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Evaluating the use of EN 14078 for determination of biodiesel in diesel blends sold in the Brazilian market

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HIGHLIGHTS

- Biodiesel sold in Brazil uses mixture of raw-materials.
- EN 14978 standard method evaluation for biodiesel determination in diesel blends.
- The use of EN 14978 may be done only when calibrated with the exact biodiesel.
- The use of EN 14978 may be done only when no chemical degradation took place.

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ABSTRACT

In Brazil, the National Agency of Petroleum, Natural Gas and Biofuels (ANP) is a regulatory agency responsible for monitoring the distribution and sale of fuels. After the introduction of biodiesel in Brazil, problems began to emerge as well as questions regarding the quality of diesel fuel in the country. One of the problems is related to the determination of biodiesel content in the diesel available in fuel stations. This work shows that biodiesel prepared from different feedstock during storage suffers oxidative degradation leading to different oxygenated compounds. The presence of these biodiesel oxidation products affects the accuracy of the result provided by the standard method EN 14078 in relation to the content of biodiesel in diesel. The result showed determination errors of almost 100%. Indeed, a B5 blend after accelerated oxidation was determined using EN 14078 as B10. Another problem observed using EN 14078 was that in countries like Brazil, where different oleaginous or alcohol are used to produce biodiesel, it is mandatory to calibrate the method with the same biodiesel present in diesel blends. Indeed, it was observed important changes in the position of the stretching related to the ester carboxyl group according to the raw materials used to prepare the biofuel, leading to significant errors in the biodiesel content determination.

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1. Introduction

Biodiesel was introduced in the Brazilian energy market by government through the Brazilian Program of Production and Use of Biodiesel (PNPB), regulated by the law 11,097 of January 13, 2005 [1]. According to the law, the use of diesel/biodiesel blendwas initially optional up to 2% *v*/*v* (B2), and subsequently increased until the mandatory use of 5% *v*/*v* (B5) in 2013. However, a considerable increase in the production capacity of the biodiesel industry anticipated this goal, and the mandatory use of B5 blends started in January, 2010. An interesting aspect of PNPB was not to have a specific technological route or preferred feedstock.

The first regulation of pure biodiesel (B100) was done by the National Agency of Petroleum, Natural Gas and Biofuels (ANP) in the Resolution ANP 42 of November 24, 2004. This resolution recognizes biodiesel as a mixture of alkyl esters of fatty acids of vegetable or animal origin, and has 27 parameters of quality. Although less extensive than the text of the Federal Law 11,097, this resolution also allows the use of any technology for biodiesel production and any feedstock, not restricting the use of any alcohol or any source of fatty material. This resolution has been reedited since 2004, and currently the resolution ANP 14, from May 11, 2012, is in effect. It should be noted that in all resolutions the definition

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of biodiesel was maintained, as well as the allowance of using any raw-material, being only changed the specifications for the required quality parameters for biodiesel.

The commercial diesel, which after PNPB is a diesel/biodiesel blend, is regulated by resolution ANP 65 of December 9, 2011. Among various quality parameters for commercial diesel, the biodiesel content (BX) shall be in accordance with the law (currently 5% *v*/*v*), with an admitted variation of 0.5%. According to this resolution, the method adopted for the analysis is the European Standard Method EN 14078. This method uses a univariate calibration plot by the height of the C=O bond absorption at 1745 cm^{-1}, setting the base line by a straight line between the points 1820 cm^{-1} and 1680 cm^{-1}. Another standard method described in the resolution for the determination of the biodiesel content in diesel is the Brazilian Standard Method NBR 15568. However, if divergent values occur, the final result is given by EN 14978.

In Brazil, a preferred feedstock for producing biodiesel would not be expected to exist as a result of its vast territory and huge variations in edaphoclimatic conditions. However, soybean oil has a well-structured supply chain and accounts for over 95% of vegetable fats and oils production in Brazil. For this reason, soybean oil has been the main feedstock for the biodiesel industry, corresponding for approximately 80%, as showed in Fig. 1a [2]. It should be noted that at the beginning of the industrial production of biodiesel in Brazil, only soybean, palm-tree and beef tallow had significant market share. After January, 2010, other feedstock, such as cottonseed oil, frying oil, sunflower oil, as well as pork and chicken fats, began to emerge (Fig. 1b). It is possible to depict from Fig. 1b that these alternative materials are increasingly present in the biodiesel production, even with seasonal variations. In addition, it is known by reports that biodiesel is being produced from more than one feedstock in the same batch, for instance, processing a mixture of soybean oil and beef tallow together to achieve a biodiesel that matches the specification regarding Rancimat oxidation stability and cold filter plugging point [3].

Since January, 2010, when B5 became mandatory, a growing claim emerged from the business associations of various segments of the chain of fuels [4]. These complaints reported sludge formation in diesel tanks which were not observed prior to blending biodiesel in fossil fuel. The sludge formation was attributed to microbial or chemical degradation (oxidation) of biodiesel. It was reported that, in addition to a visually observed deterioration, this sludge caused blockage of pipes, filters and pumps [5]. The complaints of fuel entrepreneurs seem appropriate, because the data from the Monitoring Program of the Quality of Liquid Fuels (PMQC, from ANP) [6] show a clear tendency in the increase of nonconformities after the mandatory use of biodiesel. Fig. 2 shows the percentage of non-conformity samples detected by ANP since the creation of PMQC. It is possible to observe a continuous drop in the rate of non-conformity for diesel sold in Brazil after the monitoring program. However, it becomes clear from Fig. 2 that after the addition of biodiesel, which starts with B2 blend in 2008, the rate of non-conformity begins to increase gradually until

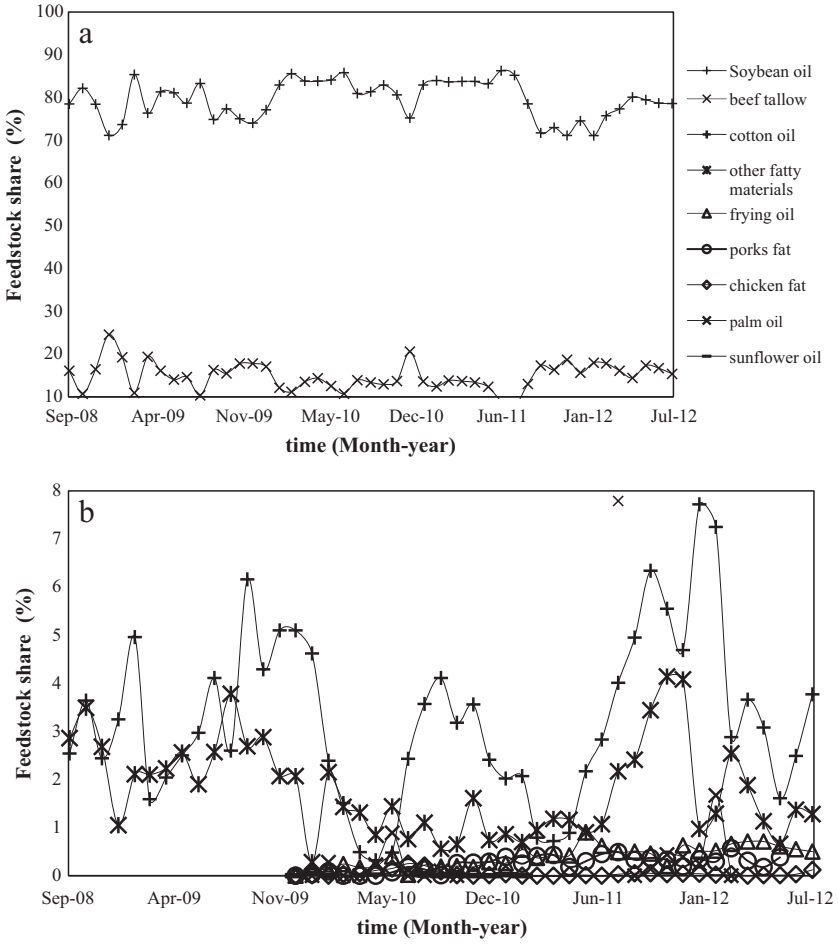

Fig. 1. (a) Percentage of feedstocks used in biodiesel production over time and (b) percentage of feedstocks with a maximum of 8% of contribution used in biodiesel production over time [2].

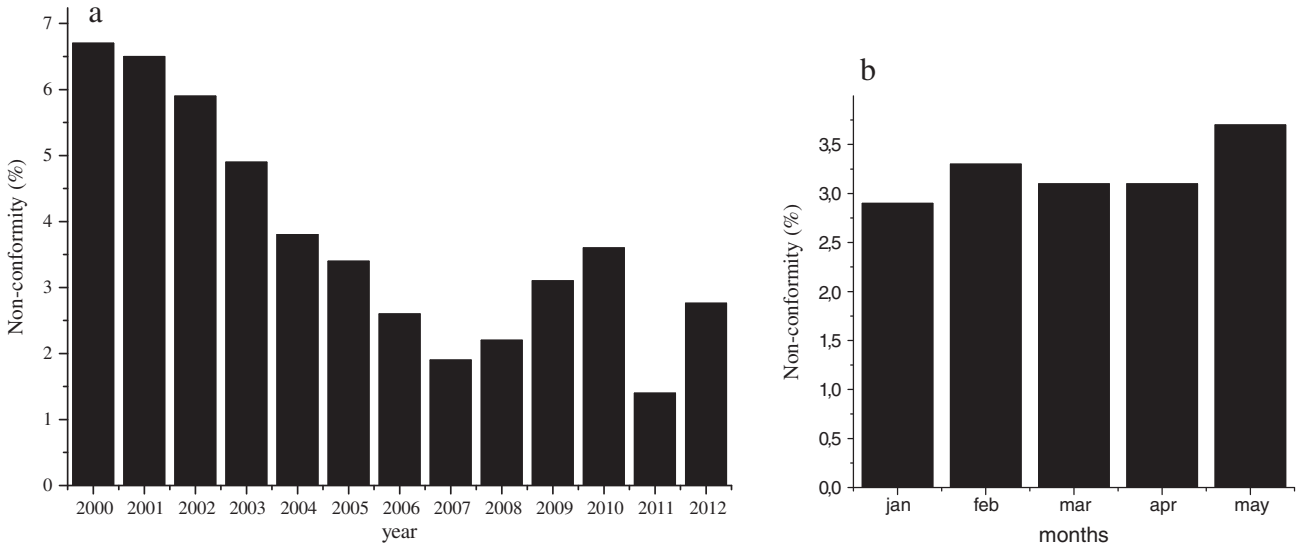

Fig. 2. Content of diesel samples in non-conformity: (a) in 2012 and (b) for the year 2013 (graphics build using data from ANP bulletins available on reference [2]).

2010. Furthermore, it is also shown in Fig. 2b that in 2013 the rate of non-conformity reached the highest value since the biodiesel was introduced in the Brazilian energy market.

In Fig. 3 are shown the amount of samples with unconformities according to the different specification. It becomes clear from this figure that more than the main reason of the unconformities is related to the aspect and the amount of biodiesel in the blend. Note that in 2012 the unconformities related to sulfur content increased significantly because the specification for sulfur content changed during 2012 from 1800 ppm to 500 ppm.

In this context, wherein the national biodiesel is produced from various feedstocks and some reports strongly indicate oxidation problems during storage, this work aims to evaluate if the standard EN 14078 is a suitable method to determine the content of biodiesel in diesel in the Brazilian conditions.

2. Experimental

2.1. Preparation of biodiesel samples

Biodiesel was prepared as described before [7]. The first step was the dilution of potassium hydroxide in alcohol (methanol or ethanol) under constant magnetic stirring. The solution was transferred to a round bottom flask and vegetable oil (castor or soybean oil) was added. The reaction medium was kept under continuous stirring for 2 h at 40 °C. Then, the stirring was stopped and a two phase system was obtained: an upper layer containing fatty acid esters and a bottom one containing glycerin, which were easily separated by decantation. The final product was obtained after neutralization with a 5% phosphoric acid solution, followed by washing with distilled water until neutral pH was achieved in the aqueous phase. The product was subjected to a new reaction until the content in methyl or ethyl esters was greater than 96.5% in order to achieve ANP specification for B100. The composition of the biofuel was determined by high performance liquid chromatography (HPLC) according to the method described before [7].

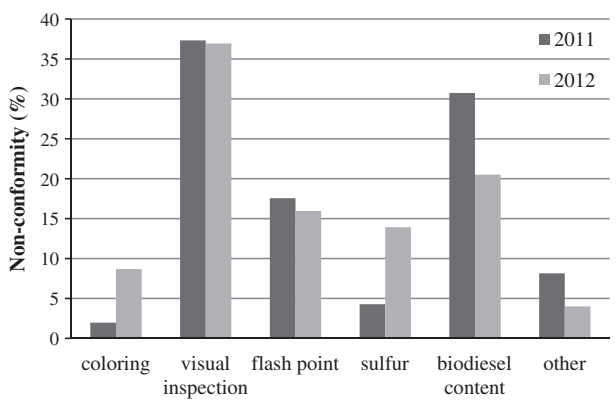

Fig. 3. Amount of samples with unconformities according to the different specification (graphics build using data from ANP bulletins available in Ref. [2]).

2.2. Preparation of B5 blends

The synthesized biodiesel samples were used in the preparation of different blends with diesel S500 (pure diesel containing 500 ppm of sulfur), gently granted by COPAPE (Guarulhos-SP). Four B5 blends were prepared according to EN 14078 using ethyl and methyl biofuels obtained from soybean oil and castor oil.

2.3. Aging of the blends using method ASTM D 5304-06

The aging of the blends and of B100 was performed by accelerated oxidation using an adapted procedure from the oxidation stability standard method described in ASTM D 5304-06. According to this method, the sample is placed inside an autoclave, pressurized with oxygen (8 atm) and kept standing at 90 °C for 16 h. In this work this procedure was performed in the presence of a cupper bar inside the autoclave because during the storage and commercialization of the diesel/biodiesel blends in the fuel station several components that are in contact to the fuel contains this metal, such as check valves and inline filters [8,9].

2.4. Determination of biodiesel content in diesel by infrared

The determination of biodiesel content in the blends was performed according to EN 14078 standard method. The spectra were obtained on an infrared spectrometer with Fourier transform (FT-IR) from Shimadzu model IR-Prestige-21, with a wave number

range from 400 to 4000 cm^{-1}, a resolution of 4 cm^{-1} and absorbance from 0.1 to 3.8 absorbance units. The sample was placed in a cell with KBr windows, with 0.5 mm optical path, and each spectrum was obtained from the average of 32 scans, using cyclohexane as reference.

2.5. Determination of biodiesel content in diesel by GC–MS–SIM

The content of biodiesel in the B5 blend prepared with soybean methyl esters, in particular, was also determined by gas chromatography coupled to mass spectrometry using selected ion monitoring mode (GC–MS–MSI) according to the method developed and validated by Faria and co-workers [10]. B5 sample obtained from soybean methyl esters was analyzed before and after aging by ASTM method D 5304-06.

GC–MS analyses were performed in a Hewlett Packard 6890 gas chromatography coupled to a Hewlett Packard 5973 MSD Instrument (Agilent Technologies, Avondale, USA) with electron impact ionization (70 eV ionization energy). A DB-1 HT capillary column (J&W, USA) with a 0.25 mm internal diameter, 12 m and 0.10 μm phase film diameter was used. The carrier gas was helium at a flow of 1.7 mL min^{-1}. The temperature program was 80 °C to 150 °C at a rate of 10 °C min^{-1}, then increased to 180 °C at a rate of 5 °C min^{-1} and finally to 300 °C at a rate of 25 °C min^{-1} with a final isothermal period of 5 min. The injector and interface temperatures were held at 290 °C and 300 °C, respectively, and the run time was 22.8 min. The sample volume of 1.0 μL and the split mode with a ratio of 1:20 was used.

Calibration graph in SIM mode was built up in a range from 1.5% to 7.5% *w*/*v* of biodiesel in diesel using pentadecanoylpropanoate as internal standard (IS). The samples were analyzed in SIM mode for quantification measurements. SCAN mode was used in the mass range of 40–500 u for confirmation of the spectral data. Table 1 presents the retention times, according to the temperature program used, and the characteristic fragments selected for qualitative and quantitative determinations.

The samples for analyses were prepared in a vial by the addition of 50 μL of B5, 100 μL of a 2170 mg L^{-1} internal standard solution and completed to 510 μL with ethyl acetate solvent.

2.6. Analysis of soybean methyl esters (B100) by GC–MS

A sample of soybean methyl esters (B100), in particular, was analyzed by GC–MS before and after aging by ASTM method D 5304-06. A solution of approximately 4000 mg L^{-1} was prepared by dissolving 20 mg of B100 in 5 mL ethyl acetate solvent. 1 μL of the solution was injected in a Hewlett Packard 6890 gas chromatography coupled to a Hewlett Packard 5973 MSD Instrument (Agilent Technologies, Avondale, USA) with electron impact ionization (70 eV ionization energy), using the same column described in Section 2.5. The carrier gas was helium at a flow of 1.2 mL min^{-1}. The temperature program was 100 °C to 140 °C at a rate of 5 °C min^{-1} and with a isothermal period of 5 min at 140 °C, then increased to 200 °C at a rate of 5 °C min^{-1} and finally to 280 °C at a rate of 15 °C min^{-1}. The injector and interface temperatures were held at 290 °C and the run time was 30.3 min. The split mode with a ratio of 1:20 was used. SCAN mode was used in the mass range of 40–500 u.

Table 1
Retention time (t_R) and selected characteristic ions (ions for quantitative analysis in bold).

Compounds	t_R (min)	Characteristic ions (*m*/*z*)
Pentadecanoylpropanoate	9.0	182/210/**255**
Methyl linoleate	10.1	220/262/**263**

3. Results and discussion

3.1. Determination of biodiesel content in diesel by infrared (EN 14078)

Initially, a calibration plot (Fig. 4) was built using standard solutions with known concentrations of biodiesel in cyclohexane as determined by EN 14078 and presented linear correlation coefficient of 0.9996. It is important to highlight that the network of laboratories that participate of the PMQC performs the standardization using the same reference sample, distributed by ANP for all laboratories, usually soybean oil methyl esters. Thus, to be as close as possible to the real analysis routine in Brazil, this single calibration plot was used for all determinations in this work, independent of the biodiesel feedstock or aging process.

Next, the content of biodiesel in the B5 blends was determined by the standard method EN 14078 using the calibration graph. Fig. 5 shows the FT-IR spectra in the region between 1820 and 1680 cm^{-1} for B5 blends prepared with the four types of biodiesel synthesized. It can be seen at Fig. 5 that changing the alcohol for both oilseed, it alters both the position of the wave number that has the maximum absorption band related to the C=O stretching of the ester as the maximum value of absorbance. Changing the oleaginous, the maximum absorbance value shifts for both alcohols. This value is lower for both methyl and ethyl biodiesel obtained from castor oil. The explanation for these two variations is quite simple. The variation of the position of the maximum absorption with the change of methyl to ethyl radical is probably a result of the increased donation of electronic density by ethyl substituent. The observed difference in maximum absorbance between samples of methyl or ethyl biodiesel from castor oil and soybean oil is probably a consequence of the variation of the molar concentration existent due to the presence of a hydroxyl group in the chain of the majority ester of castor oil (methyl ricinoleate) or due to the presence of one more methylene in the alkoxy group.

As describe by EN 14078, to calculate the concentration of biodiesel in diesel should be considered the baseline between 1820 and 1680 cm^{-1} and the maximum absorption should be collected at 1745 cm^{-1} (this wavenumber was market by a vertical line in Fig. 5). Although the four samples have been prepared with the same percentage *v*/*v* concentration, the absorbance value will not be the same, as would be observed for B5 samples obtained from identical starting material. The main consequence of the differences observed in the position of the maximum absorbance, as well as the value of the maximum absorbance itself, is an apparent dependence on the calculated biodiesel content and the feed stock used for biodiesel production. Indeed, the biodiesel content in these four blends are shown in Table 2. It is worth mentioning that the calculation of the content of biodiesel using a calibration plot built up using soybean methyl esters leads to dramatic analysis errors when used with other biodiesel, much higher than the 0.5% allowed by ANP 14 of May, 2012 resolution.

In sequence, a B5 blend of soybean methyl esters was aged by accelerated oxidation in the presence of cupper and Fig. 6 shows the spectrum of the sample after aging. The determination of biodiesel content in this sample by EN 14078 before and after the aging procedure gave the value of 4.7% and 9.6% of biodiesel in diesel, respectively. Comparing the spectra shown in Figs. 5 and 6, it is observed the presence of a broad absorbance in the region of C=O stretching after aging, which seems to be the result of many overlapping bands. Probably, these bands are related to the presence of degradation oxygenated products obtained from

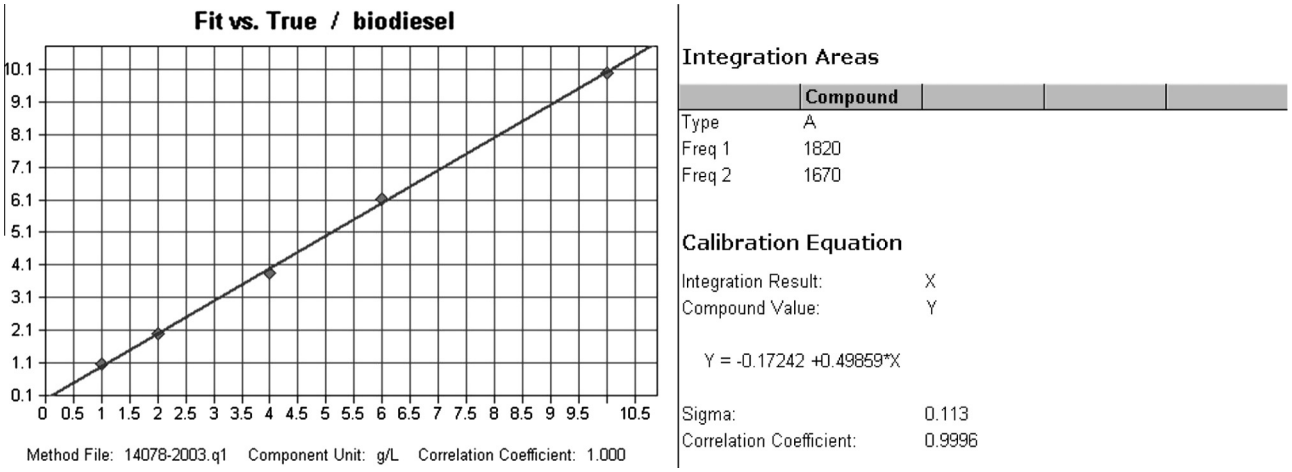

Fig. 4. Calibration graph for soybean methyl esters by EN 14078 standard.

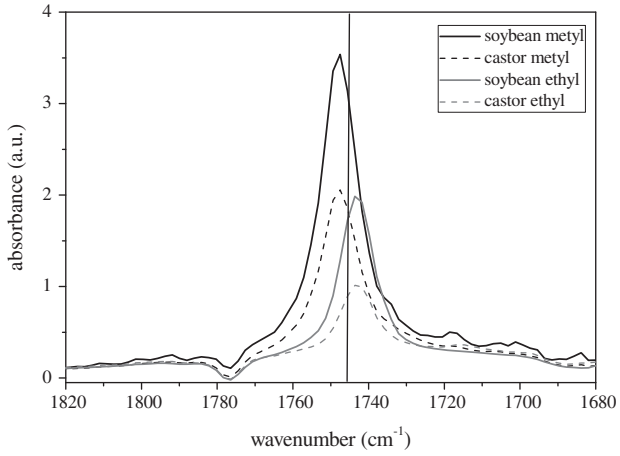

Fig. 5. Infrared spectrum emphasizing the region of C=O stretching for B5 blends using four different biodiesels.

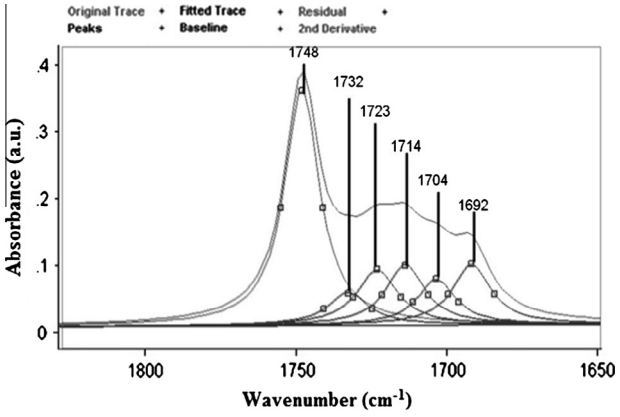

Fig. 6. Infrared spectrum of a Brazilian diesel/biodiesel blend, emphasizing the region of C=O stretching.

Table 2
Biodiesel content in diesel determined by EN 14078 for B5 blends prepared with 4 different biodiesels.

Biodiesel	Real % *v*/*v*	Experimental % *v*/*v*
Soybean methyl esters	5.0	4.7
Soybean ethyl esters	5.0	2.7
Castor methyl esters	5.0	3.0
Castor ethyl esters	5.0	2.2

Table 3
Results of analysis by GC–MS–SIM.

Calibration equation	$\boldsymbol{Y} = 0.8655\boldsymbol{X} + 0.6054$
R^2	0.9847
Content of biodiesel in diesel	
B5 before aging	4.8%
B5 after aging	1.9%

Y = methyl linoleate area/internal standard area.
X = methyl linoleate concentration/internal standard concentration.

the oxidation of C=C bonds present in unsaturated compounds of biodiesel and diesel.

It is noteworthy that an infrared spectrum does not show isolated absorptions for each phenomenon of absorption that occurs in the sample, but the sum of all of them. Considering each phenomenon of absorption as a Gaussian (band), the absorbance value at a particular wavenumber is the sum of the height of each Gaussian in this position. The deconvolution tool of program Grams AI was used for an approximate determination of absorbance of each band at wave number 1745 cm^{-1}, using the Gaussian analysis process. During the process of deconvolution, the number of bands expected to be found was randomly chosen. This procedure was repeated until find the Gaussian that after the corresponding sum generated a spectrum identical to the original one. The result can be seen in Fig. 6, which shows that the broad absorbance in C=O region of the infrared spectrum after the test of oxidative stability is the result of the sum of different bands related to various degradation products containing C=O bonds. A new determination of biodiesel in the aged blend was done considering only the band related to the ester group. The band has a maximum near 1745 cm^{-1} and 4.6% of biodiesel in diesel was found. This result is close to 4.7%, which was the value found before aging.

3.2. Determination of biodiesel content in diesel by GC–MS–SIM

The content of biodiesel in B5 blend prepared from soybean methyl esters was also determined by GC–MS–SIM before and after the aging procedure. Table 3 presents the calibration equation and

Table 4
Composition of B100 sample before and after the aging procedure.

t_R (min)	Ester	Area %	
		$B100_{before}$	$B100_{after}$
9.1	Methyl 9-oxo-nonanoate	ND	0.1
14.3	Methyl 10-oxo-8-decenoate	ND	<0.1
19.4	Methyl tetradecanoate	0.1	0.1
23.8	Methyl hexadecenoate	0.1	0.1
24.4	Methyl hexadecanoate	13.1	14.6
26.2	Methyl heptadecanoate	0.1	0.1
27.1	Methyl octadecadienoate	50.5	45.4
27.2	Methyl octadecenoate	30.2	32.2
27.5	Methyl octadecanoate	5.3	6.0
29.1	Methyl eicosenoate	0.2	0.5
29.3	Methyl eicosanoate	0.4	0.8

ND: not detected.

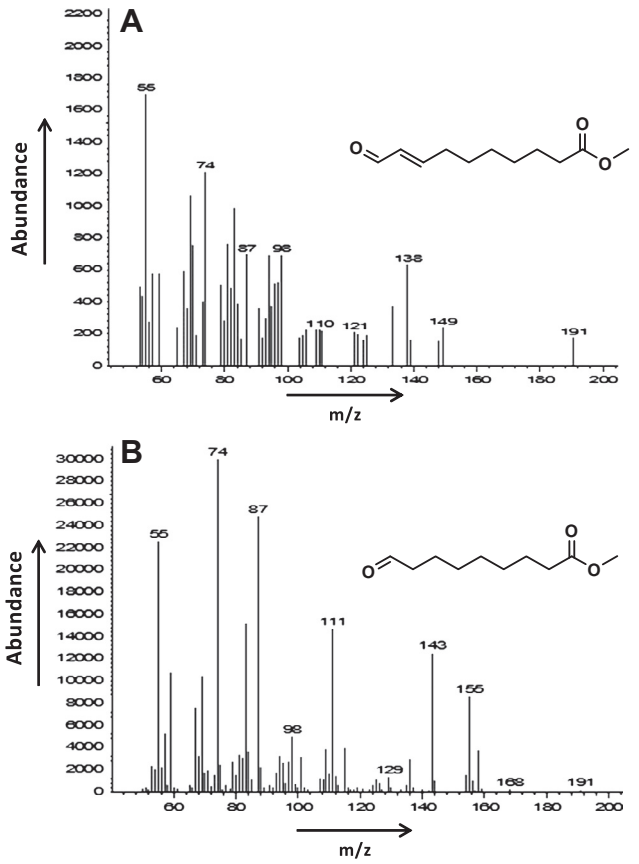

Fig. 7. Mass spectra of oxidation products: (A) methyl 10-oxo-8-decenoate; and (B) methyl 9-oxo-nonanoate.

the R^2 value of the calibration graph built in this method and the content of biodiesel in diesel before and after the aging procedure.

According to GC–MS–SIM analysis, the B5 blend prepared from soybean methyl esters presented 4.8% of biodiesel. After aging, the biodiesel content was reduced to 1.9%, different from the value obtained by IR analysis that showed an increase of biodiesel content to 9.6%. The result obtained by GC–MS–SIM highlights the degradation of methyl esters in the blend after aging, since the method is based on quantification of methyl linoleate ester, through the ion m/z 263. Thus, the method provides another information that enhances the occurrence of carbonyl bands originated from oxidation products, as well as the band of C=O bond from biodiesel methyl esters.

3.3. Analysis of soybean methyl esters (B100) by GC–MS

The objective of the analysis of B100 by GC–MS before and after the aging procedure was to identify evidence of oxidation products from biodiesel. Table 4 lists the identified compounds, their retention times and area percentage.

The results show a reduction of 10% in area of methyl linoleate content after sample aging. In addition, two products formed by oxidation of the double bond of methyl linoleate were identified: methyl 10-oxo-8-decenoate and methyl 9-oxo-nonanoate. Fig. 7 shows the mass spectra of these oxidation products.

The mechanism of lipid peroxidation is well described in the literature [11]. The hydroperoxides are unstable and form a variety of secondary oxidation products including aldehydes and short chain fatty acids. Each hydrocarbon chain cleavage in a C=C bond leads to the formation of two aldehyde molecules. This means that for the oxidation of one molecule of methyl oleate, for example, two additional carbonyl groups are generated. Thus, the oxidation products maintain the C=O bond related to the ester in their structures and incorporate C=O bond of aldehyde derived from oxidative degradation. The increase of C=O bonds in the blend of fuel raises the number of bands in the region 1680–1820 cm^{-1} in IR spectrum and, consequently, leads to the increase of the maximum absorption at 1745 cm^{-1}. This effect causes an increase of biodiesel content in the blend that is not real, but it is a strong indication of degradation of the fuel.

4. Conclusion

EN 14078 is widely used in Brazil to determine biodiesel content in diesel/biodiesel blends, but it can be subject to misinterpretation arising from several causes. In fact, the method seems to be quite accurate and precise when applied to a single feedstock. However, for a biofuel market where different feedstocks are used, as is the case of Brazil, the exact composition should be known to perform an appropriate calibration graph, which is almost unfeasible because of the peculiarities in the Brazilian biodiesel market. Moreover, one should be sure that the sample did not suffer oxidation during transportation or storage prior to use EN 14078 because the oxygenated compounds produced during the degradation of biofuel will affect the accuracy of the result.

Possibly, due to the characteristics of the Brazilian biodiesel program PNPB, the most appropriate method to be used in the determination of biodiesel content in diesel cannot consider only one variable, as used by EN 14078. Multivariate methods that use PLS and neural networks, have shown to be able to accurately determine not only the content of biodiesel as well as the type of feedstock used in its production [12]. Indeed, we believe that due to the characteristics of biodiesel production and use policies in Brazil, the country may need to develop its own standard methods, probably different from the one used in Europe and in the United States where there is homogeneity of feedstock.

Acknowledgements

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References

[1] Pousa GPAG, Santos ALF, Suarez PAZ. History and policy of biodiesel in Brazil. Energy Policy 2007;35:5393–8.
[2] http://www.anp.gov.br/?pg=65538&m=biodiesel&t1=&t2=biodiesel&t3=&t4=&ar=0 &ps=1&cachebust=1368284671630 [accessed 15.07.14].
[3] http://jcrs.uol.com.br/site/noticia.php?codn=151139 [accessed 15.07.14].
[4] http://www.fecombustiveis.org.br/blogs/direto-da-redacao/fecombustiveis-mantem-posicionamento-sobre-biodiesel.html [accessed 15.07.14].

[5] http://www.fecombustiveis.org.br/images/stories/relatorio2011/pdf/relatorio fecombustiveis11.pdf [accessed 15.07.14].
[6] http://www.anp.gov.br/?pg=65402&m=pmqc&t1=&t2=pmqc&t3=&t4=&ar=0&ps=1 &cachebust=1405454216189 [accessed 15.07.14].
[7] Carvalho MS, Mendonça MA, Pinho DMM, Resck IS, Suarez PAZ. J Braz Chem Soc 2012;23:763–9.
[8] http://zeppini.com.br/produtosInterna.asp?id=11&i= [accessed 15.07.14].
[9] http://www.zeppini.com.br/produtosInterna.asp?id=24&i=I [accessed 15.07.14].
[10] Faria RCM, Rezende MJC, Rezende CM, Pinto AC. Desenvolvimento e validação de metodologia de análise de misturas biodiesel:diesel utilizando cromatografia gasosa-espectrometria de massas. Quim. Nova 2007;30:1900–5.
[11] Schneider C, Porter NA, Brash AR. Routes to 4-hydroxynonenal: fundamental issues in the mechanisms of lipid peroxidation. J. Biol. Chem. 2008;283: 15539–43.
[12] Oliveira JS, Montalvão R, Daher L, Suarez PAZ, Rubim JC. Determination of methyl ester contents in biodiesel blends by FTIR-ATR and FTNIR spectroscopies. Talanta 2006;69:1278–84.