

Study of the operational conditions for ethyl esters production using residual frying oil and KF/clay catalyst in a continuous system

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SUMMARY: The transesterification of residual frying oil (RFO) with pressurized ethanol was carried out in a continuous reactor containing KF/clay as a heterogeneous catalyst. In the experiments, different oil:ethanol mass ratios were evaluated at 275 and 300 °C and 20 MPa. In the sequence, the operational stability of the catalyst was evaluated for 8 hours, as well as the conduct of the reaction in two steps (testing new and recycled catalyst). An esters yield of ~90% was achieved at 275 °C, for 15 min and at 1:1.5 oil:ethanol mass ratio. Under these conditions, the catalyst provided a stable yield in the first 3 hours of operation, and a total decrease of 29% after 8 hours. This result can be attributed mainly to the leaching of the K⁺ cations for the reactions in which the catalyst was exposed to long operating times. The two-step reaction served to increase the RFO conversion to esters, with low thermal decomposition.

KEYWORDS: *Ethyl esters; Heterogeneous catalyst; Residual frying oil.*

RESUMEN: *Estudio de las condiciones para la producción de ésteres etílicos utilizando aceite de fritura desechado y catalizador KF/arcilla en un sistema continuo.* La transesterificación de aceite de fritura desechado (AFD) con etanol presurizado se llevó a cabo en un reactor continuo que contenía KF/arcilla como catalizador heterogéneo. En los experimentos, se evaluaron diferentes relaciones de cantidad de aceite:etanol a 275 y 300 °C y 20 MPa. En la secuencia, se evaluó la estabilidad operativa del catalizador durante 8 horas, así como la conducta de la reacción en dos pasos (prueba de catalizador nuevo y reciclado). Se logró un rendimiento de ésteres de ~ 90% a 275 °C, 15 min y una relación de aceite:etanol de 1:1,5. En estas condiciones, el catalizador proporcionó un rendimiento estable en las primeras 3 horas de funcionamiento y una disminución total del 29% después de 8 horas. Este resultado se puede atribuir principalmente a la lixiviación de los cationes K⁺ para las reacciones en las que el catalizador estuvo expuesto durante las condiciones de funcionamiento. La reacción de dos pasos permitió aumentar la conversión de AFD a ésteres, con baja descomposición térmica.

PALABRAS CLAVE: *Aceite de fritura desechado; Catalizador heterogéneo; Ésteres etílicos.*

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1. INTRODUCTION

The search for renewable fuels, less polluting and more economically and technologically viable has intensified, especially those that meet the worldwide demand and replace fossil fuels. Biodiesel is an attractive option to meet this demand, and has similar physicochemical properties to mineral diesel (Shehata, 2013). Transesterification, which involves the reaction between triglycerides and a short-chain alcohol to produce esters, as the main product, and glycerol, is an attractive method for converting oils and fats into biodiesel. Residual frying oils (RFO) are an interesting alternative for making biodiesel economically competitive, with its economic viability restrained by the high prices of raw materials, even to a greater extent than technological or processing limitations. It is estimated that about 75% of the cost of production is related to the processing of raw material (Mahlia *et al.*, 2020).

In addition, the improper disposal of RFO leads to environmental damage, where harmful discharge pollutes large amounts of water, which is exacerbated by high production, which in Brazil reached around 1.2 million tons per year (of waste oils and fats) (Aprobio, 2018). Another advantage to using RFO is the significant decrease in agricultural land which is necessary for the planting of oilseeds used for the extraction of the oil used in the production of biodiesel.

Although RFO is attractive, the frying process leads to changes in its properties due to exposure to high temperatures, and the transfer of water from the food to the oil, resulting in the hydrolysis of triacylglycerols, and formation of free fatty acids (Ouanji *et al.*, 2016). RFO may also contain polar compounds, which associated with the presence of a high concentration of free fatty acids and water, hinders the progress of the reaction (Fonseca *et al.*, 2018). In a study by Campanelli *et al.* (2010) the authors found a low reaction rate by applying the conventional transesterification process, requiring high residence times to achieve complete conversion. There are also reports on the formation of oxidized polymers, dimers, triacylglycerol, and diacylglycerides, where some of these components cannot be converted into esters (Gonzalez *et al.* 2013.).

The presence of water and free fatty acids in the RFO triggers hydrolysis and saponification reactions, respectively (Álvarez-Mateos *et al.*, 2019). When the conventional method is used for homoge-

neous alkaline catalysis for biodiesel synthesis, in addition to consuming catalyst, it causes low ester yield (Kusdiana and Saka, 2004). The method using alcohol under pressurized conditions was reported by some authors as tolerant to the presence of these compounds in the oil (Kusdiana and Saka, 2004; Tan *et al.*, 2010), without compromising the yield of the reaction. In this method alcohol is used in conditions close to or above the critical point of temperature and pressure. Under these conditions, modifications occur in the properties of the solvent, such as increased density, solubility and mass transfer and decreased polarity of alcohol, in addition to reducing the viscosity of the oil (Kusdiana and Saka, 2004; Osmieri *et al.*, 2017). Thus, high yields are obtained in short reaction times without the use of catalyst (He *et al.*, 2007), and it is possible to maximize the ester yield by adjusting the temperature, pressure and amount of alcohol employed in the process, as they influence the solubility between phases (Hegel *et al.*, 2008).

However, in order to obtain high conversion values of triacylglycerols in esters, the use of this method requires operation at high temperatures and pressures, together with a large amount of alcohol used in the reaction medium (Silva and Oliveira, 2014). The combination of the residence time and the reaction temperature is fundamental for the effectiveness of the process, since an increase in both results in better yields, but also propitiates parallel reactions of thermal decomposition. The increase in temperature causes isomerization reactions of the type cis to trans in the double bonds of the esters, polymerization (formation of dimers), pyrolysis of fatty acids in smaller compounds and hydrogenation (Liu *et al.*, 2016; Quesada-Medina and Olivares-Carrillo, 2011). Regarding the composition of the oil, it is emphasized that the soybean oil commonly used for frying food can contain from 52 to 54% linoleic acid (Gonzalez *et al.*, 2013), and according to a study carried out by Quesada-Medina and Olivares-Carrillo (2011), for the transesterification of soybean oil with methanol, the thermal decomposition reactions of the linoleic ester intensified as the temperature increased, with a reduction in ester content reported at 300 °C.

Some studies have investigated improvements in the process, so that it is possible to work under milder conditions of temperature and pressure, thus mitigating the hindrance of thermal decomposition and

using lower ethanol volumes in the process, without compromising the high efficiency in reaction yield. To that end, researchers in the area have evaluated the use of heterogeneous catalysts under pressurized conditions in the batch reactor, such as Nano-MgO (Wang and Yang, 2007), CaLaO (Teo *et al.*, 2015), carbohydrate-derived (Lokman *et al.*, 2016) and CH₃ONa (Zeng *et al.*, 2017), perceiving high catalytic efficiency, reusability, low mass loss, possibility for reuse of catalyst without loss of catalytic efficiency, and elevation of ester yield even with small amounts of catalyst.

The transesterification under pressurized conditions conducted in a continuously operated reactor applying heterogeneous catalysts was poorly reported. Among the available studies, McNeff *et al.* (2008) made use of a zirconia-based catalyst, noting an increase in the conversion to esters, from 14.1 to 98% with the use of catalyst. Mazanov *et al.* (2016) reported a yield of 77.51% in a non-catalytic reaction, and 97.46% with the use of SrO/Al₂O₃. Krohn *et al.* (2011) and Maçaira *et al.* (2011) also investigated the use of heterogeneous catalysts in a continuous system under supercritical conditions, using titania porous catalyst and acid resin, respectively. Both concluded that the use of heterogeneous catalysts resulted in shorter operating time. The application of the heterogeneous catalyst has also been successfully reported by Visioli *et al.* (2019) in a reaction using methyl acetate. The authors reported that the use of γ -alumina catalyst increased the production of esters by 33%.

Alves *et al.* (2014) describe the efficiency of using inorganic salts such as potassium fluoride (KF) impregnated with clay as a catalyst in the transesterification to obtain biodiesel. The catalyst was used in a low-pressure batch reactor and the catalyst showed high efficiency in terms of ester yield, low mass loss and morphological stability. Catalysts prepared from clay have a crystalline structure that can be modified in a controlled manner by means of various treatments to optimize their use as catalysts. Such treatments consisted of the modification of the specific area and porosity, thus facilitating the access of the molecules of reagents to the active sites (Alves *et al.*, 2014; Centi and Perathoner, 2008). In addition, smectites are abundant in nature and have a high surface area (Nagendrappa, 2011), an important feature in heterogeneous catalysts, which, together with its

versatility and low cost, makes clay a promising catalyst or catalytic support in several processes.

The use of KF/clay catalyst in a pressurized medium for the synthesis of ethyl esters was reported in a previous study (Zempulski *et al.*, 2020) in which the performance of the catalyst was verified for 3 h of operation in 225 to 300 °C, verifying low variation in the ester yield at 275 and 300 °C. Moreover, after the transesterification, it was verified that the potassium resulting from the impregnation remained in the catalyst, and that the roughness of the particles and agglomerates of the catalyst were not affected by the experimental conditions employed. and the morphological characteristics of the catalyst were maintained.

Thus, the application of a low-cost residual oil for the production of biodiesel is currently of special interest especially from the environmental perspective concerning the re-use of waste, as well as the production of renewable fuel. In addition, through technology that uses pressurized conditions, the reaction takes place in short residence times, and the use of clay-based catalysts that are easy to obtain contributes to higher ester yields and allows for milder operating conditions. Based on the context described, the purpose of this work was to evaluate the continuous production of ethyl esters from residual frying oil (RFO), using ethanol under pressurized conditions in the presence of a heterogeneous catalyst based on clay impregnated with potassium fluoride. The effects of the oil to ethanol mass ratio at 275 and 300 °C and different residence times were evaluated. Under the conditions of higher ester yield, the stability of the catalyst was evaluated for 8 hours of operation. The reaction was further carried out in two stages, using new catalyst and recycled in the second step. The catalyst was characterized after its use and compared with the catalyst inserted into the reactor.

2. MATERIALS AND METHODS

2.1. Materials

The substrates used were residual frying oil obtained from a local restaurant (Umarama - PR) and ethanol (Panreac, 99.9% purity). The composition of the RFO was previously reported by Zempulski *et al.* (2020), and its free fatty acid and water contents were 1.16 wt% and 0.16 wt%, respectively. For the

preparation of the catalyst, Brazilian sodium smectite clays were used from deposits located in the states of Paraná and Paraíba, and potassium fluoride $\text{KF}\cdot 2\text{H}_2\text{O}$ (Synth, 98% purity). For the characterization analyses methyl heptadecanoate (Sigma-Aldrich, > 99% purity), heptane (Anhydrol), potassium hydroxide, methanol (Panreac, 99.9%), sulfuric acid (Anidrol, 98%), boron trifluoride (Sigma-Aldrich, 14% in methanol), monolein (Sigma Aldrich, $\geq 98\%$), 1,3-diolein (Sigma Aldrich, $\geq 95\%$), glycerol trioleate (Sigma Aldrich, $\geq 98.5\%$), derivative N-methyl-N-(trimethylsilyl)-trifluoroacetamide (MSTFA, Sigma Aldrich, $\geq 98.5\%$) were used.

The catalyst used in this work was based on the study of Alves *et al.* (2014), where the clay was crushed (< 60 mesh) and wet-impregnated with potassium fluoride at the concentration of $1.7 \text{ mol}\cdot\text{L}^{-1}$. The suspension, a 15% clay and potassium fluoride solution (mass concentrate), was maintained in a blanket and reflux ($80 \text{ }^\circ\text{C}$, 30 min), followed by drying ($110 \text{ }^\circ\text{C}$, 24 h). The mass obtained from clay and KF was de-agglomerated in a mortar until a fine powder was obtained. The final stage consisted of the formation of granules, where the powder was compacted in a hydraulic press with a 5-ton pressure, de-agglomerated, and classified in sieves. The granules used in the work were in the range of $710 \text{ }\mu\text{m}$ to 1 mm obtained with the aid of sieves.

2.2. Experimental procedures

The reactions, carried out in duplicate, served to investigate the influence of the oil-to-ethanol mass ratio of 1:1, 1:1.5 and 1:2 (equivalent to the oil-to-ethanol molar ratios of 1:20, 1:30 and 1:40, respectively). The tests were conducted using a catalyst mass of 2 g in the catalyst bed (these conditions correspond to an oil-to-catalyst ratio of 8:1, 6.4:1 and 5.4:1, respectively) at 275 and $300 \text{ }^\circ\text{C}$. The catalyst mass and temperatures were defined based on the results obtained by Zempulski *et al.* (2020), which provided the experiments the highest ester content and in the case of the selected temperature range did not show any loss in catalytic activity (in 3 h of reaction). The pressure was maintained at 20 MPa based on previous studies (Gonzalez *et al.* 2013; Trentini *et al.* 2018), and the residence times evaluated were 15, 30 and 45 min.

The experimental apparatus where the reactions were performed was previously described

(Zempulski *et al.*, 2020), and operated in continuous mode. The reaction mixture (RFO + ethanol) was kept under constant stirring (mechanical stirrer, IKA RW20) and pumped into the system using an isocratic pump (Waters 515 HPLC). The heating and maintenance of the operating temperature was done in a furnace (Sanchis, BTT1050-00), where the reactor was placed. The reactor consisted of 3 parts: pre-heating zone, catalytic tubular reactor (internal diameter of $9.5 \times 10^{-3} \text{ m}$), and non-catalytic tubular reactor, whose total volume was 35.15 mL. The catalytic tubular reactor was filled with glass beads of medium diameter of 4 mm at the ends and the catalyst (previously activated in a muffle - 48 h, $200 \text{ }^\circ\text{C}$). To avoid mass losses to the system, sintered steel filters ($2 \text{ }\mu\text{m}$, Allcron) were arranged at the ends. Before collection sampling, the samples were cooled by indirect heat exchange, using a thermostatic bath (Tecnal TE - 184). The residence time was calculated by dividing the empty volume of the reactor (mL) by the flow of substrates (mL min^{-1}) and counted after the system entered steady state, considering 2.5 times the residence time. After the reaction, unreacted ethanol was recovered using a rotary evaporator (Marconi, MA 120) coupled with a vacuum pump (Quimis®, 0955V).

The stability of the catalyst was performed under the experimental conditions (catalyst mass, oil-to-ethanol mass ratio, temperature and residence time) that provided not only high yield but also low thermal decomposition, resource savings (energy for temperature rise and ethanol employed). This step was performed from the addition of 2 g of catalyst in the catalytic tubular reactor and as soon as the adopted experimental conditions were reached the reaction mixture (oil + ethanol) was then pumped into the system. The reaction consisted of operating the reactor for a period of 8 h with sample collection every 30 min after reaching steady state.

Under the same experimental conditions as those selected to assess catalyst stability, the reaction was carried out in two steps. The procedure previously described (Abdala *et al.*, 2014; Trentini *et al.*, 2018) was used, which consisted primarily of collecting the sample and removal of glycerol. The removal of glycerol was performed by adding distilled water and *n*-hexane to the reaction product obtained to form immiscible phases. The mixture was centrifuged and the phase containing esters was carried to the oven

for evaporation of ethanol and *n*-hexane. Then, ethanol was added to the sample (without glycerol) and the mixture was pumped into the reaction system. In the second step, the system was filled with fresh catalyst and recycled catalyst (used for a period of 3 h). After the reaction, the recycled catalyst was washed with ethanol and *n*-hexane to remove possible products adhered to the catalyst. It was then dried in an oven (100 °C for 24h) for later re-use.

2.3. Analytical methods

The collected samples were monitored for preparation: evaporation of unreacted ethanol, removal of glycerol, addition of internal standard (methyl heptadecanoate) and dilution in heptane. One μL of the diluted sample was injected into a gas chromatograph (Shimadzu, GC-2010 Plus) equipped with an automatic injector (Shimadzu, AOC-20i Autoinjector), Shimadzu Rtx-Wax capillary column (30 m x 0.32 mm x 0.25 μm) and flame ionization detector. Nitrogen was used as the carrier gas and the samples were injected in split mode (1:20). The injector and detector were kept at a temperature of 250 °C and the heating ramp for the oven was as follows: it started at 120 °C, followed by an increase to 180 °C at 15 °C $\cdot\text{min}^{-1}$ and then to 240 °C at 6 °C $\cdot\text{min}^{-1}$, as described by Trentini *et al.* (2018).

The ester yield (Equation 1) was obtained through the convertibility of the RFO (89.52 \pm 0.88 wt%) as determined using methodology proposed by Gonzalez *et al.* (2013), which refers to the maximum conversion of ethyl esters that can be achieved from the RFO.

$$FAEE \text{ yield } (\%) = \frac{\text{esters content}}{\text{convertibility}} \times 100 \quad (1)$$

Thermal decomposition was determined according to Vieitez *et al.* (2009), and consisted of derivatizing of the compounds (mono, di and triglycerides and ethyl esters) present in the samples with methanolic solution of BF_3 and analyzed by gas chromatography. The decomposition of the samples was obtained from Equation 2:

$$\text{Decomposition } (\%) = \left[1 - \left(\frac{\sum P_i}{P_{16}} \right)_s \times \left(\frac{P_{16}}{\sum P_i} \right)_0 \right] \times 100 \quad (2)$$

Where was the sum of all ethyl ester percentages, P_{16} was the percentage of 16 ethyl ester (considered the most stable), and the subscripts 0 and S indicated the original oil and sample, respectively.

For the quantification of mono-, di- and triglycerides, the sample was derivatized with MST-FA (15 minutes at room temperature) and diluted in heptane (Trentini *et al.*, 2019). The prepared samples were injected (2 μL) into a gas chromatograph (Shimadzu, GC-2010 Plus) equipped with capillary column Zebtron ZB-5HT inferno™ (10 m x 0.32 mm x 0.10 μm), flame ionization detector and column injector. The following oven temperature gradient was applied: initially the column was held at 50 °C for 1 minute, and then heated to 180 °C at a rate of 15 °C $\cdot\text{min}^{-1}$, then at 230 °C at a rate of 7 °C $\cdot\text{min}^{-1}$ and at 380 °C at 10 °C $\cdot\text{min}^{-1}$ and held at this temperature for 5 min. The detector temperature was 380 °C and the heating program of the injector was: initial temperature of 60 °C for 1 min. then heated to 380 °C at a rate of 10 °C $\cdot\text{min}^{-1}$ and held for 10 min at this temperature. For the quantification of the compounds, a calibration curve with the standards of triolein, diolein and monolein were used (Trentini *et al.*, 2019).

2.4. Catalyst characterization

After the reaction, the catalyst recovered from the reactor was washed with ethanol and *n*-hexane and dried in an oven (Zempulski *et al.*, 2020). The characterization of the catalysts was obtained by X-ray fluorescence analysis (XRF, Spectro Philips MagiX); X-ray diffraction (using the XRD apparatus, Siemens Kristalloflex), in the range of $4^\circ < 2\theta < 40^\circ$, using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ nm}$, 40 kV, 40 mA as radiation incident) with a nickel filter, and speed of 0.5° min^{-1} and; Fourier transform infrared spectroscopy (spectrometer FTIR Bomem MB-Series) in the range of 4000 and 500 cm^{-1} , using a resolution of 4 cm^{-1} ; and scanning electron microscopy (SEM) (Quanta 440 microscope FEI), coupled to an energy dispersive spectroscopy (EDS). In the SEM analysis, the powder samples were dispersed onto a double-sided carbon tape, and subsequently metallized with a thin layer of gold by sputtering.

2.5. Analysis of data

All reactions and analyzes were performed, at least, in duplicate. The means and standard devia-

tion of each assay were submitted to ANOVA using Excel® 2010 software and Tukey's test (95% confidence) was applied to determine whether there was a significant difference between samples from the different operating conditions studied. The principal component analysis (PCA) was carried out using the Statistica 8.0 software (StatSoft™, Inc.). The principal components were derived from a correlation matrix.

3. RESULTS

3.1. Effect of mass ratio oil to ethanol

Figure 1 shows the values obtained in terms of ethyl ester yield for the reactions conducted by varying the oil-to-ethanol mass ratio (1:1, 1:1.5 and 1:2) at different residence times. It can be observed at 275 °C (Figure 1a) that the addition of ethanol to the reaction had a greater influence on the initial minutes of the reaction (15 min), for the other evaluated times there was an increase in the ester yield only when the oil-to-ethanol mass ratio was increased from 1:1 to 1:1.5. The highest yield obtained at this temperature was ~90% in 15 min of reaction. At a temperature of 300 °C (Figure 1b), the highest ester yield, obtained in 15 min, was for the oil-to-ethanol mass ratio of 1:2. Similarly, for other ratios and residence times, the increase in ethanol did not influence the yield of esters. From the general analysis of the data obtained in Figure 1, it appears that higher yields were obtained in short residence times and that the addition of a high concentration of ethanol to the reaction (above 1:1.5) was not necessary to obtain a high yield of esters at the evaluated temperatures, which is advantageous, considering the lower mass ratio of oil-to-ethanol and low reaction time to obtain high ester yields.

Increasing the proportion of ethanol in the reaction mixture benefits the conditions of mass transfer in the reaction medium (Biktashev *et al.*, 2011). It can also increase the contact area between the alcohol and triglycerides, thus shifting the balance of transesterification to the formation of products (Campanelli *et al.*, 2010; Silva and Oliveira, 2014). In addition, the addition of alcohol to the reaction medium decreases the critical temperature of the reaction mixture (Osmieri *et al.*, 2017). As an example, for the mass ratios of 1:0.5, 1:1 and 1:2 (oil:methanol), the critical temperatures are 345.93, 305.85

and 282.20 °C, respectively (Bunyakiat *et al.*, 2006). Thus, the greater availability of alcohol in the reaction medium, the better the possibility of conducting the reaction at a milder temperature, still resulting in a high reaction rate (Hegel *et al.*, 2008).

Silva *et al.* (2010) reported that the mass ratio 1:1 seemed to be the most adequate in terms of ester yield and reagent savings for the reaction between soybean oil and ethanol at 300 °C. He *et al.* (2007) found that the increase in ethanol-to-oil mass ratio resulted in an increase in yield, and this behavior was maintained until the ratio of ~1:1.5. Xu *et al.* (2016) indicated that when working with excess alcohol in supercritical conditions, it must be considered that alcohol at its critical point acts not only as a reagent, but also as a solvent, which dissolves the oil present in the reaction mixture and produces an almost homogeneous reaction. The same researchers found that an excess of alcohol could impair the reaction yield because the reagents were too diluted. High concentrations of ethanol can lead to a reduction in reaction rates, which prevents the chemical balance of the reaction from being achieved. It is also important to mention that a high mass ratio may be unfavorable, as more intense processes are required for the separation and evaporation of alcohol (Bunyakiat *et al.*, 2006).

Regarding the temperature applied to the reaction, it was noted that in general, raising the temperature from 275 to 300 °C resulted in a low increase in ester yield for the evaluated residence times. Lin and Tan (2014) also found that even by raising the operating temperature (from 280 to 300 °C), ester yields remained similar (~95%) for the reaction between coconut oil and methanol (mass ratio 1:1), with 40 g of MnO₂ catalyst and 11 MPa. Visioli *et al.* (2019) reported ~60% ester content for the reaction between macauba oil and methyl acetate (mass ratio 1:2.5), with 2 g of γ -alumina catalyst, at 275 and 300 °C.

Figures 1c and 1d show the percentages of thermal decomposition of the fatty acids present in the samples obtained and it was verified from these data that thermal decomposition is influenced by residence time and temperature. For the initial minutes of reaction, there was low decomposition, and by increasing the residence time, a thermal decomposition of up to 15% was noted, similarly, by raising the operating temperature from 275 to 300 °C (45 min); in the mass ratio of 1:2, thermal decomposition went

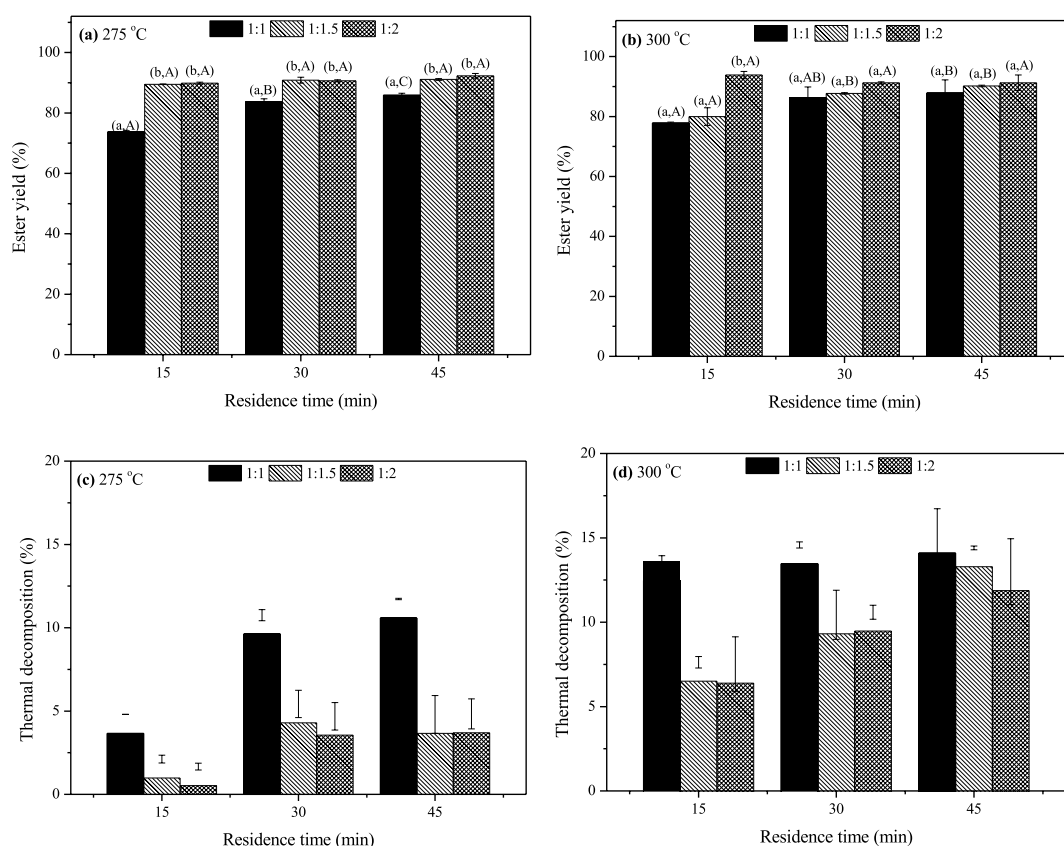


FIGURE 1. Effect of oil-to-ethanol mass ratio on the ester yield for the reactions conducted at 20 MPa using 2 g catalyst and thermal decomposition. Means followed by same letters do not differ statistically ($p > 0.05$) in lower case for the oil-to-ethanol mass ratio (with the same residence time), and upper case for the residence time (with the same oil-to-ethanol mass ratio) using ANOVA (Tukey's test). Values are presented as mean \pm standard deviation ($n=4$).

from ~5 to 15%, respectively. It was also possible to verify that a greater amount of ethanol in the reaction mixture contributed to lower percentages of thermal decomposition at the temperatures evaluated. Thermal decomposition for reactions with waste oil and ethanol has also been reported by Trentini *et al.* (2020), with values of ~20% for 275 and 300 °C, and by Abdala *et al.* (2014), who obtained ~6 and 12% decomposition at 275 and 300 °C, respectively.

The observed thermal decomposition intensified at 300 °C when the oil used for the reactions was composed mainly of linoleic fatty acid, which is less stable at high temperatures compared to saturated and monounsaturated esters, as found by Trentini *et al.* (2019). They reported ~23% reduction in the amount of linoleic ester used by raising the operating temperature from 275 to 300 °C, thus verifying that the decomposition of esters is strongly dependent on the operating temperature. Therefore, temperatures above 300 °C should be avoided, as close to this

temperature, unsaturated esters are consumed due to thermal decomposition.

Regarding the reactions that occur with thermal decomposition, linear thermal dimerization generally occurs in monounsaturated and polyunsaturated esters, forming acyclic structures of the dimers. A mixture of monocyclic and cyclic dimers of six members can cause other compounds to be formed, such as oligomers, polymers, isomers and thermal cracking products (Quesada-Medina and Olivares-Carrillo, 2011). In addition to reducing the yield in esters, thermal decomposition can influence the quality of the biodiesel obtained due to the increase in viscosity and crystallization temperature related to the accumulation of decomposition products (Liu *et al.*, 2016).

In order to reduce the dimensionality of the data set related to the effect of operational variables on the ester yield (EY) and thermal decomposition (TD) of the reaction products, the principal component analysis (PCA) was performed, using the data from

the Table 1. Figure 2 shows the biplot (PC1xPC2) of scores and loadings obtained from a correlation matrix. The two main components (PCs) explained a total cumulative variance of 100% of the data. The vectors of the variables under study form an angle of 90 °, which indicates that there is no correlation between EY and TD.

The PCA formed 2 trend groups. Group A is formed by samples that presented higher EY, since it is close to the vector of this variable. This group is mainly composed of samples obtained at 275 °C, in residence times of 15 to 45 min and oil-to-ethanol mass ratio of 1:1.5 and 1:2, except for sample 6 (obtained at 15 min and 300 °C). These results confirm that the increase in residence time (30 to 45 min) and oil-to-ethanol mass ratio (1:1 and 1:2) did not affect EY, since under these conditions, samples with similar characteristics were obtained. Group B contains samples that showed higher TD and was mainly secreted by reaction products obtained at a temperature of 300 °C and residence time of 45 min, regardless of the oil-to-ethanol mass ratio. This indicates that

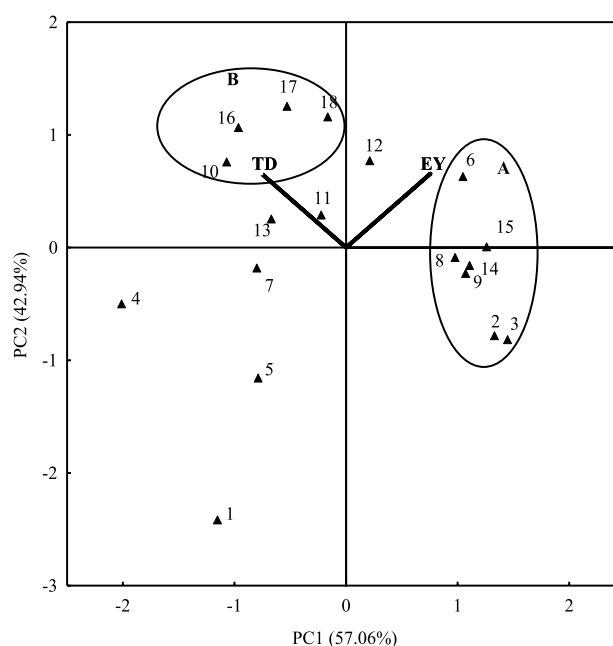


FIGURE 2. Principal component analysis (PCA) of the ester yield (EY) and thermal decomposition (TD) of reaction products obtained under different conditions of temperature (275 and 300 °C), residence time (15 to 45 min) and oil-to-ethanol mass ratio (1:1 to 1:2). The conditions for 1 to 18 are described in TABLE 1.

TABLE 1. Experimental data set of the effect of operational variables on esters yield and thermal decomposition used in the principal component analysis.

Run ¹	Residence time (min)	Temperature (°C)	Oil-to-ethanol mass ratio	EY ² (%)	TD ³ (%)
1			1:1	73.77±0.40	4.80±0.01
2		275	1:1.5	89.50±0.10	2.12±0.23
3	15		1:2	89.85±0.32	1.67±0.20
4			1:1	77.80±0.31	13.58±0.36
5		300	1:1.5	79.97±2.96	7.62±0.34
6			1:2	93.85±1.21	7.51±1.62
7			1:1	83.68±1.00	10.76±0.33
8		275	1:1.5	90.85±0.97	5.43±0.82
9	30		1:2	90.65±0.32	4.68±0.82
10			1:1	86.24±3.61	14.58±0.18
11		300	1:1.5	87.68±0.25	10.44±1.46
12			1:2	91.21±0.37	10.59±0.42
13			1:1	85.86±0.67	11.72±0.04
14		275	1:1.5	91.08±0.30	4.79±1.13
15	45		1:2	92.27±0.78	4.83±0.90
16			1:1	87.83±4.41	15.22±1.51
17		300	1:1.5	90.19±0.28	14.41±0.11
18			1:2	91.25±2.58	12.99±1.95

¹all experiments were conducted at 20 MPa, ²ester yield and ³thermal decomposition. Each value in the table represents the mean ± standard deviation (n = 4).

the increase in temperature and residence time contributed to TD. Sample 10 (obtained at 300 °C, 30 min and oil-to-ethanol mass ratio 1:1) is also represented by this group due to the lower mass of ethanol used at a high temperature. Samples 2 and 3 showed lower TD, since the opposite variable was found in the opposite quadrant. This result was attributed to the lower temperature and residence time employed in this case.

In short, from the results obtained (Figures 1 and 2), it was possible to verify that similar ester yields were obtained with oil-to-ethanol mass ratio of 1:1.5 and 1:2. In addition, the thermal decomposition became accentuated by increasing the residence time, as well as the operating temperature from 275 to 300 °C. It was also noted that raising the operating temperature resulted in a maximum percentage increase of only 5% in ester yield and intensified thermal decomposition (2.6 times). Thus, the operating conditions of 275 °C, 15 min and oil-to-ethanol mass ratio of 1:1.5 were promising to conduct the reaction and verify the stability of the catalyst.

3.2. Catalyst stability

The stability of the catalyst was evaluated for the reaction conducted at the residence time of 15 min, for a period of 8 h after reaching a steady state, at 275 °C, using 2 g of catalyst and oil-to-ethanol mass ratio of 1:1.5. The results for yield in ethyl esters are presented in Figure 3.

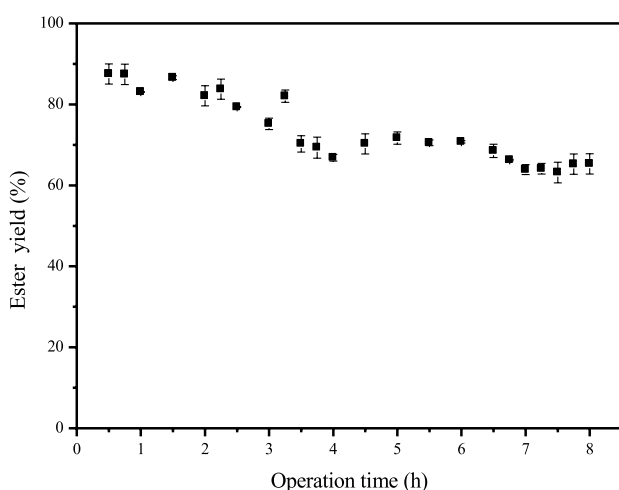


FIGURE 3. Stability of the KF/clay catalyst at 275 °C in terms of ethyl ester yield, using oil-to-ethanol mass ratio of 1:1.5, 2 g of catalyst and residence time of 15 min. Values are presented as mean \pm standard deviation (n=4).

In the first 3 hours of operation, the catalyst remained stable, providing average values for ester yield of $84.26 \pm 2.75\%$. After the mentioned period, there was a slight reduction in the yield, $\sim 15\%$, and the values remained stable at the time of 3 to 6 h of operation, when again a reduction of $\sim 29\%$ was verified in relation to the initial yield (30 min), and from this period the yield remained close to $65.30 \pm 1.60\%$ until the evaluated operation time (8h). According to Simões *et al.* (2020) with a loss of up to 15% in catalyst activity, it can still be reused. Ensuring catalyst stability is of great importance for industrial applications and reducing the cost of biodiesel production (Zhang *et al.*, 2018). Therefore, the results obtained suggest that the KF/clay catalyst has considerable stability and can be used continuously for ~ 6 hours of operation.

The stability of the catalyst used in the transesterification reactions in a continuous and pressurized reactor was investigated by other researchers. Jesus (2010) used 4 g of hydrotalcites in pressurized methanol at 300 °C, 15 MPa and residence time of 7 min, and observed that the ester content remained unchanged for 24h. Visioli *et al.* (2019) analyzed the reaction of macauba oil and methyl acetate using 2 g γ -alumina catalyst and found that the catalyst remained stable in the evaluated period (8 h) at 225 and 275 °C, with no loss in activity of the catalyst.

Regarding the catalyst stability in reactions conducted in a batch reactor, Teo *et al.* (2015) evaluated the activity of the catalyst for 5 cycles of 10 min and found a reduction of $\sim 25\%$ in the esters yield in the fourth cycle, for the reaction between *Jatropha curcas* L. oil and methanol, with 1 wt.% of CaLaO catalyst, at 240 °C. In the study by Ribeiro *et al.* (2018) the reuse of the γ -alumina catalyst at 300 °C was reported for 8 cycles of 60 min each, with a reduction of 12.47% in ester content after the seventh cycle.

3.3. Two-step reaction

Based on the results obtained in the first step of the reaction with KF/clay catalyst, a second step was conducted to investigate the influence of the recycled catalyst and the new catalyst in the reaction. The first-step sample (time 0) was obtained in 15 min of reaction, 275 °C, oil-to-ethanol mass ratio 1:1.5 and 2 g of catalyst, and used to conduct the second step, under the same operating conditions with residence times of 15, 30 and 45 min. The esters and inter-

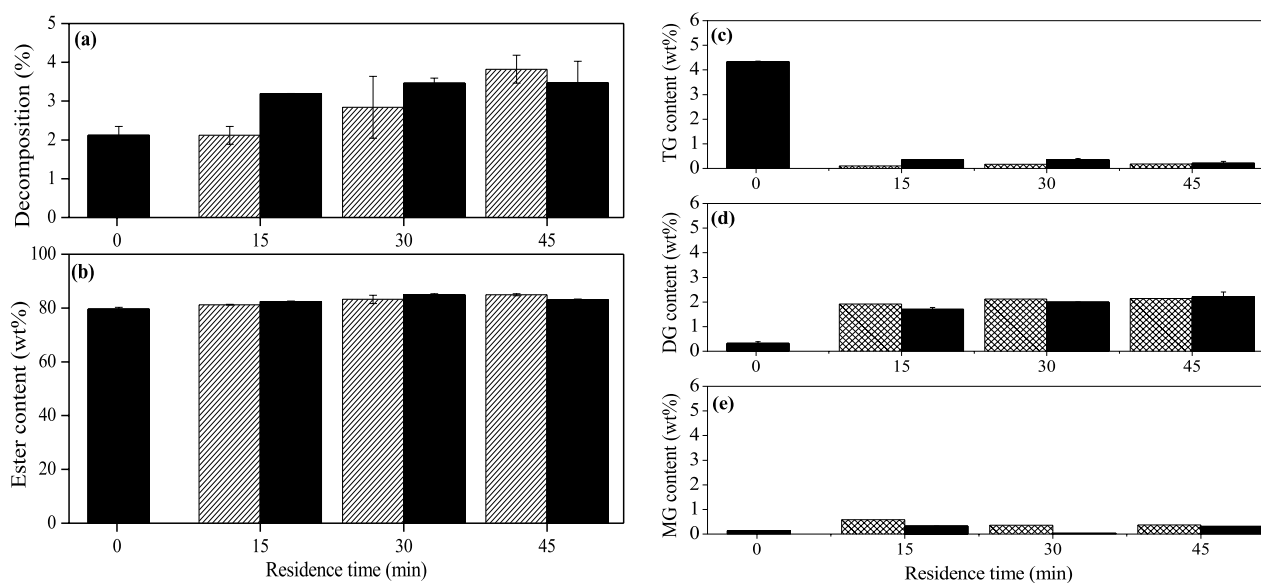


FIGURE 4. Reaction products obtained in two-step reaction at 275 °C, 20 MPa, oil-to-ethanol mass ratio 1:1.5 and applying 2 g of recycled catalyst (▨) and new catalyst (■): (a) ester content, (b) thermal decomposition, and content of (c) triglycerides, (d) diglycerides and (e) monoglycerides. Values are presented as mean \pm standard deviation ($n=2$).

mediate compound contents obtained are presented in Figure 4, as well as the values for percentage of thermal decomposition.

Applying the second reaction step, it was possible to verify that using recycled and new catalysts, they provided an increase of $\sim 6.6\%$ in the ester content, respectively. Trentini *et al.* (2018) carried out the reaction in two steps, using lipids from grease trap waste and ethanol, in which the ester content increased from ~ 70 to 72% . Regarding thermal decomposition (Figure 4b), this was higher than that found in the first reaction step, reaching values of $\sim 3.8\%$. However, these decomposition values are still low, since numbers between 6-7% are reported in the literature for reactions with residual oils and the same temperature range as in this study (Abdala *et al.*, 2014; Trentini *et al.*, 2020).

Figure 4c shows a reduction in the triglyceride content (TG), compared to the first reaction step (time 0), with $> 99\%$ consumption. In contrast, increases in diglyceride (DG) and monoglyceride (MG) contents were observed, (Figures 4d and 4e, respectively). The contents in intermediate compounds (DG and MG) obtained using a reaction step was 0.46 wt%, which increased to 2.50 - 2.53 wt%; while the content in triglycerides decreased from 4.34 to 0.19 - 0.36 wt%. Santos *et al.* (2018) reported the presence of ~ 12 wt% of intermediate com-

pounds, in ~ 30 min, 279 °C and 20 MPa for the reaction between acidic oil and ethanol, and Trentini *et al.* (2020) reported that 11.23 wt% unreacted compounds remained from the reaction with residual oil/crambe oil mixture (27/75) at 300 °C, 20 MPa and 30 min. Thus, the low levels found for the components in this study indicate the high conversion of residual frying oil into ethyl esters. The esters present in the samples, together with the intermediate components and the decomposed components total the convertibility content of the residual frying oil.

The execution of the second reaction stage for both tested catalysts was effective, and resulted in an increase in the ester content, low decomposition and still low content of unreacted compounds, proving the efficiency of the application of this process. According to the ANP 45/2014 (Brazil) (ANP, 2014) the limit for MG, DG and TG in biodiesel is 0.70 , 0.20 and 0.20 wt%, respectively, so the values obtained for MG and TG are in accordance with the legislation.

3.4. Comparison to the literature

Table 2 shows the comparison of the results obtained in this study with reports regarding the use of heterogeneous catalyst under pressurized conditions using a continuous reactor to obtain esters, as well as

TABLE 2. Comparison of the results obtained in this study with those reported in the literature for transesterification in continuous process.

Oil	Alcohol	T (°C)	P (MPa)	Oil-to-ethanol molar ratio	Catalyst/mass	Ester yield (%)	Reference
Frying oil	ethanol	275	20	1:20	KF/clay (2g)	94.85	This work
Soybean	methanol	300	15	1:30	Hydrotalcites (4g)	91.8	Jesus (2010)
Alga	methanol	340	15	1:31	Porous titania ²	94.7	Krohn <i>et al.</i> (2011)
Soybean	methanol	440	22.7	1:73.7	Base Modified Zirconia ²	98.2	McNeff <i>et al.</i> (2008)
Sunflower	methanol	205	25	1:253	acidic catalyst resin (Nafion SAC-13) 9g	88.2	Maçaira <i>et al.</i> (2011)
Rapessed	ethanol	350	30	1:20	Al ₂ O ₃ (2%wt)	97.86	Mazanov <i>et al.</i> (2016)
Frying oil	ethanol	300	20	1:204	Catalyst free	87	Abdala <i>et al.</i> (2014)
Frying oil	ethanol	325	15	1:305	Catalyst free	82.2	Gonzalez <i>et al.</i> (2013)
Waste oil	ethanol	300	15	1:156	Catalyst free	74	Fonseca <i>et al.</i> (2018)
Waste oil	ethanol	300	20	1:39	Catalyst free	~50.53	Trentini <i>et al.</i> (2020)

¹*n*-hexane as co-solvent in the process, molar ratio of 1:90 methanol:*n*-hexane; ²The authors did not inform the mass or concentration of catalyst employed; ³ CO₂ was employed in the process (mass ratio of 25:75 methanol:CO₂); ⁴ *n*-hexane was used as co-solvent in the process (20% wt in relation to ethanol); ⁵ water was employed in the process, 5% wt (in relation to ethanol); ⁶Hydroesterification - a previous hydrolysis step was carried out with a mass ratio of 1:1 (oil:water) and 50% *n*-hexane (in relation to the oil mass) and subsequent esterification reaction

research using RFO in pressurized conditions, without using a catalyst.

As seen in Table 2, for reactions conducted using catalysts and refined oils, ester yields close to this research were obtained; however, the use of residual frying oil represents an ecologically better, low-cost option (Hajjari *et al.*, 2017). In the studies carried out by Jesus (2010) and Krohn *et al.* (2011) methanol, alcohol of better efficiency in transesterification, was used, due to the lower activation energy compared to ethanol, which implies a higher reaction rate. However, they were not able to obtain results higher to those reported in this study, in addition, the production of biodiesel through ethanol is more attractive, as it is a reagent obtained from renewable sources (Soares and Andreozzi, 2011). McNeff *et al.* (2008) and Mazanov *et al.* (2016) reported higher yields than this study, although the reactions were carried out at higher temperatures (440 and 350 °C, respectively).

The researchers Maçaira *et al.* (2011), also using a catalyst, reported a lower yield than that obtained in this research for the reaction at ~200 °C, lower than the critical alcohol temperature, which may have influenced the low ester yield when compared to this study. The esters yield obtained in this study was high when compared to other studies (Table 2) that also used residual frying oil (Abdala *et al.*, 2014; Fonseca *et al.*, 2018; Gonzalez *et al.*, 2013;

Trentini *et al.*, 2020). Fonseca *et al.* (2018) reported 74% esters through hydro-esterification at 300 °C. However, a previous hydrolysis step was performed in this study. It is important to mention that not even the addition of co-solvent (*n*-hexane) and water to the reaction, as performed by Abdala *et al.* (2014) and Gonzalez *et al.* (2013) respectively, resulted in a higher yield than reported in this study. Therefore, the presence of the KF/clay catalyst in the reaction was essential to achieving high ester yield.

In this work, oil-to-catalyst mass ratios of 8:1, 6.4:1 and 5.4:1 (oil to ethanol mass ratio 1:1, 1:1.5 and 1:2, respectively) were used, and high performance was achieved with the application of a low cost and residual oil for the production of renewable fuel, and under milder temperature conditions. It should be noted that for most cases, reactions using catalysts seek to conduct the reactions under less severe conditions, as it allows to reduce energy consumption (Andreo-Martinez *et al.*, 2020). In this way, the conditions reported in this study, which promoted high yield in esters, applying residual oil, ethanol and lower temperature are advantageous, highlighting the effectiveness of the KF/clay catalyst in the production of biodiesel. In addition, the catalyst used is easy to obtain and comes from clay, a cheap and natural source which can be of great interest for the various benefits linked to its use.

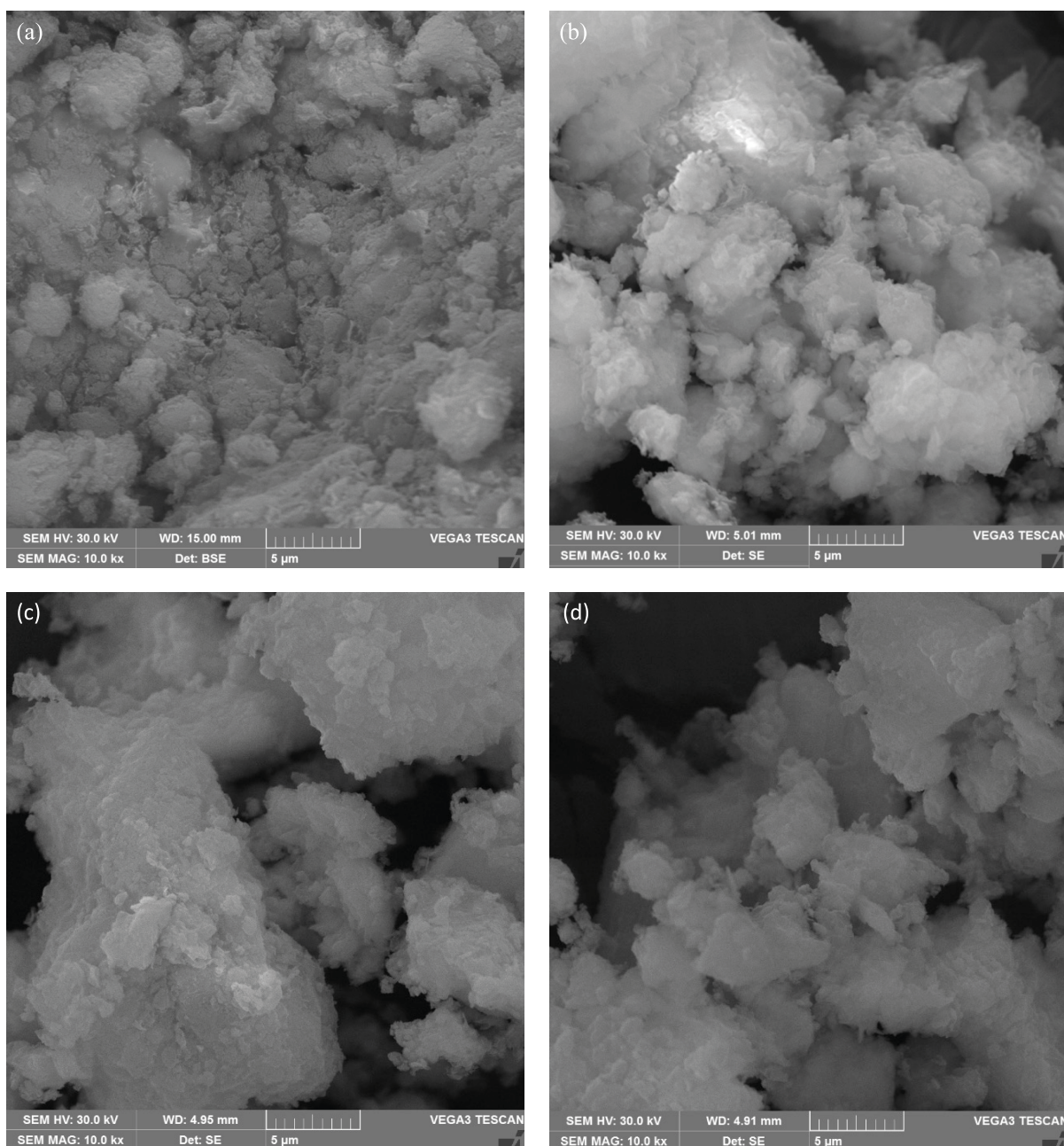


FIGURE 5. Micrographs: (a) catalyst before use, and catalyst recovered after the reactions of (b) stability (8 h); (c) two steps (recycled) and (d) two-step (new catalyst).

3.5. Catalyst characterization

The micrographs of the catalyst employed in the reactions, before and after the reactions of stability and two steps (recycled and new catalyst) are set forth in Figure 5. Note that the recovered catalyst samples (Figures 5b-d) resemble the catalyst before being used in the processes (Figure 5a), maintaining

the rough-appearance characteristic of this process. Even after exposure to the conditions of temperature and pressure employed, the granules of the catalyst were not destroyed, which suggests that the stages of compaction and granulation were successful, and that the material performed well during the reaction time. Thus, the conditions employed in the studied reactions did not significantly modify the morpho-

TABLE 3. Analysis of energy dispersive spectroscopy (EDS) of catalyst and recovered catalyst.

Elements (%)	Catalyst (KF/Clay)	Recovered catalyst		
		Estability	Two steps (recicle)	Two steps (new catalyst)
C	3.6	15.55	12.4	5.73
O	36.2	46.39	45.58	44.95
Na	0.7	0.71	0.57	0.56
Mg	1.2	1.24	1.01	1.08
Al	3.6	3.03	2.66	2.80
Si	18.5	11.88	13.92	17.87
Ca	ND	0.33	0.39	0.28
Fe	0.6	0.16	0.14	0.19
K	16.5	4.58	6.27	8.46
F	19.4	16.03	17.06	18.08

logical characteristics of the catalyst, indicating that the compacting process was effective for the possibility of its application in pressurized and continuous processes.

The quantification of the elements present in the catalyst before and after the reactions is in Table 3, obtained from the semi-quantitative analysis of energy dispersive spectroscopy (EDS).

The presence of fluoride (19.4%) and potassium (16.5%) in the catalyst sample is due to the impregnation process with potassium fluoride salt. It can be observed that in the recovered samples there was a decrease in these components (mainly potassium), being more accentuated for the catalysts that were exposed for the longest time to the operational conditions (stability reaction and 2 stages with recycle). The activity of the catalysts found is due to the basic sites generated precisely in the impregnation with KF, since the active sites correspond to the fluoride ions themselves and to the negatively charged oxygen atoms located in their vicinity, and the presence of K^+ cations distributed around the active sites generating the basicity of the catalyst (Alves *et al.*, 2014; Boz *et al.*, 2009; Endalew *et al.*, 2011). Thus, the results from the EDS analysis (Table 3) indicate that the leaching of these elements resulted in a drop in yield over the 8 h operation in the stability reaction (Figure 3). When the two-step reactions were compared (Figure 4), the catalyst submitted to reuse showed lower yield than the reaction with a new catalyst, showing the occurrence

of leaching of these elements (F and K). The other elements present in the catalyst originated from clay, which is composed of several types of minerals and their composition can vary. The catalyst recovered after the reactions had a higher carbon content, which may be due to remaining oil residues and esters in the sample, even after washing. It is worth noting that the EDS results are semi-quantitative, and that the percentages shown in Table 3 represent the average composition of five selected regions within each analyzed micrograph.

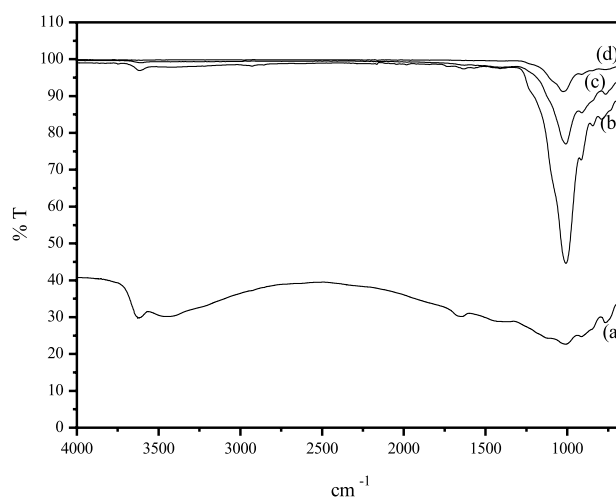


FIGURE 6. Infrared spectra for (a) catalyst and recovered catalyst after the transesterification reaction: (b) stability; (c) two steps, new catalyst and (d) two steps, recycled catalyst.

Figure 6 s shows the infrared spectra for the catalyst samples before (a) and after the stability reactions (b), two steps with new catalyst (c) and two steps using recycled catalyst (d). The vibration bands that appear between 650 and 1200 cm^{-1} correspond to Si-O and Si-O-Al vibrations, and are typical of quartz and montmorillonite clay minerals, with bands appearing between 700 and 900 cm^{-1} to the octahedral layers of clay. These vibrations remain even on the catalysts subjected to the reactions. In the range of 900 to 1100 cm^{-1} there is the characteristic SiO bond elongation, being more evident in the catalyst after use in the reactions (b-d), probably due to the leaching of the K^+ ion, which is responsible for the catalyst activity. Thus, the structure of the clay becomes more evident and for this reason, the increase in the band attributed to the SiO bond present in the minerals of the clay occurs. The 3500 to 3800

cm^{-1} range corresponds to the O-H elongation. The bands in the region of $1250\text{--}1750\text{ cm}^{-1}$ correspond to the treatment of the clay with KF. Bands in the range of $1600\text{--}1700$ represent H-O-H and correspond to adsorbed water, present only in sample (a).

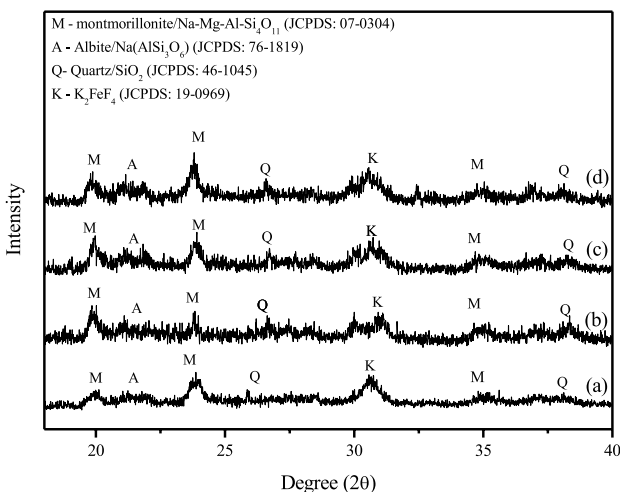


FIGURE 7. X-ray diffractometry for (a) catalyst and recovered catalyst after reactions from: (b) stability (c) Two steps, recycled catalyst (d) two-step, new catalyst.

In Figure 7 the XRD for the catalyst is presented before and after the use of stability reactions, two steps with new catalyst and recycled catalyst. The crystalline phases identified in the samples were montmorillonite ($\text{Na-Mg-Al-Si}_4\text{O}_{11}$), quartz (SiO_2) and albite ($\text{Na(AlSi}_3\text{O}_8)$), a type of feldspar. These phases were already predicted, as they are crystalline phases commonly found in bentonite clays. The peaks present in the catalyst (Figure 7a) remain similar in the catalysts recovered after use in the reactions (Figure 7b-d). There is also a crystalline phase in the catalyst, corresponding to the treatment with potassium fluoride, and it can be observed that the leaching shown in the EDS (Table 3) and FTIR (Figure 6) of the K^+ element is also evident in the XRD, mainly in the reaction which stood exposed for the longest operating conditions (stability, Figure 7b).

It is worth mentioning that there is some possibility for the development of a more stable catalyst in order to reduce the leaching of active species such as K^+ and F^- . According to the results obtained in this work, given the reactor operating conditions (temperature, flow and pressure practiced), it is believed that there is an “excess” of K^+ and F^- , which even-

tually are not interacting properly with the surface of the clay particles (weak interaction), in order to withstand the experimental conditions of temperature and pressure, which in turn, are not mild. Thus, it is necessary to conduct a future study to evaluate the amount of the KF saline precursor used in the impregnation, which can guarantee that the ideal content of K^+ and F^- ions capable of forming stable active sites on the catalyst surface.

4. CONCLUSIONS

In this work, the production of ethyl esters using residual frying oil and ethanol in a pressurized medium was investigated in the presence of the KF/clay catalyst. The results indicate that increasing the mass ratio of oil-to-ethanol resulted in ester yields close to those for the ratios of 1:1.5 and 1:2, in 30 and 45 min, with a mass ratio of 1:1.5 being sufficient to achieve balance. Raising the operating temperature from 275 to $300\text{ }^\circ\text{C}$ resulted in greater thermal decomposition of the esters. Conducting the reaction in one step at $275\text{ }^\circ\text{C}$, 20 MPa , mass ratio of oil-to-ethanol of 1:1.5 and 15 min provided maximum ester yield of $\sim 90\%$. Under the best operating conditions, the stability of the catalyst was evaluated for a period of 8 h, which provided consistent results in the first 3 h, and the yield decline in esters by 29% throughout the reaction, mainly due to potassium leaching. Conducting the reaction in two stages made it possible to obtain a higher yield in esters ($\sim 94.85\%$), using recycled catalyst and new catalyst, in addition to low thermal decomposition and higher consumption of TG. The conditions employed in the reactions did not cause significant changes in the morphology of the catalyst.

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