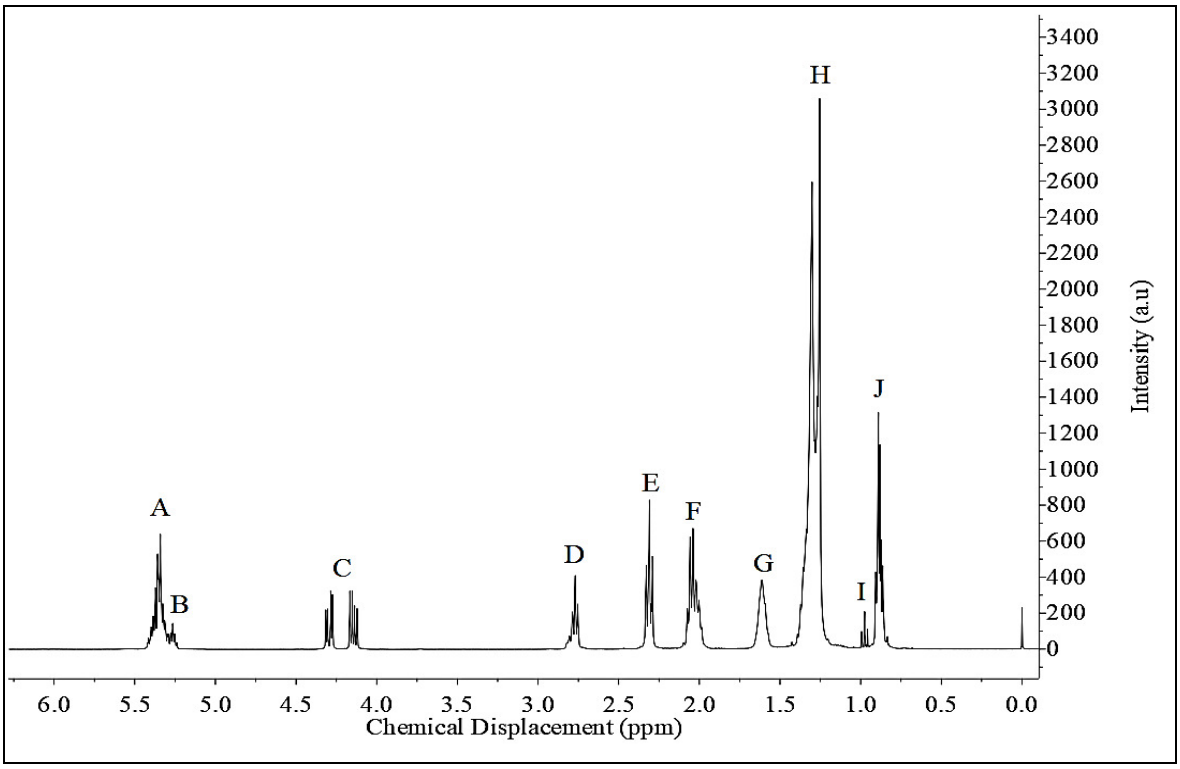

Figure 1. *^{1}H NMR spectra of residual frying oil treated by stream drag method.*

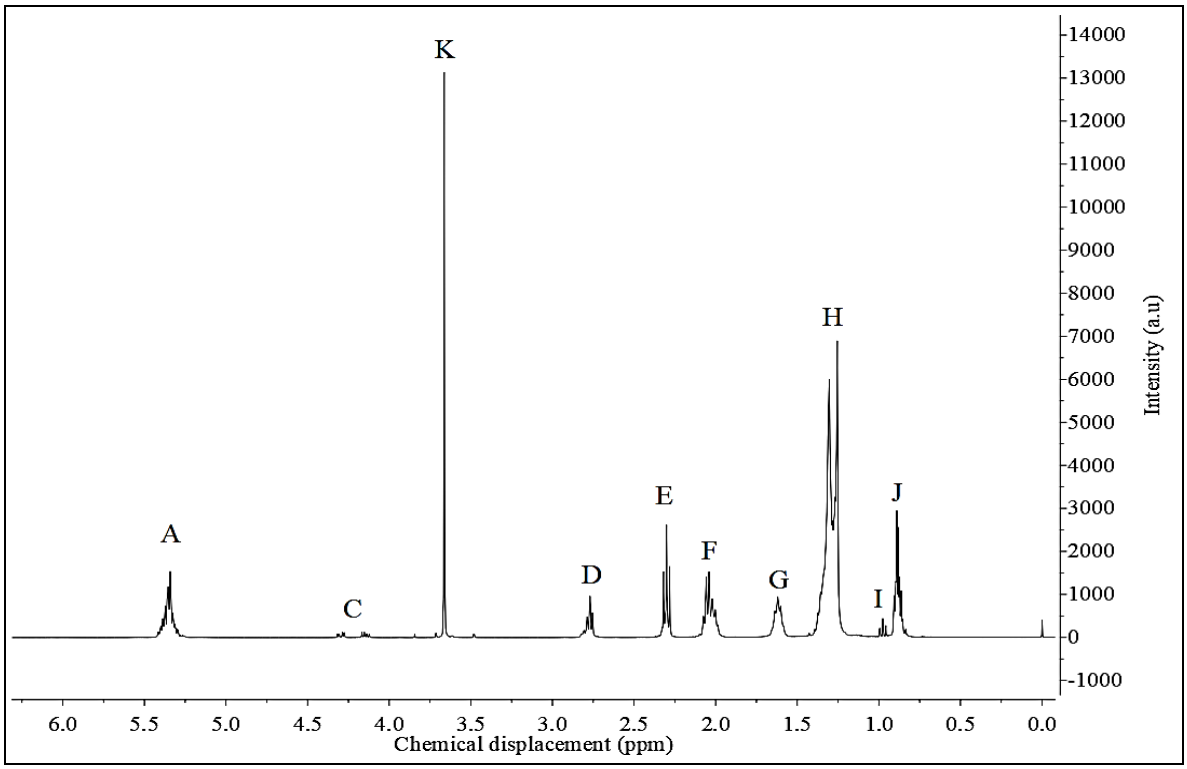

Figure 2. *^{1}H NMR spectra of biodiesel from frying residual oil*

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1. Varma, R. S.; Singh, A. P.; J. Indian Chem. Soc., 1990, 67, 518.

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3. Vidotti, M.; Silva, M. R.; Salvador, R. P.; de Torresi, S. I. C.; Dall'Antonia, L. H.; Electrochimica Acta (2007), doi:10.1016/j.electacta.2007.11.029.

It is recommended to give composite references instead of a list of separate references. The style of composite references is as follows:

4. Varela, H.; Torresi, R. M.; J. Electrochem. Soc. 2000, 147, 665; Lemos, T. L. G.; Andrade, C. H. S.; Guimarães, A. M.; Wolter-Filho, W.; Braz-Filho, R.; J. Braz. Chem. Soc., 1996, 7, 123; Ângelo, A. C. D.; de Souza, A.; Morgon, N. H.; Sambrano, J. R.; Quim. Nova 2001, 24, 473.

Patents

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5. Hashiba, I.; Ando, Y.; Kawakami, I.; Sakota, R.; Nagano, K.; Mori, T.; Jpn. Kokai Tokkyo Koho 79 73,771 1979. (CA 91:P193174v)

6. Kadin, S.B.; US Pat. 4,730,004 1988. (CA 110:P23729y)

7. Eberlin, M. N.; Mendes, M. A.; Sparrapan, R.; Kotiaho, T. Br PI 9.604.468-3, 1999.

Books

With editors

8. Regitz, M. Multiple Bonds and Low Coordination in Phosphorus Chemistry; Regitz, M.; Scherer, O. J., eds.; Georg Thieme Verlag: Stuttgart, 1990, cap. 2.

Without editors

9. Cotton, F.A.: Wilkinson, G.; Advanced Inorganic Chemistry, 5th ed., Wiley: New York, 1988.

Computer programs (software)

10. Sheldrick, G. M.; SHELXL-93; Program for Crystal Structure Refinement; University of Gottingen, Germany, 1993.

Theses

11. Velandia, J. R.; Ph.D. thesis, Federal Rural University of Rio de Janeiro, Brazil, 1997.

Presentations at meetings

12. Ferreira, A. B; Brito, S. L.; Abstracts, 20th Annual Meeting of the Brazilian Chemical Society, Poços de Caldas, Brazil, 1998.

Internet pages

13. http://www.sbq.org.br/jbcs, accessed June 2001. (minimal of information requested)

Unpublished material

For articles accepted for publication: Magalhães, U. H.; J. Braz. Chem. Soc., in press.

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