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Esterification of oleic acid employing sulfonated polystyrene and polysulfone membranes as catalysts

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Abstract

In the present study, catalytic activity of dense, porous, electrospun membranes of polysulfone (PSF) and polysulfone with sulfonated polystyrene (PSF_PSS) have been evaluated in reactions of esterification of oleic acid with methanol, in times that varied from 10 to 480 minutes. Conversion to biodiesel has been confirmed by FTIR and quantified through gas chromatography. The results showed the catalysts used were effective in the esterification reaction studied and the PSF_PSS electrospun membrane has presented the best conversion to methyl oleate, reaching 70.5% in a 10-minute reaction and 95.8% in a 240-minute reaction, when methanol:oleic acid molar ratio of 10:1, 5% of catalyst and temperature of 100 °C were used. Considering the performance of solid catalysts described in literature, mainly related to reaction times and conversion of the process, this study reveals a promising feasibility of using electrospun membranes of PSF_PSS for developing a heterogeneous acid catalyst aimed to biodiesel synthesis.

Keywords: *biodiesel, esterification, membranes, polysulfone, sulfonated polystyrene.*

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1. Introduction

Increasing population, urbanization and industrialization induce to a drastic need of energy. It is estimated that the global demand for energy will increase from almost 286 million barrels of oil equivalent per day (mboe/d) in 2018 to more than 357 mboe/d in 2040, with an average increase of around 1% per year[1]. The main energy source to the whole world is fossil biofuels, which includes all conventional sources of energy, such as petroleum-based, methane and coal. Due to the non-renewable nature of these resources, systematic rise in energy import prices and environmental factors, the interest in alternative sources of energy is increasingly growing[2]. In this context, biodiesel emerges as a biofuel that has similar properties to diesel fuel and has several benefits, such as being renewable, biodegradable, non-flammable, non-toxic, non-explosive and with low level of sulphur and pollutants emissions[3,4].

Alkyl fatty acid esters, or biodiesel, may be produced by transesterification of triglycerides or by esterification of free fatty acid with short chain alcohols in the presence of a catalyst[5]. The transesterification reaction performed with homogeneous alkaline catalysts is the technology commonly applied in biodiesel industry, presenting high yields, moderate operation conditions and fast reaction rates. Nevertheless, when oils with high acidity and moisture are applied with basic catalysts, production effectiveness decreases due to saponification reactions[2,6,7]. Although homogeneous acid catalyst is insensitive to free fatty acid content and has the potential to simultaneously perform esterification and transesterification reactions, the process has some disadvantages, such as equipment corrosion, slow reaction rates and great amount of effluents to be treated, increasing environmental pollution and production costs[6,8]. Thus, solid acid catalysts are a promising replacement to the process, since they are easily recovered and reused in the reaction, avoid reactor corrosion problems and reduce the stages of product purification[3,4]. Recently, fatty acid esterification from long hydrocarbon chain fatty acids in the presence of acid catalysts has drawn great interest, since the esters produced can also be applied as biofuels[9]. Comprehensively considering, heterogeneous acid catalysts as sulfated zirconia[10], ion exchange resin[11], materials based on carbon[7], zeolite[12] and heteropoly acids[13] are good examples of solid catalysts to this reaction, once they display relatively high catalytic activity in moderate conditions[14]. When it comes to esterification reaction mechanisms, the process of biodiesel acquisition occurs with the formation of an oxonium ion through protonation of the fatty acid, thereby increasing the electrophilic character of carbonyl group and facilitating the nucleophilic attack from the alcohol in order to produce a tetrahedral intermediate. Subsequently, this intermediate goes through rearrangement, a water molecule is withdrawn, the ester is formed and the catalyst is recovered[2], as shown in Figure 1.

Functional polymer materials, such as microspheres and membranes, chemically modified with acid groups are also viable options to overcome deficiencies and replace liquid acids in several organic reactions (transesterification and esterification, among them). The most used in heterogeneous acid catalysis are sulfonic resins (cation exchangers), Nafion non-porous resins and Amberlyst macroporous resins being the most common[15]. In literature, there are many papers which report the use of acid polymer materials as solid catalysts in reactions aiming biodiesel production[16-21].

Polystyrene (PS), a thermoplastic polymer with good mechanic and insulating properties widely used in beaker production, transparent packing for foods, audio/video packaging, and light bulbs caps, among others[22], may be easily modified through sulfonation reactions to be applied as solid catalyst[18]. Meanwhile, a careful control of its degree of sulfonation (DS) is needed, considering some materials with high DS - for being soluble in water - would have little application in heterogeneous catalysis[23]. Also belonging to the thermoplastic class, there is polysulfone (PSF), a polymer formed by two monomers, bisphenol-A and diphenyl sulfone, which has great mechanic resistance, good dimensional and thermic stability, adequate flexibility, and high chemical and hydrolytic stability[24,25]. This polymer has been broadly used in resin manufacturing are allocated to the construction of

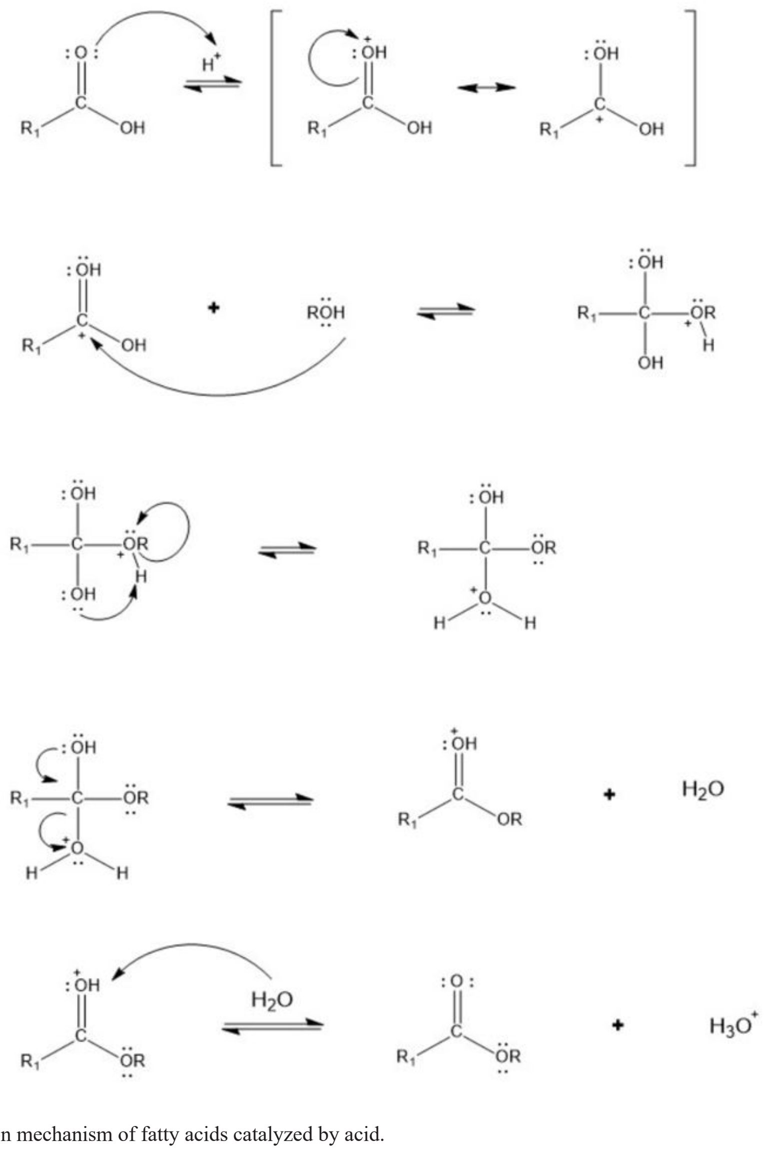

Figure 1. Esterification mechanism of fatty acids catalyzed by acid.

parts and equipments in electrical and automotive engineering, household and medical equipments and also as membrane materials for being highly thermostable[26].

Considering this context, the preparation and characterization of dense (D), porous (P) and electrospun (E) membranes of polysulfone and polysulfone with sulfonated polystyrene (PSF_PSS) had been reported in a previous paper generated in our laboratory, aiming a preliminary evaluation of their catalytic properties in esterification reactions from oleic acid with methanol[27]. Due to the obtained results that illustrated the good performance of PSF_PSS membranes as heterogeneous acid catalysts in the reactional time of two hours, esterification experiments have been expanded in the work reported in the present paper, ranging reaction times, with the aim of improving the maximum obtainable conversion, linking the catalytic activity with physical and chemical properties from different membranes.

2. Materials and Methods

2.1. Materials

For the esterification reaction, oleic acid (Fluka Analytical) and methanol (PA, Sigma Aldrich) have been used. Dense, porous and electrospun membranes of polysulfone, with maximum degradation temperatures ($T_{máx}$) of 531, 532 and 531 °C, respectively, and dense, porous and electrospun membranes of polysulfone with sulfonated polystyrene, with $T_{máx}$ of 526, 527 and 527 °C and superficial area of ~0, 5.4 and 184.4 $m^2 g^{-1}$, respectively, have been used as catalysts in this reaction. These membranes have been produced and characterized according to the previously mentioned paper[27] using the Carl Zeiss EVO MA10 and Tescam VEGA 3 LMU microscopes, which evidenced the homogeneous structures, materials with pores and materials formed by nanofiber networks. Dense, porous and electrospun membranes, respectively, have been produced as shown in SEM micrographs in Figure 2. Potassium bromide (PA, Vetec) for infrared analysis and methyl oleate (Sigma Aldrich) for gas chromatography with flame ionization detector have also been used in the development of this paper.

The sulfonation degree (SD) of PSF_PSS membranes was determined by titration with a standardized NaOH solution 0.01 mol L^{-1}. The SD was calculated using Equation 1.

$$SD = \frac{\left(104 * M_{NaOH} * V_{NaOH}\right)}{m - \left(81 * M_{NaOH} * V_{NaOH}\right)} \quad (1)$$

Where:

104 = Molar mass of the monomeric unit (g mol^{-1}).

M_{NaOH} = Concentration of the standard NaOH solution (mol L^{-1}).

V_{NaOH}= Volume of NaOH solution spent in the titration (L).

m = Sample mass (g).

81= Molar mass of the SO_3H group (g mol^{-1}).

2.2. Esterification reaction

The catalytic performance of PSF and PSF_PSS membranes has been evaluated in the previously mentioned paper[27] in esterification reactions from oleic acid with methanol in a two-hour time. In this present paper, catalytic activity from membranes has been evaluated in different reactional times, ranging from 10 to 480 minutes. For this reaction, 5% of catalyst was added to methanol and the compound was kept resting for 24 hours. Afterwards, this solution was put into a Parr reactor, model 4848, together with oleic acid. The alcohol:oleic acid molar ratio was 10:1 and the reaction occurred at 100 °C. At the end of the process, the catalyst was removed from the reactional mean by simple filtration, and the product was submitted to evaporation under a reduced pressure process in order to withdraw excessive water and methanol.

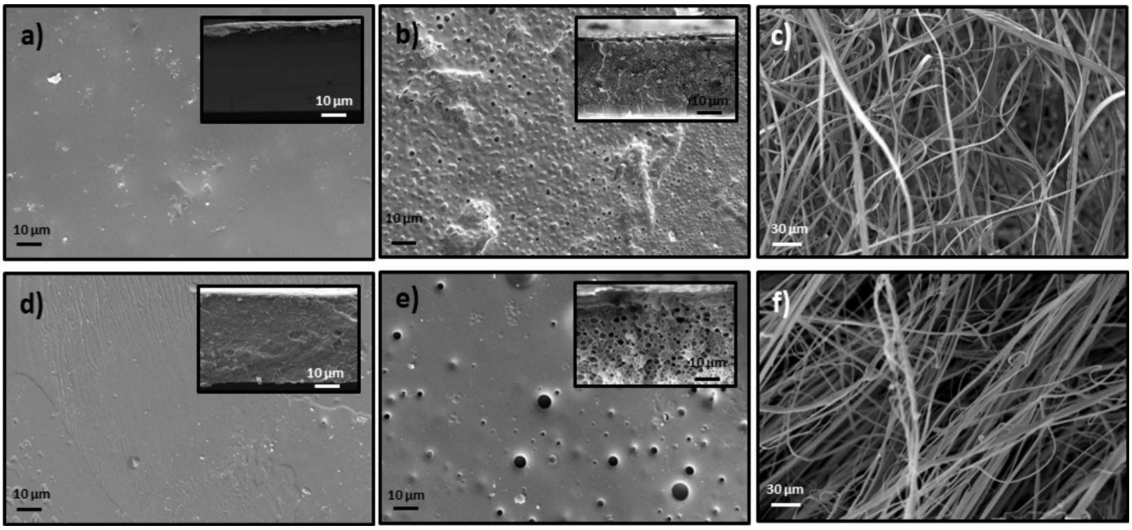

Figure 2. SEM of membranes: (a) PSF Dense (magnification 2,000x); (b) PSF Porous (magnification 2,000x); (c) PSF Electrospun (magnification 250x); (d) PSF_PSS Dense (magnification 2,000x); (e) PSF_PSS Porous (magnification 2,000x); (f) PSF_PSS Electrospun (magnification 250x)[27]. The inset shows SEM images of the fractured surface on their respective membranes (magnification 5,000x).

The catalyst reuse test was performed for the PSF_PSS-E 10 min membrane. The catalysts were separated by simple filtration, washed with 10 mL anhydrous ethanol and 10 mL water, followed by a drying at 70 ºC for 3 h.

2.3. Characterization techniques

Analyses of characterization performed to the obtained methyl esters included Fourier transform infrared (FTIR) and gas chromatography with flame ionization detector (GC-FID).

FTIR spectra, using a Shimadzu IRPrestige-21 equipment, has been used to identify functional groups in the samples by KBr method and registered in the range of 4000 – 400 cm^{-1} [28].

For quantifying the methyl ester formation, an analytical curve from methyl oleate standard has been elaborated, being the analyses from the standard and the conversion products performed in a Thermo® gas chromatograph, model Focus GC. The temperature of the column oven was kept in isotherm to 190 °C. Other technique elements included: split injection, with flux division 1:10 and temperature of 250 °C; flame ionization detection, with temperature detection of 250 °C; injection of 1 µL sample; total analysis time for each sample of 5 minutes. Applied column: capillary column of stationary poly (ethylene glycol), Carbowax brand, 30 m length, 0.32 mm intern diameter and 0.25 µm film thickness.

3. Results and Discussions

The polymeric catalyst activity is influenced by the incorporated sulfonic groups providing acidic sites for the esterification. Thus, the PSF_PSS membranes were evaluated for the sulfonation degree and obtained a SD value equal to 24%.

Figures 3 and 4 show spectra from products obtained by esterification using PSF and PSF_PSS membranes, respectively, in all reaction times studied. As the main characteristic changes of oleic acid conversion in biodiesel are focused in the 1800 to 1100 cm^{-1} region, only this will be presented to make the discussion easier. Analyzing the spectra, it is observed that the band in 1710 cm^{-1} corresponding to the stretching from C=O bond of acids is more pronounced in products that used PSF membranes, proving that there was not oleic acid full consumption in these esterification reactions. Band in 1742 cm^{-1} assigned to C=O bond from esters is more pronounced in products obtained when PSS_PSF membranes have been applied as catalysts, pointing an increase in biodiesel formation. Furthermore, stretching from O-CH$_3$ bond located in 1196 cm^{-1}, typical of methylic biodiesel, is more evident in product spectra obtained when PSF_PSS membranes catalyzed the reaction, showing greater oleic acid conversion to methyl oleate in these reactional systems[8,29,30].

Biodiesel quantification produced by the esterification reactions has been performed by GC-FID and an analytical curve has been built to determine the concentration of methyl oleate formed. Linear regression proved to fit well to data, with linear regression coefficient of 0.998, by the internal standard method. Biodiesel conversion values obtained in catalyzed reactions by dense, porous and electrospun membranes of PSF and PSF_PSS, after the reaction times of 10, 30, 60, 90, 120, 240, 360 and 480 minutes are listed in Table 1.

Analyzing Table 1, it is observed that, in general, PSF membranes have presented low oleic acid conversion into methyl oleate, showing average results only in long reactional times, while PSF_PSS membranes have presented better results in all periods of time studied, reaching even satisfying

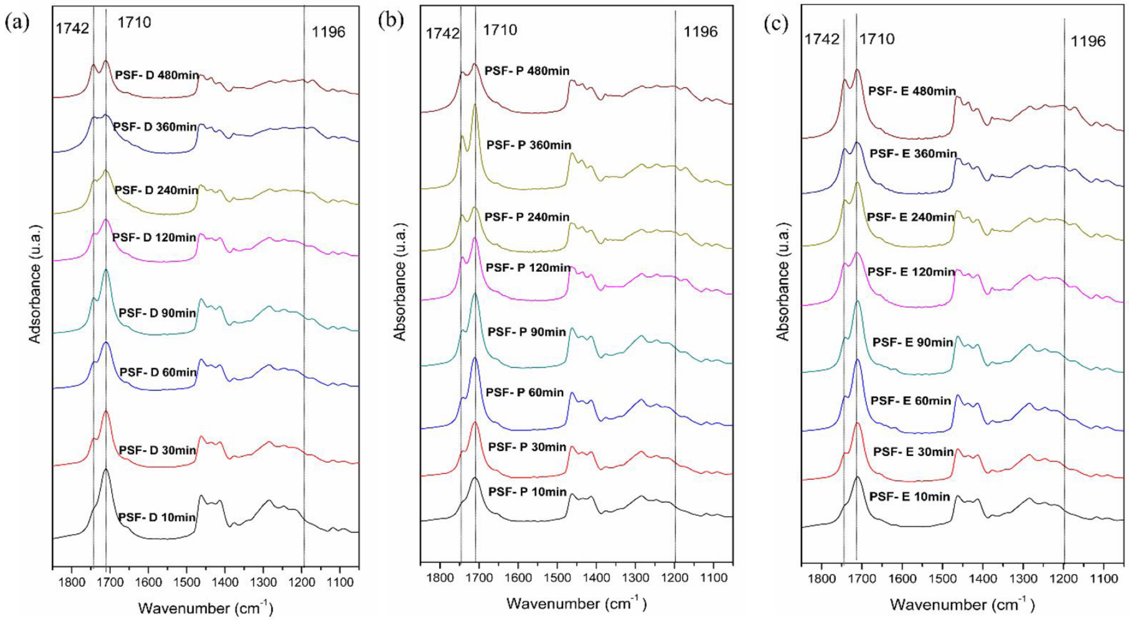

Figure 3. FTIR of membranes of PSF at all reaction times: (a) dense, (b) porous and (c) electrospun.

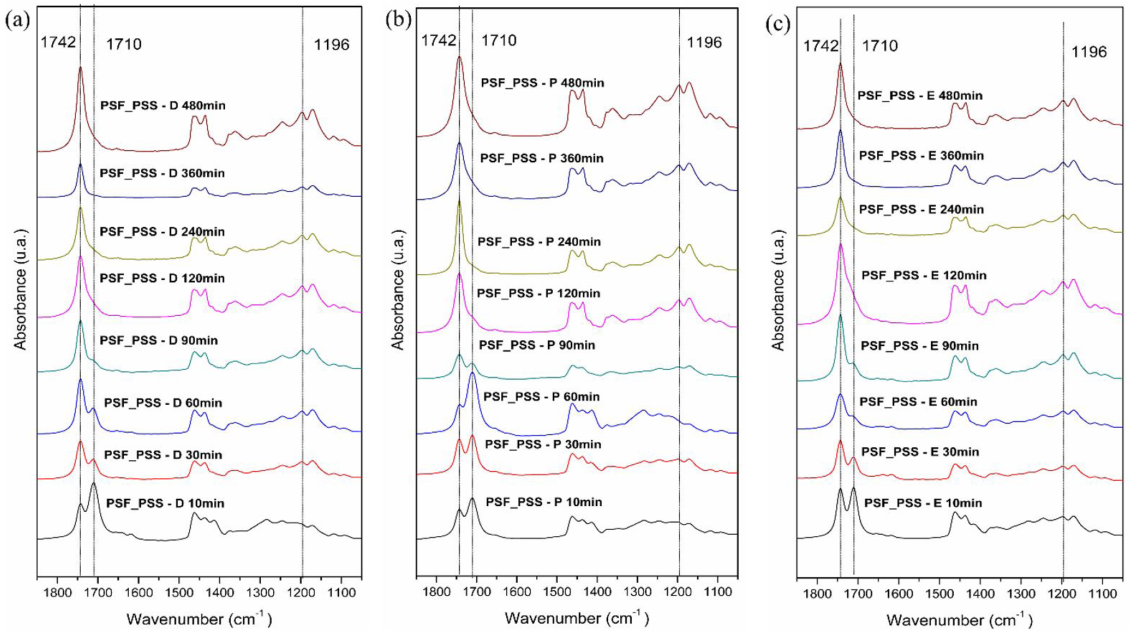

Figure 4. FTIR of membranes of PSF_PSS at all reaction times: (a) dense, (b) porous and (c) electrospun.

conversions in reaction times relatively low. PSF electrospun membrane provided a conversion of 7.5% in 10 minutes, whereas PSF_PSS electrospun membrane converted 70.5% of fatty acid to methylic ester in the same time range. Comparing the performance of porous membranes in 60 minutes of reaction, it is observed that the PSF membrane resulted in a conversion of 18.0%, whereas PSF_PSS membrane led to a conversion of 65.5%. As an example of dense membranes, a conversion of 15.7% was obtained for the PSF membrane, whereas the catalyzed reaction with PSF_PSS converted 63.9% in 90 minutes of reaction. These results showed that the presence of sulfonated polystyrene in membranes has increased the conversion efficiency, as more active acid sites were available to catalyze the reaction.

The best conversion rates found for a PSS_PSF electrospun membrane, even in short reaction times, may be attributed to its large superficial area, which allows reagents (methanol and oleic acid) to effectively spread in the catalytically active sites, increasing interaction due to better accessibility[5,11,20]. The superficial area of this membrane, for example, is approximately 34 times larger than the one from PSF_PSS porous membrane, whereas dense membrane has a superficial area near zero.

In some cases, reaction conversion rates decreased while reaction time increased. For instance, the catalyzed esterification with PSF_PSS electrospun membrane, has converted 81.4% in a 360-minute reaction, while in 480 minutes this value has dropped to 68.1%. This may be attributed to the reversibility of esterification reactions, indicating that prolonged times may cause hydrolysis of the formed ester[7,8].

A pattern of similar results had been reported in the authors' previously mentioned paper, which has evaluated the catalytic performance of these membranes in two reaction times as a function of oleic acid consumption. The values of fatty acid concentration found have shown that PSF membranes were not effective to catalyze the reaction, and better results were obtained when PSS_PSF porous and electrospun membranes were used as catalysts[27].

The use of polymer acids catalysts in esterification reactions is already the subject of study in literature. In the paper of Grossi et al.[18], oleic acid esterification has been performed using sulfonated polystyrene and a conversion of approximately 90% was found in 8 hours of reaction. Gomes et al.[20] have studied esterification of several fatty acids catalyzed by porous co-polymer poly-divinylbenzene-co-triallylamine and it was found for the oleic acid methanolysis a yield of 92% after 10 hours of reaction. Dechakhumwat et al.[5] studied the catalytic activity from a sulfonated residue derived from corn on the cob in oleic acid esterification with methanol, and they obtained a methyl oleate yield next to 80% after 8 hours of reaction. Pan et al.[21] have carried out esterification reactions using an acid catalyst obtained by sulfonation of ethylenediamine in polydivinylbenzene, and after a 4-hour reaction at 100 °C they obtained 85% conversion. Considering the conversion results obtained in the present study, one can affirm that though heterogeneous catalysis usually requires more severe reactional conditions and longer periods of time to obtain a good performance, 10 minutes of reaction were enough to obtain a significant conversion when PSF_PSS electrospun membrane was applied as reaction catalyst.

The catalyst reuse test was performed for the reaction condition: molar ratio oleic acid:methanol 1:10, temperature of 100 °C, 5% catalyst and 10 minutes of reaction for the electrospun membrane (PSF_PSS-E 10 min). Figure 5 show FTIR from products obtained by esterification in three reuse cycles.

Table 1. Percentage conversion of oleic acid to methyl oleate, measured by GC-FID.

Sample	Conversion (%)
PSF-D 10 min	**10.4**
PSF-D 30 min	**7.8**
PSF-D 60 min	**8.3**
PSF-D 90 min	**15.7**
PSF-D 120 min	**12.2**
PSF-D 240 min	**21.2**
PSF-D 360 min	**54.7**
PSF-D 480 min	**42.4**
PSF-P 10 min	**6.6**
PSF-P 30 min	**12.7**
PSF-P 60 min	**18.0**
PSF-P 90 min	**22.3**
PSF-P 120 min	**19.3**
PSF-P 240 min	**31.3**
PSF-P 360 min	**52.1**
PSF-P 480 min	**59.6**
PSF-E 10 min	**7.5**
PSF-E 30 min	**11.2**
PSF-E 60 min	**11.3**
PSF-E 90 min	**14.4**
PSF-E 120 min	**16.6**
PSF-E 240 min	**26.4**
PSF-E 360 min	**51.2**
PSF-E 480 min	**39.9**
PSF_PSS-D 10 min	**30.0**
PSF_PSS-D 30 min	**56.2**
PSF_PSS-D 60 min	**87.0**
PSF_PSS-D 90 min	**63.9**
PSF_PSS-D 120 min	**91.6**
PSF_PSS-D 240 min	**85.1**
PSF_PSS-D 360 min	**72.5**
PSF_PSS-D 480 min	**95.4**
PSF_PSS-P 10 min	**38.9**
PSF_PSS-P 30 min	**40.0**
PSF_PSS-P 60 min	**65.5**
PSF_PSS-P 90 min	**56.3**
PSF_PSS-P 120 min	**73.4**
PSF_PSS-P 240 min	**62.8**
PSF_PSS-P 360 min	**63.3**
PSF_PSS-P 480 min	**70.7**
PSF_PSS-E 10 min	**70.5**
PSF_PSS-E 30 min	**63.4**
PSF_PSS-E 60 min	**70.6**
PSF_PSS-E 90 min	**69.0**
PSF_PSS-120 min	**59.1**
PSF_PSS-E 240 min	**95.8**
PSF_PSS-E 360 min	**81.4**
PSF_PSS-E 480 min	**68.1**

Analyzing the FTIR spectra in Figure 5, it is observed that the band in 1710 cm^{-1} corresponding to the stretching from C=O bond of acids gradually increases and is more pronounced on the third reuse, proving that there was not oleic acid full consumption in these esterification reactions. The band in 1742 cm^{-1} assigned to C=O bond from esters is more pronounced in product obtained in first reuse and gradually decreases. The loss of catalyst activity may be due to a reduced surface area and reduced acid site concentration[19]. In the first reuse, the catalyst showed a higher catalytic activity and this leads to the conclusion that this catalyst presents possibilities for reuse.

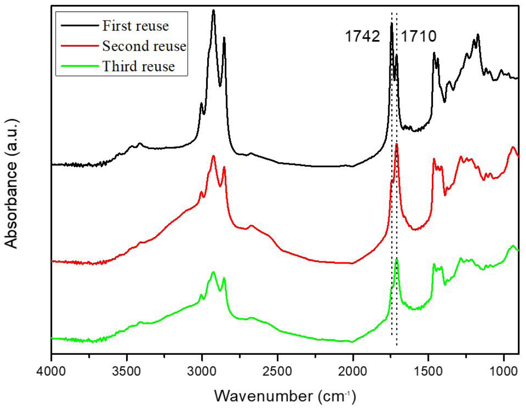

Figure 5. FTIR from products obtained by esterification using PSF_PSS electrospun membranes in three reuse cycles.

4. Conclusions

In this paper, catalytic activity from six polymer membranes of PSF and PSF_PSS were investigated in esterification of oleic acids with methanol, in different reactional times. FTIR has confirmed the formation of methylic esters and the consumption of oleic acid. And by using gas chromatography, it was possible to quantify methyl oleate formation as a reaction product. The results have shown that PSF_PSS membranes, having more acidic sites in their structure due to the presence of sulfonated polystyrene, had a better catalytic performance than PSF membranes. Having a larger superficial area, the electrospun membrane resulted in a conversion of 70.6% with only 10 minutes of reaction and 95.8% in 240 minutes. Thus, results have shown that polysulfone with sulfonated polystyrene membranes, in particular electrospun, may be successfully applied as heterogeneous catalyst acids in esterification reactions from oleic acid with methanol, aiming biodiesel production, mainly due to the good conversion achieved in short reaction times with the possibility of reusing the catalyst.

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