AN INTERFERENCE FREE ABSORPTION IN THE MID-INFRARED TO FOLLOW THE OBTAINING OF BIODIESEL BY TRANSESTERIFICATION OF WASTE FRYING OILS

ABSORCIÓN LIBRE DE INTERFERENCIAS EN EL INFRAROJO MEDIO PARA SEGUIR LA OBTENCIÓN DE BIODIESEL POR TRANSESTERIFICACIÓN DE DESECHOS DE FRITURAS

Isabel Cristina Castellanos[1*], Eliseo Avella Moreno[2], Paula M. Vargas Molina[1] and Andres M. Bejarano[1]

[1] Grupo Ciencias Básicas, Facultad de Ingeniería, Universidad EAN, Colombia.
[2] Grupo APRENA, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Colombia.

(Recibido: 02/2023. Aceptado: 04/2023)

Abstract

To trace the production of biodiesel in a base-catalyzed transesterification of waste frying oils and methanol, mid-infrared spectra were acquired by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) of the organic phases isolated from the reaction medium at 0, 5, 15, 30, and 60 minutes from the start of the process and analyzed qualitatively in comparison with the IR spectrum of the waste oil in its initial condition. Among all the signals or regions of the infrared spectrum proposed by other authors as suitable for monitoring the biodiesel content in blends, which were indeed observed in these ATR-FTIR spectra, the signal at 1195 cm^{-1}, attributable to the stretching of the bond between sp^2 carbon and oxygen in methyl carboxylate -(CO)-OCH_3 resulted in the most suitable signal to follow the biodiesel production in the reaction medium through the IR spectrum of the corresponding isolated organic

---

* iccastellan@universidadean.edu.co

doi: https://doi.org./10.15446/mo.n67.107249

phase. The signal at 1195 cm^{-1} appeared only in the infrared spectra of the organic phases containing some biodiesel, and its intensity increased steadily during the reaction. For the rest of the signals proposed in previous publications as useful for quantifying biodiesel in mixtures, it was demonstrated, by these infrared spectra, that there is interference by signals attributable to species, other than biodiesel, present in the mixture.

Keywords: biofuel, biodiesel, infrared-spectroscopy, transesterification, vegetable oils.

Resumen

Con el fin de rastrear la producción de biodiesel en una transesterificación catalizada por base de aceites usados de fritura y metanol, se adquirieron los espectros en el infrarrojo medio por reflectancia total atenuada con transformada de Fourier (ATR-FTIR) de las fases orgánicas aisladas del medio de reacción a los 0, 5, 15, 30 y 60 minutos desde el inicio del proceso y se analizaron cualitativamente en comparación con el espectro IR del aceite usado en su condición inicial. Entre todas las señales o regiones del espectro infrarrojo propuestas por otros autores como adecuadas para monitorear el contenido del biodiesel en mezclas, que efectivamente se observaron en estos espectros ATR-FTIR, la señal a 1195 cm^{-1}, atribuible al estiramiento del enlace entre el carbono sp^2 y el oxígeno en el carboxilato de metilo, $-(CO)-OCH_3$, resultó la señal más adecuada para seguir la producción de biodiesel en el medio de reacción a través del espectro IR de la correspondiente fase orgánica aislada. La señal a 1195 cm^{-1} apareció únicamente en los espectros infrarrojos de las fases orgánicas que contenían algo de biodiesel, y su intensidad aumentó de manera regular en el curso de la reacción. Para el resto de señales propuestas en publicaciones anteriores como útiles para cuantificar el biodiesel en mezclas, se demostró, por estos espectros infrarrojos, que existe interferencia por señales atribuibles a especies, distintas al biodiesel, presentes en la mezcla.

Palabras clave: biodiesel, espectroscopía infrarojo, transesterificación, aceites vegetales.

Introduction

The extraction of petroleum and the production of petroleum derivatives from increasingly large heavy crude, reserves pose additional issues to the current problems that have already been proven with the pollution of the air due to combustion. The commercial value of fossil fuels does not always reflect, and does not usually cover. The costs of the disastrous impacts of their use on health and environment [1]. These impacts range from air and water pollution [2] to the emission of hazardous chemical species in the fuel combustion-explosion process in engines, such as sulfur dioxide (SO_2) that participates in the generation of acid rain and in the promotion of corrosion processes [3].

Biodiesel is a liquid biofuel that is obtained, ideally, by the transesterification of triacylglycerol with methyl or ethyl alcohol. In order to propose the biodiesel as a substitute of fossil fuels and as an alternative to reduce traditional diesel consumption, several processes have been developed for its production, such as: transesterification of waste cooking oil [4], [5], or interesterification of vegetable oil and small esters [6] or biocatalysts [7], which currently propose biodiesel as an alternative to reduce traditional diesel consumption, that is, as a substitute for fossil fuel.

The use of biofuels has a justified opposition. The fear of the deforestation and soil deterioration, due to the monoculture of the vegetable raw materials used in biodiesel production, are among the first reasons. In addition, there has been an increase in the prices of fats and edible oils, that could threaten food security, if these are transformed into high interest inputs to the biodiesel industry, which is looking to meet the growing demand for energy [8]. Finally, the unfavorable environmental effects by carbon footprint that result from the combustion of biodiesel (instead of diesel): Because biodiesel, generates less amount of energy and higher contamination by CO_2 and CO per unit mass [9].

However, it is currently recognized that using biofuels is a favorable alternative to mitigate the pressure that is exerted by prices and by the shortage of oil reserves, and to give some treatment to the appreciable quantities of waste frying oils [10]. Therefore, as a contribution to sustainability, it seems indispensable to look for methodologies that take advantage of instrumental analytical techniques (as this work does with infrared spectrometry) so as to improve the ways of monitoring the production processes, and the quality of the biodiesel and the commercial mixtures made with this and with petroleum diesel or other fuel materials. This is in order to ensure high yields in the processes and good quality of the resulting products for the benefit of the industrialists, the consumers, and government agencies who are interested in or in charge of the control and quality assurance of the biodiesel and of the combustible mixtures that are made with some biodiesel fraction.

The main purpose of this work was to determine the signals in the ATR-FTIR spectrum of the organic phases isolated from the base-catalyzed reaction medium of transesterification of waste frying oils and methanol. These signals could provide the best indication of biodiesel production based on their signal intensity, with minimal interference from other species in the mixture. Additionally, these signals could be used to monitor the production or presence of biodiesel in mixtures containing it. Although we have already conducted investigations in that regard, this work does not intend to present a formal analytical method for the quantitative determination of biodiesel in mixtures at this stage.

Material and Methods

Material

Methanol (CH_3OH, $\geqslant$ 99.9 wt %) and sodium hydroxide (NaOH, $\geqslant$ 99 wt %), analytical grade reagents purchased from Merck. The waste cooking oil was collected from a local restaurant in Bogotá, Colombia. The oil was tested for acidity by directly titrating the oil in hot ethanol against standard sodium hydroxide solution 0.1 M, using phenolphthalein as acid-base indicator.

Experimental Procedure and Analysis

The biodiesel was obtained by transesterification in one-step [11], catalyzed with NaOH of waste cooking oils and methanol. The transesterification of used cooking oil and methanol, at oil/methanol ratio 5:1 by volume, was carried out into each one of five identical laboratory assemblies constituted of a 250 mL flat bottom flask, a bulb condenser (Allihn type), and a DLAB MS7-H550-Pro hotplate provided with magnetic stirring and a PT 1000 sensor that controls temperature within ± 0.2 ^{0}C. Each reaction was carried out under identical conditions (atmospheric pressure, 60 ^{0}C, and 9.5 g NaOH/L oil, at ratios of 7 g/L, as a catalyst, and 2.5 g/L as neutralizer of the oil acidity that was determined by titration with NaOH). The NaOH(s) dissolved into methanol was slowly added to the used cooking oil, which was preheated at 60 ^{0}C, and the reaction medium was maintained with constant stirring at that temperature for one hour. The reaction was stopped by suspension of heating at the 0, 5, 15, 30, and 60 minutes after the addition of the NaOH to each one of five different laboratory assemblies, respectively. The reaction mixture was allowed to cool and, after eight hours of cold rest in a separatory funnel, the phases (organic and aqueous) were separated.

The analysis was performed with a Shimadzu IRTracer-10 instrument with a DLATGS detector (deuterated L-alanine doped triglycene sulphate), a midinfrared (IR) source, and a single-refection attenuated total reflectance (ATR) zinc selenure (ZnSe) crystal. All spectra were recorded in the range of 340 cm^{-1} - 4700 cm^{-1}, with a spectral resolution of 2 cm^{-1} and 32 scans. The measurement of the background spectrum was performed before each analysis. The LabSolutions IR Data Collection Program was applied to record. All processing was made using Spectragryph program [12].

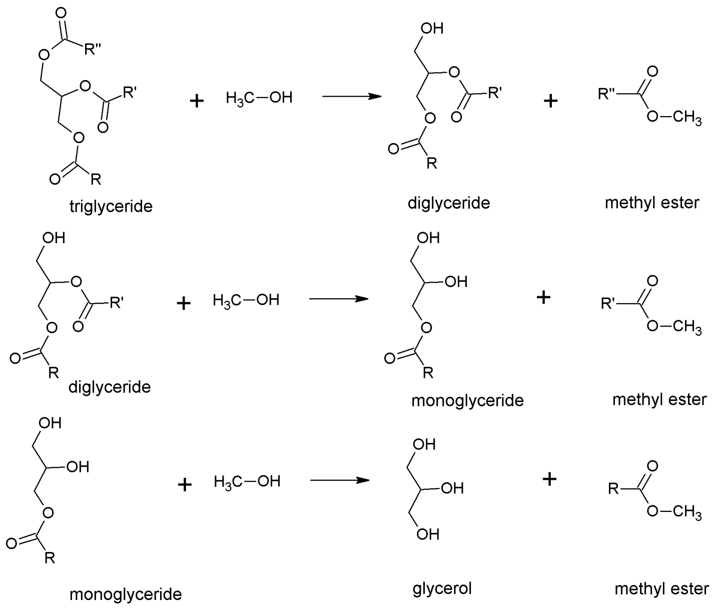
Results and discussion

The possibility of making better use of disposable waste frying oils for the production of biodiesel is not only an alternative for treating residual edible oils but also a real economic opportunity for the industry. Overcoming the challenge of obtaining biodiesel from these used oils, which constitute a raw material with various properties different from those of the refined oils they originate from, presents an appropriate contribution to the preservation of human health and the ecology of the planet. Among the considerable properties of such used cooking oils to obtain the biodiesel, the acidity is of particular importance [13]; therefore, it requires previous quantification because it determines the amount of catalyst (NaOH) that is advisable to set out in the reaction medium. In order to neutralize the acidity of the used cooking oil that was submitted to transesterification, it was necessary to use 2.5 g NaOH/L. Obtaining biodiesel from used cooking oil involves the consecutive excision of triglycerides, to diglycerides, to monoglycerides, and finally to glycerol and the production of methyl esters, each leaving acyl group by substitution of the alkoxyl fragments in the triacylglyceride by the methoxyl group of the methanol (Scheme 1).

Dark yellow, water-immiscible organic phases were separated from the reaction medium after 15 minutes of transesterification process. At lower reaction times, the coloration of the organic phase was clearer and the liquid appearance was noticeably more viscous. The biodiesel that was obtained from the separated organic phase at the end of each process time was analyzed by ATR-FTIR (Figures 1,2,3, Scheme 1).

Analyzes based on the infrared spectrum of reaction systems for obtaining biodiesel (from other raw materials), or blends of biodiesel-oil, or biodiesel-oil-diesel were found in, previously published works (Table 1); However, this is the first time that the signals of the spectrum in the MID-IR of the organic phase, isolated from the transesterification medium of used cooking oil in the obtaining of biodiesel, are studied with this degree of detail searching for the most adequate signals in order to follow the production of the biodiesel in the process.

The ATR-FTIR spectra of the organic phases with some content of biodiesel produced in the reaction and of the used cooking oil



Scheme 1: *Generalized sequence of reactions in obtaining biodiesel.*

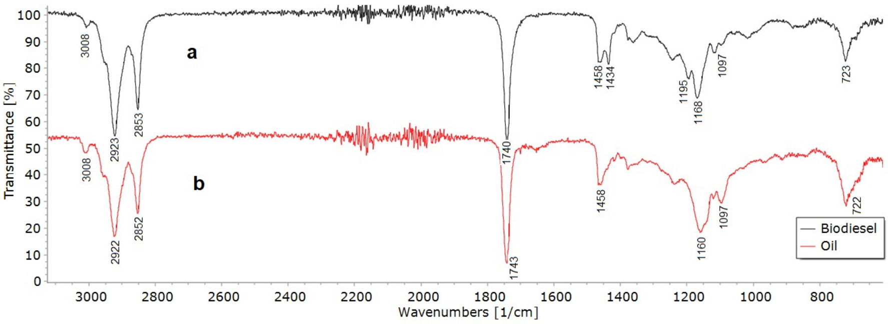


FIGURE 1. *ATR-FTIR spectra (Shimadzu IRTracer-100, ATR - ZnSe, 340-4700 cm^{-1}, 32 scans, spectral resolution of 2 cm^{-1}) of a) obtained biodiesel in the transesterification and b) disposable frying oil waste used as raw material.*

without reacting (Figure 1), showed a small absorption band at 3007 cm^{-1}, attributable to the stretching of the C-H bond of sp^2 carbons (R-CH=CHR-), another band at 722 cm^{-1} corresponding to the flexion out of the H-C-C planes in normal alkyl fragments with four or more adjacent; several bands at 2800 - 3000 cm^{-1} attributable to

Reference	Wavenumbers	Analysed sample
[14]	1743 1712	Free fatty acids in rice.
	1425-1447 1188-1200	Biodiesel blends - soybean oil.
	1700-1800 1573	Free fatty acids from salmon skin oils used for biodiesel production.
[15]	1378	Production of biodiesel from waste canola oil.
[16]	1500-1060	Production of biodiesel from Cynara cardunculus, cotton, sunflower, and sesame seeds.
[17]	3707-8140	Ethyl esters obtained from soybean oil.
[18]	1098, 1746	Biodiesel blends-soybean oil.
[19]	2746-3165 650-1909	Biodiesel blends-soybean oil.
[20]	1745	Diesel blends - biodiesel (without considering interference by residual vegetable oil).
[21]	1745	Ethyl esters obtained from soybean oil.
[22]	3699-2974 1841-925	Diesel blends - biodiesel

TABLE 1. *Signals of the IR spectrum proposed in the literature for composition analysis of systems containing biodiesel.*

the stretching of the methylene groups CH_2, and an intense band due to the stretching of the C=O bond in the carboxylate groups of the triglyceride and of the methyl ester, at 1743 cm^{-1} for the vegetable oil, and in 1740 cm^{-1} for the biodiesel, respectively. As expected for the esters [23], it was possible to observe the absorption

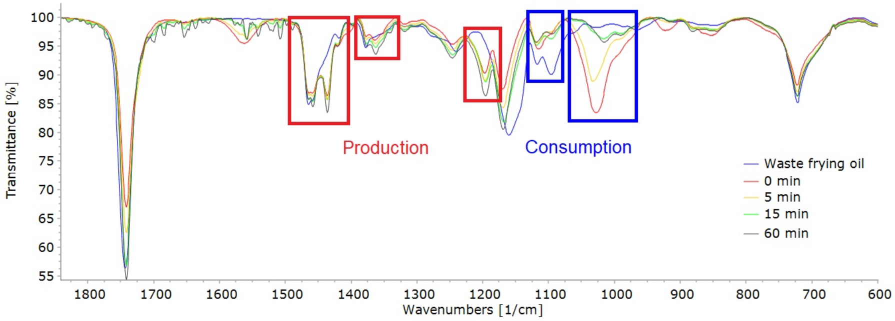


Figure 2. *Overlapped whole ATR-FTIR spectra (Shimadzu IRTracer-100, ATR - ZnSe, 340 - 4700 cm^{-1}, 32 scans, spectral resolution of 2 cm^{-1}) of the waste frying oils and the organic phases containing biodiesel isolated from the reaction medium at five different process times. Expanded regions of these IR spectra evidencing Production (1100 - 1500 cm^{-1}), and Consumption of species (1200 - 920 cm^{-1}) in the reaction mixture during the process.*

bands due to the stretching of the C-O bonds of the sp^2 carbon of the carboxylate groups, O=C-O, at 1100 - 1200 cm^{-1} in the IR spectrum of biodiesel [24]. In the same region where Ault and Pomeroy [18] registered the appearance of the band assigned to the stretching of the C-C-O and that was proposed as a useful band for the composition analysis of refined oils and biodiesel blends.

The superposition of the IR spectra of the used cooking oil and those of the organic phases with some content of biodiesel that were isolated from the reaction mixture during the transesterification (Figure 2) showed bands whose intensities varied with opposite tendencies in two particular regions of the spectra: one region in which the intensity of the signals decreased because some species were consumed, and another in which its intensity increased due to the production of other species, as the reaction progressed.

In the region of the spectrum where the intensity of the signals decreased during the reaction progress (Figure 2c), notable bands appeared at 1028 - 1018 cm^{-1} and close to 1120 - 1100 cm^{-1}, attributable to stretching vibrations of the C-O bond of sp^3 carbons. The wide band at 1028 cm^{-1} was not observed in the IR spectrum of the oil, it appeared in the spectra of the organic phase with some biodiesel content, with maximum intensity at time 0 minutes, that is, once the reaction mixture was constituted, over time it moved to 1018 cm^{-1} and its intensity decreased as time progressed in the process, therefore, it was assigned to the stretching vibration of the C-O bonds in the methanol, CH_3OH, incorporated at the beginning into the system and consumed during the transesterification, in the glycerol, $HOCH_2$-CHOH-CH_2OH.

The two bands around 1120 cm^{-1} (vibrations of symmetrical and asymmetrical stretching of the C-O bond of sp^3 carbons of the glyceryl fragment) whose absortion maximun shifted to lower wave numbers (changing the signal shape) had their maximum intensity in the spectra of the used cooking oil of the organic phase isolated at 0 minutes, evidencing this way the predominant consumption of triglycerides during the process (Figure 2). The diglycerides and monoglycerides practically do not contribute to the signals attributed to CHOH or CH_2OH groups [25] because these are species produced and consumed during the process whose solubility in the organic phases is low.

The signals at 1458 cm^{-1} (bending vibrations in the H-C-H planes of CH_2 groups, or in the H-C-C planes of CH_3 groups), at 1436, and at 1378 and 1362 cm^{-1} (bending vibrations in the H-C-H planes of CH_3) showed increase in their absorbance as an index of the concentration in the reaction medium of the species containing such groups, which were formed during the process (Figure 2). The band at 1458 cm^{-1} appeared in all the IR spectra, but those at 1436 cm^{-1} and 1362 cm^{-1} were absent in the IR spectrum of the used cooking oil, the Raw material (Figures 2 and 3). The absorbance or the integral of the band appearing at 1458 cm^{-1} includes undetermined contributions of the acyl fragments, of both the biodiesel and the raw materia, that interfere for the specific quantification of the biodiesel concentration in the reaction medium, because the measure results from non-discriminated addends of different species whose concentration varies during the process.

The band at 1436 cm^{-1} was proposed as a useful signal for the construction of quantification models of oil-biodiesel mixtures and it was attributed to the bendings in the H-C-O planes of the CH_3O group [14] (Table 1). However this band resulted unsuitable when

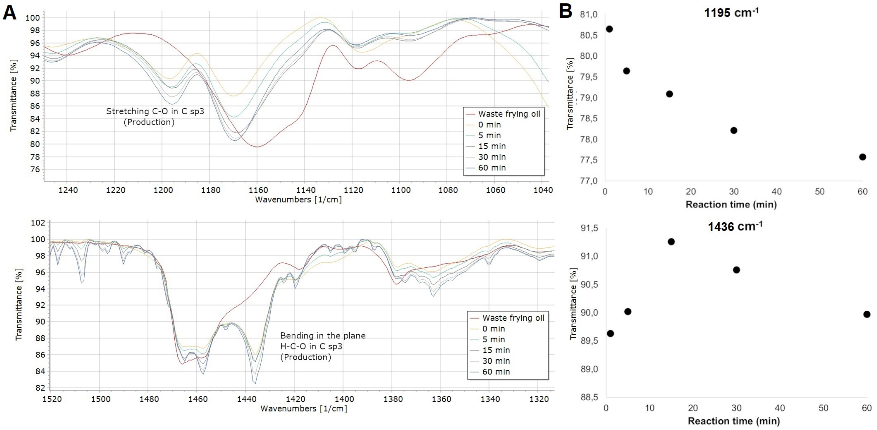


FIGURE 3. *Effect of the reaction time on the bands at 1436 cm*$^{-1}$ *and 1195 cm*$^{-1}$ *in the ATR-IR spectrum during the production of biodiesel.* ***A****. Expanded bands (1436 cm*$^{-1}$ *and 1195 cm*$^{-1}$*) of the IR spectra of the used cooking oil and the organic phases containing biodiesel isolated from the reaction medium at five different reaction times.* ***B****. Evaluation of the change in the transmittance of the bands at 1436 cm*$^{-1}$ *and 1195 cm*$^{-1}$ *as a function of the reaction time.*

quantifying differences in the biodiesel concentration in the reaction mixture at different timeframes of the transesterification progress, because the intensity of the band at 1436 cm^{-1} increased up to a maximum (at 15 minutes of the process), but then decreased and showed irregular and non-linear dependence of the absorbance in relation to the concentration of the biodiesel obtained in each time during the process (Figures 2 and 3). This behavior was attributed to the presence of transient species in the reaction (di- and monoglycerides) and it indeed evidenced the lack of linear correlation between the concentration of biodiesel produced and the reaction time.

The signal at 1378 cm^{-1} (bending in the H-C-H planes in methyl groups) had its greatest intensity in the spectrum of the used cooking oil or just at the beginning of the process in the series of spectra of the organic phase with some content of biodiesel and showed a small irregular decrease in its intensity as the process progressed. This behavior was explained mainly due to the CH_3 groups at the end of the chain of the tri-, di-, and monoglycerides of the free fatty acids and of the biodiesel, and in a minimal part, to the OCH_2 groups of the little glycerol remaining in the organic phase. This signal was previously proposed as a useful signal to quantitatively track the process of transesterification by MID-IR [15], but it suffers from the same drawback noted above for the bands at 1436 cm^{-1} and 1458 cm^{-1}. In total, it incorporates indeterminate addends whose concentration varies during the transesterification.

The signal at 1362 cm^{-1} (bendings in the H-C-H planes of the CH_3 group of the methanol) appeared in the IR spectra of the organic phase with some biodiesel content, it had maximum intensity at 0 minutes and it was absent in the spectrum of the used cooking oil, showing that the methanol turned out diluted while the methyl carboxylate fragment, $-(CO)-O-CH_3$, of the biodiesel was concentrated as the process progressed.

The bands at 1098 cm^{-1} and 1116 cm^{-1} (C-O stretching in the carboxylate groups), -(O=C-O)-, proposed as useful signals to determine the composition in mixtures of oil and biodiesel [18] (Table 1), appeared in all the IR spectra (Figure 2) and showed irregular decrease of their intensity as the reaction advanced. Similar to the band close to 1116 cm^{-1} in the IR spectrum of the used cooking oil, in the spectra of the organic phases that contained a little more biodiesel, the bands at 1098 cm^{-1} and 1116 cm^{-1} moved at higher wave number in the course of the process, similar as the band close to 1160 cm^{-1} shifted to 1170 cm^{-1} in the IR spectrum of the raw material (used cooking oil). All these bands are attributed to the stretching of the C-O of the sp^2 carbon in the carboxylate fragment of tri-, di- and monoglycerides, therefore, their absorptions constitute total results of indeterminate addends that may vary within the time of the process, then, all these bands do not allow to determine the participation of oil and biodiesel in the composition of such reaction mixtures or in blends containing biodiesel.

The band at 1195 cm^{-1} (stretching of the C-O bond on the side of the sp^2 carbon in the methyl carboxylate fragment, $O=C-O-CH_3$, appeared exclusively in the IR spectra of the organic phases with some biodiesel content, and its intensity always increased during the course of the process (Figure 3). Since the band at 1195 cm^{-1} does not incorporate interferences attributable to phenomena typical of groups in chemical species different to the biodiesel that is present in the organic phase, it seems the most appropriate of the bands in the MID-IR spectrum to follow the kinetics of production of biodiesel through the spectra in the MID-IR of the crude organic phases isolated from the transesterification medium, when quantifying based on the intensity or the integral of the band (it is the area measured within the polygonal formed by the baseline and the contour of the signal), in order to establish the ratio of biodiesel produced to unreacted oil at any time during the process, and also to establish the composition of mixtures of biodiesel with oil, or with diesel and oil, since unlike to other proposed signals (Table 1).

In accordance with the Lambert-Beer-Boguet Law, the variations in the transmittance percentage, related to the absorbance, of this signal in the course of the reaction correspond to changes in the concentration of the methyl carboxylate fragments, typical of the biodiesel, which are enriched in the medium, as the process progresses. This well agrees with the intensification of the band at 1436 cm^{-1} (bending in the H-C-O plane of the CH_3O group) in the spectra, when the isolated organic phase of the reaction medium that contained the biodiesel was washed with distilled water in order to remove salt, methanol, and glycerin (Figures 2 and 3). Prior to this work, the signal at 1195 cm^{-1} had not been proposed individually and specifically for the purposes of monitoring the production or to determine the composition of mixtures containing biodiesel, nor in transesterifications from virgin oils, or from used cooking oils, treated as waste(Table 1) [22, 26–28].

Conclusions

The bands in the ATR-FTIR spectra in the MID-IR of the organic phases isolated from the reaction mixture at different times showed their potential to monitor the production of biodiesel during the transesterification catalyzed with base of used cooking oil and methanol. Particularly, the band at 1195 cm^{-1} only appeared in the ATR-FTIR spectra of organic phases containing biodiesel, and its intensity increased as the biodiesel content in the organic phases isolated from the reaction mixture increased according to the progress of the reaction (Figure 2 and 3). It was independent of any change in concentration of the other species present in the reaction mixture over any time throughout the process. Therefore, this work postulates the band at 1195 cm^{-1} as the most suitable band in the MID-IR spectrum of the organic phase isolated from the transesterification medium to monitor the production of biodiesel during the progress of the reaction or to determine the composition of blends containing biodiesel.

Acknowledgements

This study was supported by the Universidad EAN, in the Basic Sciences area of the Engineer Faculty, and by the Universidad Nacional de Colombia, in the APRENA investigation group of the Chemistry Department at the Science Faculty. The authors declare their affiliation to one or other institution, respectively, and they appreciate the support received from these two academic institutions which operate in Bogotá (Colombia).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] P. R. Epstein, J. J. Buonocore, and et al., Ann. N. Y. Acad. Sci. **1219**, 73 (2011).

[2] D. O'Rourke and S. Connolly, Annu Rev Environ Resour **28**, 587 (2003).

[3] Environmental Protection Agency (EPA), Acid rain. (accessed 7 february 2019).

[4] A. R. Mohammed and C. Bandari, Biofuels **11**, 409 (2017).

[5] T. A. Degfie, T. T. Mamo, and Y. S. Mekonnen, Sci. Rep. **9**, 1 (2019).

[6] N. Akkarawatkhoosith, A. Kaewchada, C. Ngamcharussrivichai, and A. Jaree, Bioenergy Res. **13**, 542 (2020).

[7] P. E. Ahranjani, M. Kazemeini, and A. Arpanaei, Bioenergy Res. **13**, 552 (2020).

[8] K. Mathiesen, *The Guardian. Are biofuels worse than fossil fuels? (accessed 7 February 2019).*

[9] E. Avella-Moreno, MOMENTO **44**, 35 (2012).

[10] M. Hirtzer, *U.S. renewable fuel credits pressured by biodiesel tax credit optimism (accessed 7 February 2019).*

[11] M. L. Pisarello, M. Maquirriain, P. S. Olalla, V. Rossi, and C. A. Querini, Fuel Process. Technol. **181**, 244 (2018).

[12] F. Menges, Spectragryph - optical spectroscopy software. Version 1 (2016).

[13] J. F. García Martín, M. López Barrera, M. Torres-Garcia, Q.-A. Zhang, and P. Álvarez-Mateos, Processes **7**, 304 (2019).

[14] W.-B. Zhang, Renewable Sustainable Energy Rev. **16**, 6048 (2012).

[15] M. A. Dubé, S. Zheng, D. D. McLean, and M. Kates, JAOCS **81**, 599 (2004).

[16] N. Siatis, A. Kimbaris, C. Pappas, P. Tarantilis, and M. Polissiou, JAOCS **83**, 53 (2006).

[17] M. G. Trevisan, C. M. Garcia, U. Schuchardt, and R. J. Poppi, Talanta **74**, 971 (2008).

[18] A. P. Ault and R. Pomeroy, J. Chem. Educ. **89**, 243 (2011).

[19] M. F. Ferrão, M. de Souza Viera, R. E. P. Pazos, D. Fachini, A. E. Gerbase, and L. Marder, Fuel **90**, 701 (2011).

[20] D. M. Pinho, V. O. Santos, and et al., Fuel **136**, 136 (2014).

[21] G. G. Shimamoto, L. F. Bianchessi, and M. Tubino, Talanta **168**, 121 (2017).

[22] V. H. J. d. Santos, E. D. C. Bruzza, J. E. de Lima, R. V. Lourega, and L. F. Rodrigues, Energy & Fuels **30**, 4905 (2016).

[23] P. J. Larkin, *Infrared and Raman spectroscopy: principles and spectral interpretation* (Elsevier, 2018).

[24] B. H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications* (J. Wiley & Sons, 2004).

[25] C. G. Chol, R. Dhabhai, A. K. Dalai, and M. Reaney, Fuel Process. Technol. **178**, 78 (2018).

[26] S. O'Donnell, I. Demshemino, M. Yahaya, I. Nwandike, and L. Okoro, EIJST **2**, 137 (2013).

[27] T. Yuan, E. Akochi-Koble, D. Pinchuk, and F. R. van de Voort, Intern. j. renew. energy biofuels. **2014**, 1 (2014).

[28] N. N. Mahamuni and Y. G. Adewuyi, Energy & Fuels **23**, 3773 (2009).