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Article

$SnSO_4$ as Catalyst for Simultaneous Transesterification and Esterification of Acid Soybean Oil

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O biodiesel é um biocombustível biodegradável e não tóxico produzido a partir de recursos renováveis. Sua produção industrial ocorre pela transesterificação catalítica de óleos vegetais refinados com metanol ou etanol. Os custos de produção do biodiesel podem ser reduzidos pelo uso de matérias-primas não refinadas, cujos preços são inferiores aos dos óleos vegetais refinados. Neste trabalho estudou-se o uso de sulfato de estanho(II) ($SnSO_4$), como catalisador para a transesterificação e esterificação simultânea de matérias-primas modelo com altos teores de ácidos graxos livres. Analisou-se a influência de parâmetros experimentais, a lixiviação do catalisador bem como a sua capacidade de reutilização. Obteve-se rendimento elevado (92%) para uma matéria-prima modelo contendo 70% (m/m) de ácidos graxos livres (ácido oleico), a 100 °C, sob pressão autógena, 5% (m/m) de $SnSO_4$ em excesso de etanol, após 3 h de reação. O catalisador foi reutilizado por dez vezes sem decréscimo significativo no rendimento de biodiesel.

Biodiesel is an alternative biodegradable and non-toxic biofuel produced from renewable resources. Industrially, it is produced by catalytic transesterification of refined vegetable oil with methanol or ethanol. Biodiesel production costs can be reduced by using non-refined feedstocks whose market prices are lower than those of refined vegetable oils. This work studied the use of tin(II) sulfate ($SnSO_4$), as catalyst for the simultaneous transesterification and esterification of model acid oil containing high levels of free fatty acids. The influence of experimental parameters, catalyst leaching as well as its reusability was investigated. For a model feedstock containing 70 wt.% of free fatty acids (oleic acid), the highest biodiesel yield (92%) was obtained at 100 °C, under autogenous pressure, using 5 wt.% of $SnSO_4$ in excess of ethanol after 3 h of reaction. The catalyst was reused ten times without significant decrease in biodiesel yield.

Keywords: biodiesel, esterification, model acid oil, $SnSO_4$, tin catalysts

Introduction

The growing concern on the environmental problems, such as greenhouse gas emissions, has driven the development of researches aiming at sustainable solutions. In this context, the production of biofuels from renewable resources and environmentally non-aggressive processes appears as an interesting alternative to reduce the problems related not only to the environmental pollution but also to the long-term supply of fossil fuels.

Biodiesel is a non-polluting alternative fuel produced from renewable resources, such as vegetable oils or animal fats, whose chemical and physical properties closely resemble those of the petroleum diesel fuel. It consists of a mixture of fatty acid alkyl esters (FAAE), which is mainly produced by the catalytic transesterification of refined vegetable oils with short carbon-chain alcohols (methanol or ethanol) (Figure 1). Homogeneous strong base catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides, are the most industrially used due to their low cost and high performance under milder conditions, although they require the use of refined

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feedstock. The reaction also occurs in the presence of acid catalysts but under stronger reaction conditions and having as disadvantage the risks of corrosion of the equipment.

The costs of biodiesel production by transesterification are generally higher than those of petrodiesel production. According to Atabani *et al.*[1] the refined feedstock represents 75% of the overall biodiesel production cost. The alternative to reduce these costs is the use of non-refined feedstock whose price is low in the market. However, in order to use this type of feedstock, it is necessary to develop catalysts that are able to catalyze the transesterification of vegetable oils and the esterification of free fatty acids. Esterification is the reversible reaction of a fatty acid with an alcohol producing ester and water (Figure 2).

The most used acid catalysts for transesterification/esterification reactions are strong acids or metal oxides or salts, which may be heterogeneous or homogeneous. The use of the basic catalysts traditionally employed for transesterification reactions must be avoided because they promote saponification in the presence of acid feedstocks, which reduces FAAE yield and make the phase separation steps difficult. Esterification may even occur in the absence of catalyst; however, due to the weak acidity of carboxylic acids, the reaction is extremely slow and requires several days to reach equilibrium under typical reaction conditions.[2]

Commonly, H_2SO_4 is the catalyst used for esterification, however, substantial reactor corrosion and great generation of wastes, including salts formed due to neutralization of the mineral acid, are negative aspects of its use. The development of alternative catalysts for the esterification of free fatty acids (FFAs), based on Lewis acids, which are less corrosive and operate under mild conditions could allow the production of biodiesel in more competitive costs, in processes of environmental impact.[3] Tin compounds either in the oxide form or as its salts are extensively tested as catalysts for esterification and transesterification reactions.[3-9] Tin(II) cations are strong Lewis acids and when compared with other transition cations, the following order of acidity is observed: $Sn^{2+} >> Zn^{2+} > Pb^{2+} \sim Hg^{2+}$.[10] Mello *et al.*[11] studied the use of SnO as heterogeneous catalyst for FFA esterification with methanol. In this study, the reaction reached equilibrium with yields ranging from 80 and 90% after 3 h. Furthermore, they observed that tin(II) oxide (SnO) maintained its catalytic activity around 70% (time: 1 h), even after ten reuses in esterification reaction. One study that used $SnCl_2.2H_2O$ in homogeneous phase proved that esterification of FFA achieves high yields under mild reactions, suggesting tin chloride as a promising acid-catalyst for the production of biodiesel.[3]

The use of sulfated metal oxides in biodiesel production has also received attention. The use of sulfated tin oxide (SO_4/SnO_2) has shown strong surface acidity.[12] Lam *et al.*[6] investigated the use of SO_4/SnO_2 for biodiesel production from cooking oil, in the range between 1 to 8 wt.%, at 150 °C, for 3 h and using methanol/oil ratio equal to 10. The yield of fatty acid methyl ester (FAME) increased with increasing catalyst concentration until a value in which higher increments no longer increased the yield of FAME, reaching a maximum around 70%.

However, the use of these compounds is not yet fully clarified and other precursors can be tested, especially when used in reactions with high content of fatty acids, as well as in ethanol, since world biodiesel production is typically carried out employing methanol.[13] The use of methanol has been based on low cost compared to ethanol.[14] Methanolysis

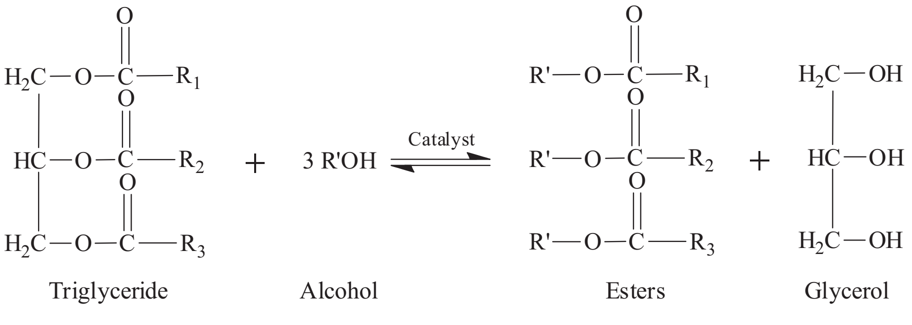

Figure 1. Fatty acid alkyl ester production by catalytic transesterification.

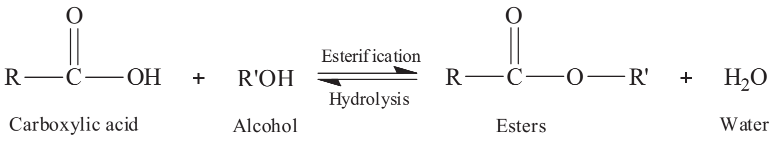

Figure 2. Esterification reaction.

is also faster than ethanolysis due to higher reactivity of the methoxide ion and easier in terms of phase separation (glycerol and esters). Meanwhile, the most environmentally friendly process is ethanolysis, since ethanol can be produced from biomass and high yield biodiesel can also be obtained. On the other hand, methanol is highly toxic and hazardous, its use requires special precautions while ethanol is simple to manipulate.

In the present work, the use of tin(II)-based compounds, particularly tin(II) sulfate, as catalysts for the simultaneous transesterification and esterification of soybean oil with high free fatty acid contents with ethanol was studied.

Experimental

Materials

Model acid feedstocks are used to simulate wastes of vegetable oil refining processes and are prepared by mixing a vegetable oil with different amounts of fatty acid. In this work, feedstocks were made by mixing stearic or oleic acid (85 wt.%, Vetec Química Fina, Brazil) and soybean oil (< 0.3 wt.% of acidity) in different proportions, and these mixtures were named “model acid oils”.

The catalyst tested was tin(II) sulfate ($SnSO_4$, 96 wt.%), but tin(II) chloride ($SnCl_2.2H_2O$, 98-103 wt.%) was also evaluated. All solids were supplied by Vetec Química Fina (Brazil) and were used without any previous treatment. Sulfuric acid (H_2SO_4, 95-97%, Merck) was used as reference.

Catalytic tests

The catalytic tests were carried out under autogenous pressure, in a 50 mL stainless steel batch reactor, equipped with temperature, pressure and agitation control. The influence of temperature (80-130 °C) and catalyst concentration (0.5-7 wt.%, based on the amount of oil + FFA) was investigated. The reaction time was kept constant and equal to 3 h and the amount of ethanol used was 3.5 times the stoichiometric amount for FFA esterification and soybean oil transesterification.

Acid content and free fatty acid (FFA) conversion

The acid content in the feedstock and the acid conversion were determined by titration with sodium hydroxide. In a typical procedure, 0.5 g of the sample (feedstock or reaction product after catalyst removal) was diluted in 25 mL of anhydrous ethanol containing 3 drops of phenolphthalein and then titrated with 0.1 mol L^{-1} NaOH solution.

Simultaneous monitoring of the esterification and transesterification processes (gas chromatography)

At the end of each catalytic test, the system was rapidly cooled down to room temperature and the catalyst was separated by centrifugation. The liquid phase was transferred to a separation funnel and the phase with lower density, which contains the ethyl ester mixture, was separated and then heated in rotary vacuum evaporator for elimination of water and ethanol. Afterwards, 20 µL of this phase were diluted in 480 µL of methyl heptadecanoate solution (internal standard, 9.6 g L^{-1} solution in *n*-hexane); the masses of the aliquots were taken for the calculations. A VARIAN CP 3380 chromatograph equipped with a CPWAX 52 CB capillary column (30 m × 0.25 mm × 0.25 µm) and a flame ionization detector was used. Injector and detector temperatures were 280 and 300 °C, respectively. The oven was initially kept at 200 °C for 4.5 min, then it was heated up to 250 °C at a heating rate of 20 °C min^{-1}, and kept at this temperature for 5 min. Hydrogen was used as the carrier gas at a 2 mL min^{-1} flow rate; column pressure was set at 20 psi and the split injection ratio at 1:20.

For the catalytic tests using the model acid oil with oleic acid, fatty acid ethyl ester (FAEE) yield expressed in terms of weight percentage corresponds to the contribution of both transesterification and esterification reactions. In order to evaluate the relative contribution of each reaction, the total mass of esters formed was calculated by equation 1 and the mass of esters formed from esterification (ethyl oleate) was calculated from the oleic acid conversion obtained by titration. In according with the stoichiometry of the esterification reaction (Figure 2), equation 2 was applied. The molar masses used in this calculation were 282.46 g mol^{-1} for oleic acid and 310.46 g mol^{-1} for methyl oleate. Thus, the mass of esters derived from the transesterification reaction (equation 3) was expressed by the difference between the total mass of esters obtained by gas chromatography (equation 1) and the mass of esters from esterification (equation 2). Finally, the conversions for esterification of oleic acid and transesterification of soybean oil were estimated in reference to its initial masses of oleic acid and soybean oil, respectively equations 4 and 5.

$$m_T = Y \times m_S \tag{1}$$

$$m_{E.E} = n_A \times X \times M_{E.E} \tag{2}$$

$$m_{E.T} = m_T - m_{E.E} \tag{3}$$

$$X_T = \frac{m_{E.T}}{m_O} \times 100 \tag{4}$$

$$X_E = \frac{m_{E.E}}{m_A} \times 100 \tag{5}$$

where m_A is the initial mass of oleic acid (g); $m_{E.E}$ is the mass of esters from esterification (g); $M_{E.E}$ is the molar mass of esters from esterification (g mol^{-1}); $m_{E.T}$ is the mass of esters from transesterification (g); m_T is the total mass of esters (g); m_O is the initial mass of soybean oil (g); m_S is the mass of sample (g); n_A is the initial number of moles of oleic acid; X is the conversion of oleic acid (%); X_T is the esterification conversion of oleic acid (%); X_E is the transesterification conversion of soybean oil (%); and Y is the FAEE yield (%).

Sulfur in biodiesel

The determination of sulfur content in the reaction product was performed on a LECO SC632 elemental analyzer. The sample is heated to 1350 °C in an induction furnace while passing a stream of oxygen through the sample. SO_2 released from the sample is measured by an infrared detection system and the total sulfur result is provided. The biodiesel samples were read on an alumina bed to avoid loss of material by volatilization.

Catalyst leaching

$SnSO_4$ leaching in ethanol or in water was investigated since it could acidify the reaction medium and promote homogeneous catalysis. This investigation was performed through experiments conducted at similar reaction conditions in the absence of the model oil acid. The test with ethanol was performed at 60 °C, whereas that with water was carried out at 100 ºC. In the latter, the volume of water employed was equivalent to that generated by a complete conversion of the oleic acid present in the model acid oil. At the end of the tests, $SnSO_4$ was decanted and the liquid phase was titrated.

Results and Discussion

Esterification of the model acid oil

The influence of several experimental parameters, such as catalyst concentration, reaction temperature, and tin precursor, as well as the reuse of the catalysts, were investigated in the esterification of a model acid oil (70 wt.% of stearic acid + 30 wt.% of soybean oil) with ethanol catalyzed by $SnSO_4$. The results were discussed based on the FFA conversion.

Effect of $SnSO_4$ concentration

The influence of catalyst concentration on the conversion of the model acid oil was investigated in the range between 0.5 to 7 wt.%, at 100 ºC, and using an amount of ethanol equal to 3.5 times the stoichiometric value. As shown in Figure 3, the conversion of the fatty acid increased with the increase in catalyst concentration reaching a maximum at 3 wt.%. Further increase in the amount of catalyst did not influence the FFA conversion. Although 3 wt.% of catalysts is sufficient to guarantee the highest conversion, the amount of 5 wt.% was selected to conduct further experiments. It was particularly important for the experiments aiming to evaluate the reuse of the catalyst, in order to compensate any loss of catalytic material.

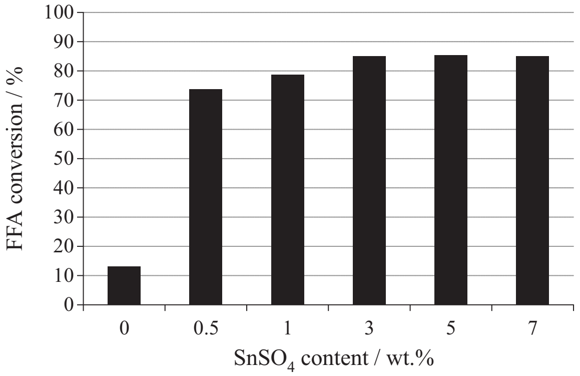

Figure 3. Effect of $SnSO_4$ concentration on the esterification of the model acid oil (stearic acid/soybean oil 70/30 m/m). Reaction conditions: T = 100 °C; $R_{EtOH/oil}$ = 3.5; reaction time = 3 h.

Effect of reaction temperature

Esterification and transesterification reactions can be considerably influenced by temperature, especially when using solid catalysts, since the high temperature helps overcome mass transfer limitations. However, the use of high reaction temperatures, especially above 200 °C, can generate undesirable products such as polar compounds and polymers.[15]

The effect of temperature on the esterification of the model acid oil (stearic acid/soybean oil 70/30 m/m) using $SnSO_4$ catalyst was investigated at 80, 100 and 130 °C. As shown in Figure 4, in this range the temperature influence was not important and good catalytic activity was achieved even at 80 °C. Taking into account our previous studies in which esterification of industrial waste organic acids were carried out at 100 °C, this temperature was selected for further tests in order to facilitate the comparison with our previous results.

Influence of tin precursor

In order to evaluate the influence of the tin precursor on the esterification of the model acid oil, tin(II) chloride was also evaluated as catalyst. Figure 5 compares the results of the model acid oil esterification catalyzed by $SnCl_2.2H_2O$

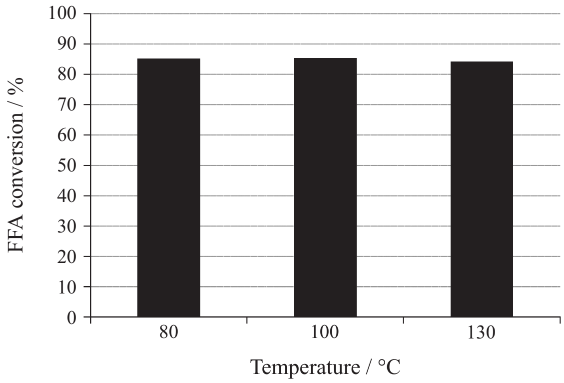

Figure 4. Influence of temperature on the esterification of the model acid oil (stearic acid/soybean oil 70/30 m/m). Reaction conditions: $R_{EtOH/oil}$ = 3.5; reaction time = 3 h; 5 wt.% catalyst.

and $SnSO_4$. The results obtained with sulfuric acid were also included, since it is a traditional catalyst in the esterification processes for biodiesel production. It can be observed that the activity of tin(II) sulfate (5 wt.%) was similar to that of sulfuric acid (1 wt.%) for the esterification of stearic acid. On the other hand, $SnCl_2.2H_2O$ (5 wt.%) was less active for the esterification reaction.

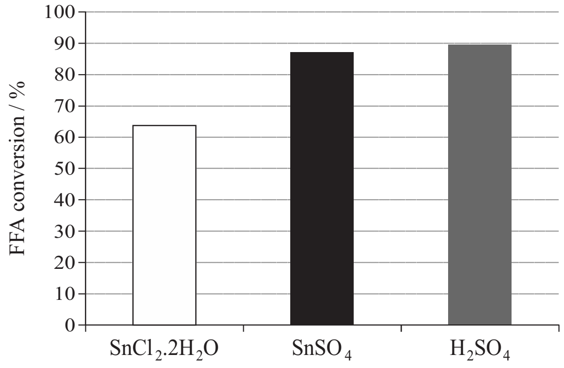

Figure 5. Esterification of the model acid oil (stearic acid/soybean oil 70/30 m/m) catalyzed by $SnSO_4$ (5 wt.%), $SnCl_2.2H_2O$ (5 wt.%), and H_2SO_4 (1 wt.%). Reaction conditions: T = 100 °C; $R_{EtOH/oil}$ = 3.5; reaction time = 3 h.

The catalytic activity of these tin(II) compounds may be related to their solubility in the reaction medium. Casas *et al.*[4] tested different tin-based catalysts (tin(II) acetate, tin(II) chloride, tin(II) 2-ethylhexanoate and tin(II) stearate) in transesterification and esterification reactions using acid vegetable oils. They observed that the solubility changes with the tin precursor. For example, tin(II) chloride was completely insoluble in sunflower oil but soluble in methanol, making it difficult to reach the triglyceride. Tin(II) acetate presents negligible solubility in triglycerides and methanol. Both showed good results in transesterification and esterification at 150 °C, reaching conversions above 90% but the use of tin(II) acetate required less time. According to the authors, the mechanism of both transesterification and esterification catalyzed by Lewis acids, as is the case of tin(II) catalysts, involves interactions between free tin(II) orbitals and the carbonyl group oxygen, decreasing the electronic density of the carbonyl carbon atom and making it more susceptible to nucleophilic attack. Thus, the carbonyl group must be easily accessible for the catalyst to start the reaction.

In the present work, it was observed that tin(II) chloride was highly soluble in ethanol, as previously observed for methanol, which prevents the contact between catalyst and the carbonyl group of (triglycerides and/or) stearic acid. This behavior can explain the lower activity when compared with tin(II) sulfate, which is insoluble in soybean oil, in fatty acids and slightly soluble in ethanol. In this case, the interactions between free tin(II) orbitals and the carbonyl oxygen are somewhat facilitated. Thus, the reaction proceeded also over the solid surface, easily accessible for ethanol and carbonyl compounds (triglycerides or stearic acid).

Another important aspect is the formation of water in the esterification reaction. $SnCl_2.2H_2O$ is also completely soluble in water (at 90 °C, under stirring, for 3 h), while $SnSO_4$ is partially soluble in the same conditions. This means that a possible leaching of both tin precursors can be occurring either by alcohol or by water.

In order to explain this fact, the catalyst leaching and its influence on catalytic activity will be further discussed in a particular topic of this paper.

Reuse of $SnSO_4$

Taking into account the good results obtained with tin(II) sulfate for the esterification of the model acid oil, its reusability was investigated not only for the model acid oil (70 wt.% of stearic acid + 30 wt.% of soybean oil) but also for a model feedstock containing 70 wt.% of oleic acid and 30 wt.% of soybean oil. As shown in Figure 6, $SnSO_4$ presented good reusability, presenting high conversion of fatty acids even after ten successive reaction cycles for both acidic mixtures.

The results presented in Figure 6 are quite similar and the fluctuations observed in the conversion of free fatty acid are probably due to experimental uncertainties associated not only with the conversion calculus but also with the reuse procedure. For the latter, before each reuse, the entire liquid phase of the previous use was removed and new reagents were added without any catalyst treatment. Since different amounts of the reaction mixture could be retained in the used catalyst, this could promote fluctuations in the conversion of each stage. As previously mentioned,

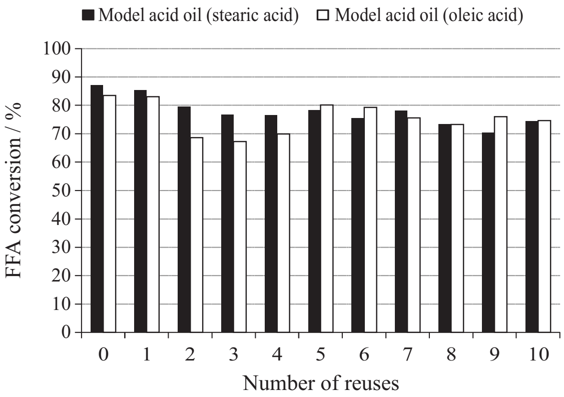

Figure 6. Reuse of $SnSO_4$ in the esterification of the model acid oil (70 wt.% fatty acid and 30 wt.% soybean oil). Reaction conditions: T = 100 °C; 5 wt.% of catalyst; $R_{EtOH/oil} = 3.5$; reaction time = 3 h.

the amount of catalyst used (5 wt.%) was sufficient to compensate the losses due to catalyst leaching.

Catalyst leaching

Although at the end of the catalytic tests the presence of the solid $SnSO_4$ could be apparently observed in the same initial amount, a possible leaching in water or ethanol cannot be disregarded. Thus, tests were conducted in order to investigate this phenomenon, showing that this catalyst can follow a pseudo-homogeneous pathway.[16]

When working with anhydrous reagents, water was absent from the reaction medium. However, esterification reaction generates water as a byproduct. Its impact on the kinetics of esterification reactions has been attributed to the hydrolysis reaction, in which ester reacts with water restoring the fatty acid.

The issue of water in the system under study has been identified as an additional problem. $SnSO_4$ was used as a heterogeneous catalyst since it is insoluble in oil. However, its solubility in water and ethanol cannot be neglected. According to Edwards *et al.*[17] and Ararat-Ibarguen *et al.*[18] tin(II) sulfate is spontaneously hydrolyzed in aqueous medium, leading to the formation of H^+ and SO_4^{2-}, which may catalyze the esterification reaction, and a precipitate identified as basic tin(II) sulfate ($Sn_3O(OH)_2SO_4$), according to the following reaction:

$$3SnSO_4(aq) + 3H_2O(l) \rightleftharpoons Sn_3O(OH)_2SO_4(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \tag{6}$$

So, the presence of water may contribute to the dissolution of part of $SnSO_4$ and modify the physicochemical properties of the reaction medium. Apart from water, there is also the possible contribution of ethanol. Suwannakarn *et al.*[19] investigated the stability of sulfated zirconia and the nature of catalytically active species in the transesterification of triglycerides. This is one of the few papers that were dedicated to the issue of deactivation of the catalyst by dissolving it in alcoholic medium, at temperatures from 100 °C. The authors concluded that the sulfate ion species were leached out and the degree of dissolution depended on the alcohol size and contacting time. They found that, in the reaction conditions, almost all catalytic activity was due to homogeneous rather than heterogeneous catalysts, as a result of catalyst leaching. The leaching pathway includes the removal of sulfate ions from the catalyst surface, which subsequently reacts with alcohol to form monoalkyl hydrogen sulfate and dialkyl sulfate in solution, as the authors indicated by ^1H nuclear magnetic resonance (NMR) studies.

In the present work, the extension of $SnSO_4$ leaching in ethanol and water was evaluated by monitoring the acidity of the medium after the leaching test. The amount of protons in the reaction medium was equal to 0.14 and 2.8 mmol $H^+ g^{-1}$ for ethanol and water, respectively, confirming the partial leaching of tin(II) sulfate along with acid generation.

For tin(II) chloride, also tested as catalyst in this work, the phenomenon was more visible than in the case of sulfate, since dissolution was apparent during the reaction and a significant increase of acidity in the reaction medium was observed, probably due to salt hydrolysis.

Silva *et al.*[7] investigated the effect of water in the residual cooking oil ethanolysis using tin(II) chloride as a catalyst. The hydrolysis of $SnCl_2$, which may be involved in steps of FFA protonation, can occur with the formation of an insoluble salt according to the following reaction:

$$SnCl_2 + H_2O \rightarrow H^+ + Cl^- + Sn(OH)Cl(s) \tag{7}$$

A suggestion to explain the higher activity of $SnSO_4$ in comparison with $SnCl_2.2H_2O$ (Figure 5) may be the largest formation of H^+ in the reaction medium with generation of water during FFA esterification.

In order to confirm the partial dissolution of $SnSO_4$, the esters formed in the catalytic tests were also analyzed to determine the presence of sulfur. These results are shown in Table 1. For the biodiesel synthesized with the $SnSO_4$ catalyst, the sulfur content in the upper organic phase, which corresponds to the ester phase, was compared to the sulfur content in the lower phase, which corresponds to a mixture of unreacted ethanol, glycerol and water (formed from the esterification reaction). It can be seen that approximately 91% of the sulfur dissolved in the reaction medium remained in the lower phase, confirming the solubility of the catalyst in the ethanol/water phase.

Table 1. Sulfur content in the reaction product of the esterification of the model acid oil (70 wt.% oleic acid and 30 wt.% soybean oil) with ethanol catalyzed by $SnSO_4$. Reaction conditions: T = 100 °C; 5 wt.% of catalyst; $R_{EtOH/oil} = 3.5$; reaction time = 3 h

Identification	Sulfur content / %
Upper phase (esters)	0.10
Lower phase	1.07
Upper phase (esters) after water washing	0.09

The upper phase (ester phase) was washed with water and the sulfur content reanalyzed. The results showed that after a simple washing, the sulfur content reduced by approximately 12%.

Thus, beyond the question of tin(II) precursor solubility in ethanol that minimizes the necessary contact between free tin(II) orbitals and the carbonyl group oxygen, there is the effect of the hydrolysis of these salts in water which can effectively promote the reaction in homogeneous phase.

Effect of FFA content in acid feedstock

In the first part of this work, the study was focused on the esterification of a model acid oil (70 wt.% of stearic acid + 30 wt.% of soybean oil) with ethanol whose results were analyzed considering the FFA conversion. The results pointed $SnSO_4$ as a promising catalyst for the synthesis of biodiesel from acid feedstocks.

In order to confirm the catalytic efficiency of $SnSO_4$, the second part of the work deals with the study of the simultaneous esterification and transesterification of soybean oil with different FFA content (oleic acid content in the mixture varying between 0 and 100 wt.%) with ethanol. The catalytic performance was analyzed taking into account the contribution of both reactions, esterification of FFA and transesterification of soybean oil, to fatty acid ethyl ester formation.

Figure 7 shows the influence of free fatty acid content in the feedstock on the conversion of soybean oil (by transesterification) and of oleic acid (by esterification) into fatty acid ethyl esters (FAEE). The conversion of pure soybean oil (ca. 50%) and of pure oleic acid (ca. 92%) was taken as reference.

The addition of 5 wt.% of FFA in soybean oil promoted the transesterification reaction catalyzed by $SnSO_4$. This improvement was maintained at the same level (conversion around 60-70%) even with the significant increase in FFA content (up to 40%). An increase to 70% of FFA caused a significant drop in conversion via the transesterification reaction. The reduction in soybean oil conversion for the feedstock containing the highest FFA content can be associated with the important increase in water content formed by the esterification reaction with the increase in FFA content, favoring the hydrolysis of FAEE. Canakci and Van Gerpen[20] studied the effect of water in acid-catalyzed transesterification reactions in homogeneous media. The test duration was 96 h with 3% acid catalyst, 60 °C, and 6:1 molar ratio. They reported that the ester production was affected even at low water concentrations (0.1 wt.%) and was almost totally inhibited when the water content reached 5 wt.%. Kusdiana and Saka[21] also investigated the effect of water in the acid-catalyzed (3 wt.% H_2SO_4) transesterification reaction of rapeseed oil with methanol, at 65 °C for 48 h. Their results showed that the presence of 0.1 wt.% of water slightly reduced the ester yield, which stayed near 90%. On the other hand, when 5 wt.% of water was added the conversion was reduced to 6%.

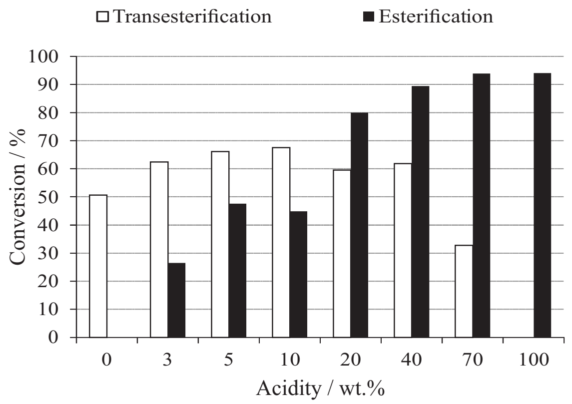

Figure 7. Comparison between FFA (esterification) and soybean oil (transesterification) conversion for the reaction of the model acid oil (oleic acid) with ethanol catalyzed by $SnSO_4$. Reaction conditions: T = 100 °C; 5 wt.% of catalyst; $R_{EtOH/oil} = 3.5$; reaction time = 3 h.

Considering the 90 wt.% conversion of oleic acid observed for the feedstock containing 70 wt.% of the acid, the amount of water in the reaction medium can be estimated as 4 wt.%, an amount that could affect the transesterification reaction as reported in the literature.[20,21]

Figure 7 shows that the conversion of FFA into FAEE increases when the oleic acid content increases in the feedstock, reaching 92% for the feedstock containing 70 wt.% of FFA. This value is similar to that observed for the pure oleic acid. This tendency can be explained considering the role played by homogeneous acid catalysis. With the increase in FFA content, the contribution of the esterification reaction also increases, as well as the presence of water in the reaction medium. Consequently, the hydrolysis of tin(II) sulfate is favored increasing the amount of H^+ ions in solution, which catalyze the esterification reaction.

Conclusion

$SnSO_4$ proved to be an interesting catalyst for the biodiesel production from feedstock with high free fatty acid content. It showed good catalytic activity in the esterification reaction with conversion levels that reached 92% using ethanol and the model acid oil (70 wt.% fatty acid and 30 wt.% soybean oil) with an amount of ethanol equal to 3.5 times the stoichiometric value and using 3 wt.% $SnSO_4$ at 100 °C for 3 h. It had already achieved a good catalyst performance at 80 °C, with conversion similar to that observed at 100 °C. Esterification increased when more catalyst was added, up to the limit of 3 wt.%, from which the conversion was maintained approximately constant. The fatty acid conversions using 5 or 3 wt.% $SnSO_4$ and 1 wt.% H_2SO_4 were almost similar. A pseudo-homogeneous reaction has been observed for ester-forming reactions using $SnSO_4$ catalyst due to hydrolysis reactions that acidify the reaction medium. Thus, $SnSO_4$ catalytic activity was also attributed to its solubility in the reaction medium. The performance of esterification with $SnSO_4$ was greater than with $SnCl_2.2H_2O$, probably due to more H^+ ions being released in the medium. Transesterification was inhibited when 70 wt.% acid content was used, probably due to water formation from the esterification reaction, which increased in this condition. Thus, $SnSO_4$ catalyst showed good reusability, since it is a non-supported catalyst and can keep its solubility for more time, minimizing deactivation. However, the use of $SnSO_4$ catalyst on a broader scale depends on a careful evaluation of the removal of the residual sulfate present in the formed esters.

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