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USE OF FTIR FOR PRELIMINARY ANALYSIS OF THE CONVERSION RATE OF OLEIC ACID TO ETHYL OLEATE[1]

USO DE FTIR PARA ANÁLISE PRELIMINAR DA TAXA DE CONVERSÃO DE ÁCIDO OLEICO EM OLEATO DE ETILA

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ABSTRACT

In the work here reported, an efficient and preliminary method to calculate the conversion rate of esterification reactions is presented, through a simple, fast and cost-effective technique, the Fourier-transform infrared spectroscopy, given that conversion rate is the percentage of ester formation when compared to the initial amount of carboxylic acid. From referential samples containing mixtures of oleic acid and ethyl oleate in different proportions, both substances purchased commercially and with a high degree of purity, a calibration curve was elaborated through linear regression, providing an equation for calculating conversion rates based on the integration of carbonyl peaks in Fourier-transform infrared spectroscopy spectra of reactants and products. The esterification of oleic acid with ethanol was verified under influence of two different solid-acid catalyst nanoparticles, niobium pentoxide and zirconium dioxide, in which the calculated conversion rates were, respectively, 38.1% and 10.4%. At the end of the work, it was possible to verify that the reported method provided a fast, simple and cheap way of obtaining esterification conversion rates, using exclusively infrared spectroscopy spectra of reaction products, which has the potential to avoid extra steps in sample preparation, consequently, reducing costs.

Keywords: Spectroscopy, Esterification, Catalysis.

RESUMO

No trabalho aqui relatado, é apresentado um método eficiente e preliminar para calcular a taxa de conversão de reações de esterificação, através de uma técnica simples, rápida e de baixo custo, a espectroscopia na região do infravermelho com transformada de Fourier, entendendo-se que taxa de conversão é porcentagem de éster formado quando comparado à quantidade de ácido carboxílico inicial. A partir de amostras referenciais contendo misturas de ácido oleico e oleato de etila em diferentes proporções, ambas substâncias compradas comercialmente e com elevado grau de pureza, elaborou-se uma curva de calibração por meio de regressão linear, fornecendo uma equação para cálculo de taxas de conversão baseada na integração de picos de carbonila em espectros de espectroscopia no infravermelho com transformada de Fourier de reagentes e produtos. A esterificação do ácido oleico com etanol foi verificada sob influência de duas nanopartículas catalisadores sólido-ácidos diferentes, pentóxido de nióbio e dióxido de zircônio, em que as taxas de conversão calculadas foram, respectivamente, 38,1% e 10,4%. Ao final do presente trabalho, foi possível verificar que

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o método aqui relatado ofereceu uma maneira rápida, simples e barata de se obter taxas de conversão de esterificação, utilizando somente espectros de espectroscopia no infravermelho com transformada de Fourier dos produtos da reação, o que possui potencialidades para evitar etapas extras na preparação de amostras, consequentemente, diminuindo gastos.

Palavras-chave: *Espectroscopia, Esterificação, Catálise.*

INTRODUCION

With increasing demand for alternative sources of energy and renewable fuels, the chemical industry has adapted to a new reality, aiming to reduce the use of certain energy precursors, such as oil and coal, since their prolonged use has caused environmental problems (ZABETI; DAUD; AROUA, 2009; PINTO *et al.*, 2012; WANG *et al.*, 2020; ALVES *et al.*, 2021). Another motivation for the diversification of energy sources is the unavailability of resources and the increase in the price of oil (BASKAR; AISWARYA, 2016; FERRER *et al.*, 2018; MURSHED; TANHA, 2021). Among the alternatives for cleaner fuels, biodiesel can be highlighted, since its use can reduce negative environmental impacts as it contains less sulfur and can be biodegradable. In addition, it can be used in conjunction with diesel itself in different proportions and does not require costly adaptations to the engines in which it is employed (MAHMUDUL *et al.*, 2017; SINGH et al, 2020).

As esters such as biodiesel have become more targeted for fuel applications, the search for different synthesis processes, catalysis and characterization of reaction products also emerged. Factors such as facility, cost-effectiveness, sustainability, yield and reaction times are some of the reasons most cited by the literature so that the implementation of esterification and transesterification reactions can be increasingly viable in industries (BASKAR; AISWARYA, 2016; AMBAT, SRIVASTAVA; SILLANPÄÄ, 2018). In this context, the characterization of esters formed in these reactions and the determination of the product conversion rate also instigate academic interest.

Biodiesel consists of esters of fatty acids. For its production, transesterification is the most commonly used synthesis route, in which the ester is produced from triglycerides and alcohols. The main renewable sources of these precursors are vegetable oils, animal fat and biomass, one of the many reasons why biodiesel has aroused more and more industrial interest. With this focus for mass production, it is important that the transesterification reaction can be catalyzed, which usually occurs by addition of bases such as potassium hydroxide or sodium hydroxide (MONTEIRO *et al.*, 2008; RESÉNDIZ-VEGA *et al.*, 2019, CARDOSO *et al.*, 2020).

In the search for catalysts for these reactions, researchers have often opted for the use of certain metal oxides such as zinc, zirconium and titanium oxides. In addition to the ability to accelerate transesterification reactions, these oxides can also act in the catalysis of esterification reactions.

The main factor leading to this catalytic property is the metal oxide's capability to provide adsorption sites, in which alcohols can have their hydroxyl group broken and subsequently react with carboxylic acids to form esters. In this process, the solid-acid catalyst does not mix with the liquid phase, which leads to another factor that favors the use of metallic oxides as catalysts of these reactions: the heterogeneous catalysis, in which there is no mixture of the catalyst in the same reaction phase, facilitating their separation, reuse, and also decreasing possible environmental problems (ZABETI *et al.*, 2009; SANI; DAUD; AZIZ, 2014; DU *et al.*, 2018; NASREEN et al, 2018).

The main equipment and techniques employed to characterize and determine conversion rates in the synthesis of esters and biodiesel are titration, gas chromatography, thin-layer chromatography, high-performance liquid chromatography, proton nuclear magnetic resonance and infrared spectroscopy (KNOTHE, 2000; MONTEIRO *et al.*, 2008, LÔBO, FERREIRA; CRUZ, 2009). However, although titration is a simple technique, it is also slow, repetitive and increases the amount of consumed reagents and generated waste. Chromatographic techniques, although accurate in determining the composition of biodiesel, tend to be more expensive and consume excess solvents. Proton nuclear magnetic resonance, which can be an easier alternative, requires high costs for its maintenance, such as using deuterated solvents. Nonetheless, in terms of determining the conversion rate of ester synthesis, literature does point out some methods that use infrared spectroscopy. When compared to other mentioned techniques, FTIR spectroscopy is able to overcome most disadvantages, with the highest hindrance being the initial cost to acquire the equipment. In addition, the technique is rapid, does not require an elaborate prior preparation of the samples and is not destructive, being ideal for a preliminary analysis of esterification and transesterification products (KNOTHE, 2001; ZHANG, 2012; BELLO; ADEKANBI; AKINBODE, 2016; SIMANJUNTAK; PANDIANGAN, 2021).

In order to determine the conversion rate in esterification and transesterification reactions using infrared spectroscopy, it is possible to elaborate a calibration curve from different proportions of fatty acid and ester, identifying the area under the characteristic peaks of each sample. Thus, a linear function can be obtained, which can be used for the calculation of the reaction yield based on the area under the characteristic peaks of the reagents and products obtained in the FTIR spectra. Mathematical methods have already been reported by the literature for the determination of the conversion rate in esters and biodiesel using FTIR spectra, mainly using partial least squares regression (PLS) and principal component analysis (PCA) (KNOTHE, 1999; BLANCO *et al.*, 2004; RABELO *et al.*, 2015; KARTNALLER *et al.*, 2016; DHARMA et al, 2016, ROSSET; PEREZ-LOPEZ, 2019). Therefore, the objective of the present work was to carry out a preliminary analysis of the products of esterification reactions catalyzed by zirconium oxide and niobium pentoxide using infrared spectroscopy, following the present trend in research for simplification and cost reduction in the characterization process of esters and biodiesel.

MATERIALS AND METHODS

Nine reference samples of oleic acid and ethyl oleate mixtures were prepared, changing their respective molar fractions, starting at 0.1 ethyl oleate for the remainder of oleic acid. Table 1 shows the samples used and the percentage of oleic acid and ethyl oleate in each.

Table 1 - Referential mixture samples used containing oleic acid and ethyl oleate.

Sample	Oleic acid molar fraction (±0.01)	Ethyl oleate molar fraction (±0.01)
1	0.900	0.100
2	0.800	0.200
3	0.700	0.300
4	0.600	0.400
5	0.500	0.500
6	0.400	0.600
7	0.300	0.700
8	0.200	0.800
9	0.100	0.900

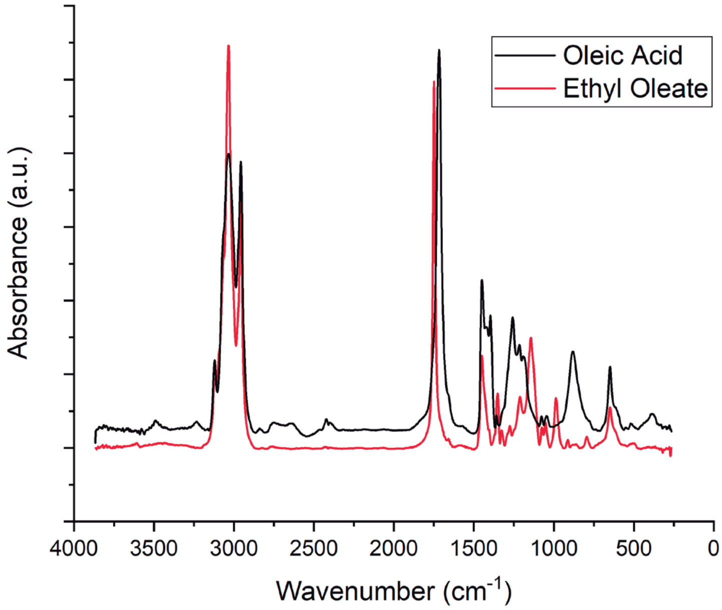
Source: authors' construction.

These samples were prepared in order to simulate what happens in an esterification reaction between oleic acid and ethanol, where oleic acid is consumed and ethyl oleate is formed. For the characterization of the samples, a Nicolet IR200 infrared spectrometer was used, obtaining the absorbance of the samples with the use of plates containing potassium bromide. The oleic acid absorbance spectrum (Sigma-Aldrich, 90%) and ethyl oleate spectrum (Sigma-Aldrich, 98%) were also characterized. The catalytic tests were done with oleic acid and ethanol in a heating plate at 333 K for one hour, in which three different samples were trialed: no catalysts, zirconium oxide catalyst and niobium pentoxide catalyst. The products were characterized with infrared spectroscopy as previously described.

RESULTS AND DISCUSSION

The absorbance spectra of both oleic acid and ethyl oleate obtained as reference can be seen in figure 1.

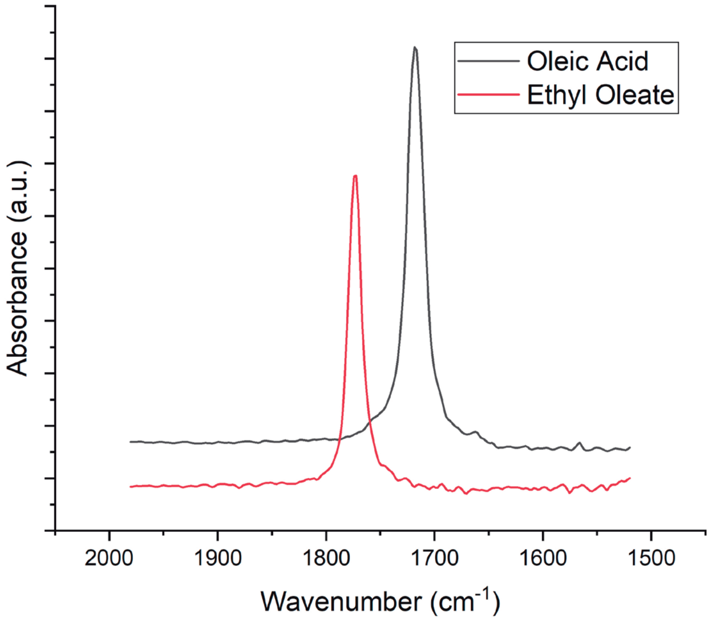
Figure 1 - Oleic acid and ethyl oleate FTIR absorbance spectra.



Source: authors' construction.

The absorbance spectrum of the oleic acid presented a well-defined peak nearing the 1717 cm^{-1} region, a region corresponding to the carbonyl group of its structure. The absorbance spectrum of ethyl oleate showed a peak in the 1747 cm^{-1} region, which corresponds to the carbonyl group of its structure (KARTNALLER *et al.*, 2016, ZHOU; NIU; LI, 2016; NIU *et al.*, 2017; SENA; NETO; PEREIRA, 2019; BASHIR; WU; KROSURI, 2021; KAUR; SAHU, 2020; SIMANJUNTAK; PANDIANGAN, 2021). Both peaks can be seen in figure 2.

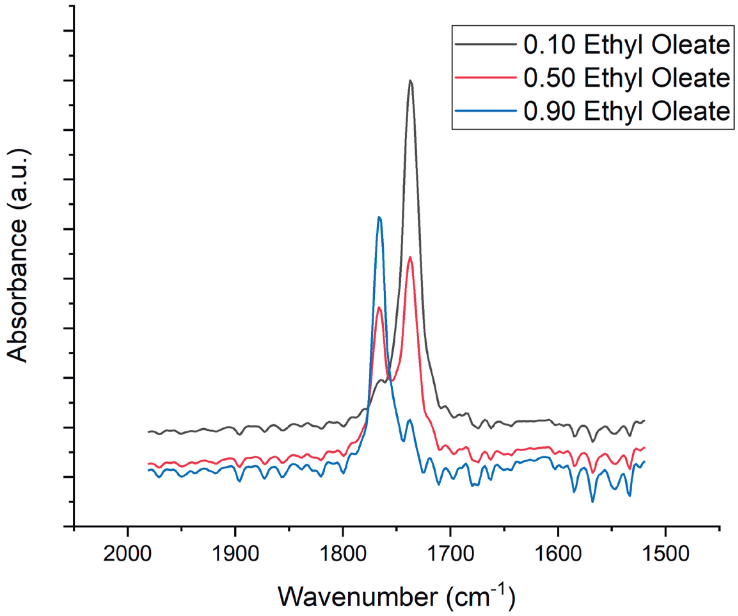
Figure 2 - Oleic acid and ethyl oleate carbonyl peaks in FTIR absorbance spectra.



Source: authors' construction.

It can be noticed that the characteristic peak of the carbonyl of ethyl oleate is not present in the spectrum of oleic acid absorbance and vice versa. Hence, the reference samples of 1 to 9 presented both peaks, as seen in figure 3. Also, the peak in the region nearing 1717 cm^{-1} decreased throughout the samples, as the molar fraction of the oleic acid also decreased. Consequently, the peak in the region near 1747 cm^{-1} increased as the molar fraction of the ethyl oleate increased, as highlighted in figure 3.

Figure 3 - Carbonyl peaks in samples 1, 5 and 9 in the FTIR absorbance spectra.



Source: authors' construction.

It was possible, with the use of appropriate software, to analyze the peaks in the range between 1680 cm^{-1} and 1800 cm^{-1} of the absorbance spectra of samples 1 to 9, separating the peaks into two gaussians and calculating their areas with integration. For samples with pure oleic acid or ethyl oleate, the same wavenumber region was analyzed, containing only a single peak representing its carbonyl group. The ratio of the ethyl oleate area ($A_{\text{ethyl oleate}}$) and its sum with the oleic acid area ($A_{\text{oleic acid}}$) allows for the calculation of the ratio between the areas under both curves, named $R_{\text{ethyl oleate}}$, as seen in table 2. This relation is shown in equation 1:

$$R_{ethyl\ oleate} = \frac{A_{ethyl\ oleate}}{A_{ethyl\ oleate} + A_{oleic\ acid}} \qquad (1)$$

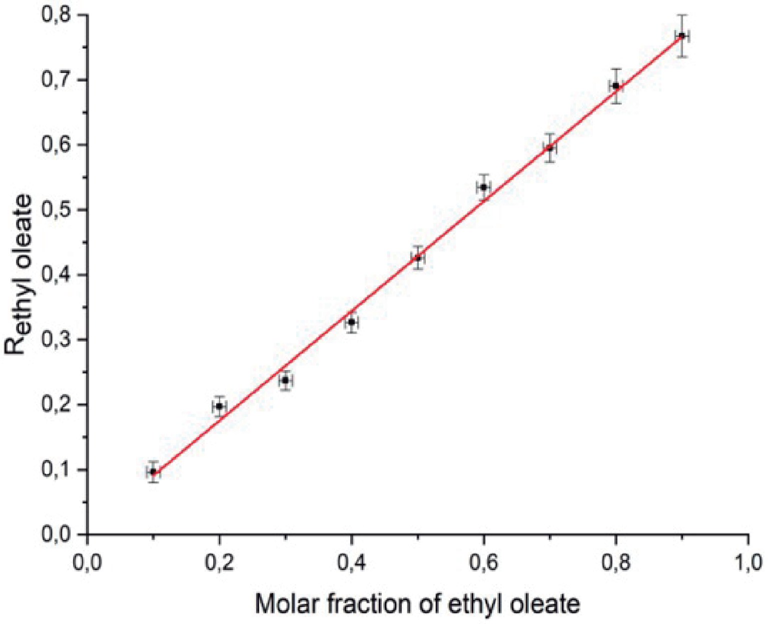
Table 2 - Areas of each gaussian and their ratio from FTIR spectra of mixture samples.

Sample	$A_{\text{oleic acid}}$	$A_{\text{ethyl oleate}}$	$R_{\text{ethyl oleate}}$
1	2.54 ± 0.04	0.27 ± 0.04	0.10 ± 0.02
2	2.22 ± 0.04	0.54 ± 0.04	0.20 ± 0.02
3	2.16 ± 0.04	0.67 ± 0.04	0.24 ± 0.01
4	1.81 ± 0.04	0.88 ± 0.04	0.33 ± 0.02
5	1.47 ± 0.04	1.09 ± 0.04	0.43 ± 0.02
6	1.14 ± 0.03	1.31 ± 0.04	0.53 ± 0.02
7	0.93 ± 0.03	1.37 ± 0.04	0.60 ± 0.02
8	0.68 ± 0.03	1.51 ± 0.04	0.69 ± 0.03
9	0.50 ± 0.03	1.64 ± 0.05	0.77 ± 0.03

Source: authors' construction.

A graph was plotted with $R_{\text{ethyl oleate}}$ depending on the molar fraction of ethyl oleate (figure 4) and linear regression was done, obtaining an equation describing the phenomenon (equation 2), which presented an error (R^2) of 0.993.

Figure 4 - Calculated calibration curve from mixture samples of oleic acid and ethyl oleate.



Source: authors' construction.

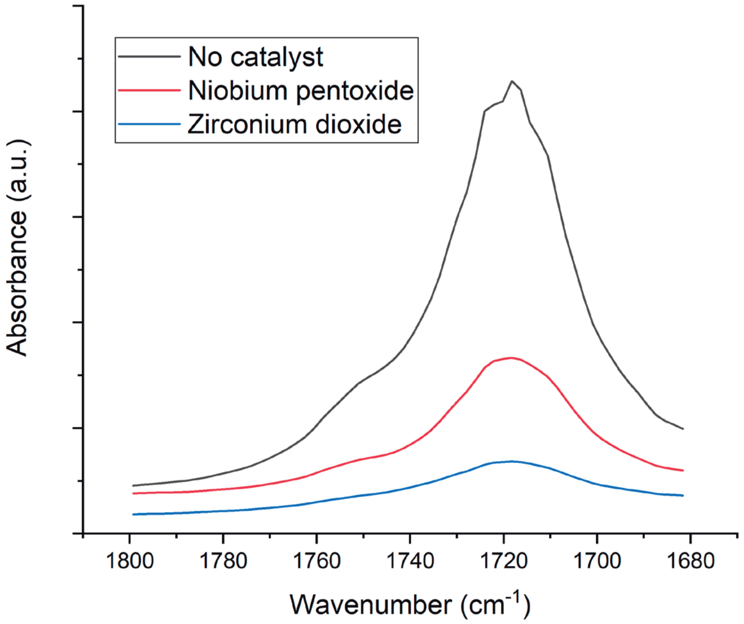
$$R_{ethyl\ oleate} = (0.844 \pm 0{,}0027)x + (0.006 \pm 0.012) \quad (2)$$

Equation 2 can be used to obtain an estimate of the conversion rate of carboxylic acid to ester. To obtain it in percentage, the equation can simply be multiplied by 100% (equation 3).

$$\%_{ethyl\ oleate} = \frac{R_{ethyl\ oleate} - (0.006 \pm 0.012)}{(0.844 \pm 0.027)} \cdot 100\% \quad (3)$$

An example of the utility of equation 3 can be seen in figure 5, where three oleic acid esterification experiments with ethanol were carried out using 7.468 mL of ethanol (Synth 99.5%) and 1.324 mL of oleic acid (Sigma-Aldrich, 90%), for 1 hour at 333 K. A test was performed without the presence of catalysts, another in the presence of 0.0122 g of ZrO_2 nanoparticles (NPs) and another in the presence of 0.0122 g of Nb_2O_5 NPs. In figure 5, the peaks in the region between 1680 cm^{-1} and 1800 cm^{-1} of the products' infrared spectra can be seen.

Figure 5 - Carbonyl peaks in FTIR spectra of esterification reaction products containing no catalyst, ZrO_2 NPs and Nb_2O_5 NPs



Source: authors' construction.

It was possible to analyze the peaks of the said interval, to separate each of the curves in figure 5 into two gaussians and to calculate their areas with integration. With these values, $R_{ethyl\ oleate}$ (equation 1) could be calculated and the value could be inserted as a variable in equation 3, thus obtaining the value, in percentage, of ethyl oleate in the sample. Calculations revealed that, in this preliminary analysis and in the given conditions, Nb_2O_5 was more effective as a catalyst for the esterification reaction, reaching 38.1% conversion rate, while ZrO_2 reached 10.4% and the non-catalyzed reaction reached 16.2%.

When compared to literature, the data for Nb_2O_5 seemed promising, reaching similar conversion rates to esterification reactions with higher temperatures, use of methanol over ethanol and the same reaction times (BRANDÃO *et al*., 2009). However, ZrO_2 showed a smaller conversion rate when compared to the non-catalyzed test, although previous works have achieved similar rates on the esterification of lauric acid at 340 K for 12 h (RACHMAT; TRISUNARYANTI; WIJAYA, 2017). Even for other esterification catalysts, similar research has observed different conversion results. A real time FTIR analysis was performed in a previous work for the conversion of oleic acid and ethanol at a temperature of 57 ºC. After one hour, depending on the catalyst, conversions could vary from less than 10% up to 60% (KARTNALLER *et al.*, 2016).

When compared to transesterification reactions, previous similar works have also identified varying yields depending on which oxide was used as catalyst. An example is the conversion of soybean oil and methanol to biodiesel, which reached 99.4% conversion and 11.0% conversion when catalyzed by CaO and MgO, respectively. The authors compared the method to gas chromatography, verifying that the calculated conversion rates were close values (ROSSET; PEREZ-LOPEZ, 2019).

CONCLUSIONS

It was verified that the technique of infrared spectroscopy here presented is promising for the preliminary determination of the conversion rates in esterification reactions, in this case, with the conversion of oleic acid into ethyl oleate being analyzed. The advantages that were discussed previously by literature were also observed, such as the ease and quickness of the method, low cost of execution, the simple preparation of the samples and the fact that they were not destroyed in the process of characterization.

In view of the production of esters and biodiesel, the main disadvantage of the method corresponded to not knowing whether contaminants or minor impurities and substances with similar functional groups were present in the reaction products. This differentiation can be done with the use of complementary and more complex techniques, such as gas chromatography or high-performance liquid chromatography.

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