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ORIGINAL PAPER

Effect of Water on the Ethanolysis of Waste Cooking Soybean Oil Using a Tin(II) Chloride Catalyst

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Abstract Biodiesel production from cheap lipid raw materials is economically welcome, but a high free fatty acids (FFA) content makes it incompatible with traditional alkaline catalysts. Although liquid mineral acids are alternatively used, serious drawbacks such as high corrosiveness and large effluent generation, as well as the impossibility of catalyst reuse compromises its application. Contrarily, solid acid catalysts appear to be an attractive option; however, the water present or generated during FFA esterification provokes the leaching and deactivation of these catalysts. Thus, in this work we have evaluated the use of tin chloride $SnCl_2$, which is less corrosive, water tolerant, and a recyclable Lewis acid catalyst, on FFA ethanolysis using waste cooking oil samples (WCO). Additionally, the main kinetic parameters of the reactions were assessed. Compared to pTSA (*p*-toluenesulfonic-acid), a catalyst also evaluated, $SnCl_2$ efficiently promoted FFA ethanolysis even in the presence of high amounts of water (ca. 0.1–5.0% w/w). Moreover, the homogeneous $SnCl_2$ catalyst was easily recovered and reused successively, without loss of activity.

Keywords Catalytic esterification · Tin chloride (II) · Free fatty acids · Biodiesel

Introduction

Biodiesel is a renewable and low-polluting fuel which consists of methyl or ethyl esters, resulting from either transesterification of glycerides or esterification of free fatty acids (FFA) [1]. However, although biodiesel provokes a lower emission of greenhouse gas, its production conventionally occurs via environmentally unfriendly processes [2]. Use of alkali or acid homogeneous catalysts generally results in the generation of large amounts of effluents and salts, which are disposed to the environment [3]. The high consumption of non-reusable catalysts, the formation of soap, as well as substantial reactor corrosion imparts negative and virtually impassable aspects of both acid or alkali-catalyzed homogeneous processes [4]. Thus, to develop efficient catalysts for the esterification of FFA is one of the challenges to be overcome and such a technology could allow the production of biodiesel with lower costs and under environmentally benign conditions [5, 6].

Therefore, acid solid-catalyzed processes are an attractive alternative to produce biodiesel directly from low-cost raw materials which generally contain high concentrations of FFA [7, 8]. Currently, efforts to develop heterogeneous catalysts for conversion of FFA into biodiesel have increased noticeably and they have been used as an alternative to avoid the serious disadvantages of homogenous catalysts [9, 10]. However, the water present or generated in the reaction medium during conversion of FFA into biodiesel results in leaching and consecutive deactivation of most heterogeneous catalysts, as well as contaminating the products [11, 12]. With this in mind, Lewis acid salt catalysts may be an attractive alternative mainly because they may be recovered from solution by simple extraction or by solvent evaporation [13]. Recently, we described the use of $SnCl_2$ in the alcoholysis of pure fatty acids [14]. Although widely used in organic synthesis, Lewis acids are little used in biodiesel production [15]. Among the few examples is the use of tin complexes in soybean oil esterification [16, 17]. However, features such as the

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complexity of their composition and the special reactors required elevate costs, thoroughly restricting its application to biodiesel production [18]. Another drawback of these catalysts is that they are effective only in FFA methanolysis. Methanol is non-renewable fuel made directly from a fossil fuel. Moreover, methanol is highly toxic, which comprise a negative aspect of their use as raw material in biodiesel production.

In this paper, $SnCl_2{\cdot}2H_2O$ catalyst, which is an easily handled Lewis acid, inexpensive, water tolerant and less corrosive than mineral acids, was assessed as a recyclable homogeneous catalyst for FFA ethanolysis using waste cooking oils samples (WCO). Since the *p*-toluenesulfonic acid (pTSA) catalyst is also used as alternative to mineral acids, it was selected for comparison to soluble $SnCl_2$. Initially, kinetic parameters were obtained for both catalytic reactions. Furthermore, the catalytic activity of pTSA and $SnCl_2$ was investigated under different initial amounts of water. Finally, the ability of the $SnCl_2$ catalyst to be recovered and reutilized was evaluated. The determination of residual Sn content in biodiesel was also performed via Atomic Absorption Spectrophotometer (AAS) analyses.

Experimental

Chemicals

All chemicals were purchased from commercial sources and used as received unless otherwise stated. Ethanol (99.9% w/w, Sigma-Aldrich) was distillated twice over phosphorous pentoxide. The $SnCl_2{\cdot}2H_2O$ catalyst was purchased from Sigma-Aldrich (Milwaukee, WI), whereas *p*-toluenesulfonic-acid (99% w/w) was acquired from Química Moderna (São Paulo, SP, Brazil). Oleic acid (99% w/w, Sigma-Aldrich) was the standard used in construction of the calibration curve for the gas chromatography analyses (GC). Hexane was purchased from Vetec (São Paulo, SP, Brazil), and utilized without prior handling. Three WCO (waste coking soybean oil) batches were obtained from the university restaurant in Viçosa (Brazil) and filtered to remove impurities.

Determination of the FFA Content of the WCO Samples: Titration Versus GC Analysis

The initial FFA content (acid number) was determined by titration, against an alcoholic KOH solution 0.01 mol L^{-1} (ASTM D664), and all measurements were performed in triplicate. Additionally, the results obtained by titration were compared with those from GC analyses. The conventional method of GC analysis (ASTM D6584) provides the total content of esters, resulting from both transesterification and esterification reactions [19]. However, only the FFA esters are the target of this study. For this reason, a modified GC analysis method was employed for the determination of FFA content. Dodecane was the internal standard used. Typically, a WCO sample (3.26 g) was reacted with a KOH aqueous solution at 60 °C, with the consequent FFA saponification. Furthermore, after three consecutive extractions with water, acid was added to the oil-free aqueous layer for conversion of fatty salts into the respective fatty acids (FA), thus resulting in a biphasic mixture. The organic phase containing the FA was extracted with hexane and after almost complete evaporation of the solvent. They were esterified with an excess of ethanol in the presence of H_2SO_4 (2% w/w) to give the FAEE (fatty acid ethyl esters). The FAEE were extracted with hexane and analyzed using a GC gas chromatograph Varian 450 GC, equipped with an FID detector and DB5 capillary column (30 m length, 0.25 mm i.d., 0.25 mm film thickness). The temperature profile used was as follows: 80 °C for 3 min, 10 °C/min up to 260 °C, a hold time of 5 min; injector temperature: 250 °C and detector temperature: 280 °C.

Effect of Initial Water Content on WCO Ethanolysis

The water produced or initially present in esterification reactions can shift the equilibrium toward the reactants. Moreover, the performance of the catalyst may also be altered. This effect was investigated in catalytic runs with initial amounts of water in the range of 0.1–5.0% w/w. Reactions were carried out in a 50-mL three-necked glass flask, equipped with a sampling system, reflux condenser, thermostatic bath and magnetic stirrer. In all the catalytic tests, ethanol was used in a large molar excess over the WCO to drive the equilibrium towards the ester formation. Typically, WCO (13.0 g, 13.2 mL), ethanol (380.0 mmol, 21.8 mL) and an adequate amount of water were mixed by magnetic stirring and heated at reflux temperature (ca. 78 °C). Finally, after the addition of the appropriate catalyst to solution ($SnCl_2{\cdot}2H_2O$, 0.30 mmol; or pTSA, 1.20 mmol), the reaction was started. Despite being a Brønsted acid, pTSA was selected for comparison because it is a homogeneous catalyst less corrosive than mineral acids and commonly used in FFA esterification reactions [20].

Reaction Progress Monitoring

The GC analyses of FAEE produced during the reaction were complicated by the presence of unreacted vegetable oil (triglycerides). For this reason, reaction progress was continuously monitored by titration of 0.5 mL aliquots, sampled at regular time intervals (ca. 10 min), against an alcoholic KOH solution 0.01 mol L^{-1} (ASTM D664). All catalytic runs were carried out in triplicate. The amount of zKOH required to react with the acid catalyst was taken into account to calculate the concentration of the FFA in solution.

Recovery/Reuse of the Homogeneous $SnCl_2$ Catalyst

A simple protocol was used for recovery of the homogeneous $SnCl_2$ catalyst [21]. At the end of the reaction, the solution was concentrated under reduced pressure and the ethanol recovered. Thus, after cooling the solution, the solid $SnCl_2$ catalyst was recovered by filtration, washed with hexane and then dried. The catalyst was reutilized in further runs. The ester layer generated was analyzed as described in "Determination of Residual Sn in Biodiesel Samples" (Fig. 1), for determination of residual tin content. This complete recovery/reutilization procedure was repeated five times.

Determination of Residual Sn in Biodiesel Samples

From the resultant non-polar layer of the recycle/reutilization protocol, three aliquots were collected. After the solvent had been removed, portions of the neat oil were collected, and their masses were precisely determined (ca. 0.5 g). For acid digestion of the samples, a mixture of HNO_3 (ca. 65% w/w) and H_2O_2 (ca. 30% w/w) was added to the neat oil drop by drop, while heating in a microwave digestion instrument (Milestone Ethos Plus Labstation with HPR-1000/10S high-pressure segmented rotor). The concentration of Sn in the ester layer was determined in an Atomic Absorption Spectrophotometer (Varian Spectra A-200 model). The samples were pumped directly into the flame at 2,700 °C (C_2H_2/N_2O) [21]. Parameters used in determining the concentration were λ (235.5 nm), and detection limit (0.1 ppm). The tin standard curve (Merck, Germany) appears to be linear within the range of 0.5–200 µg/ml.

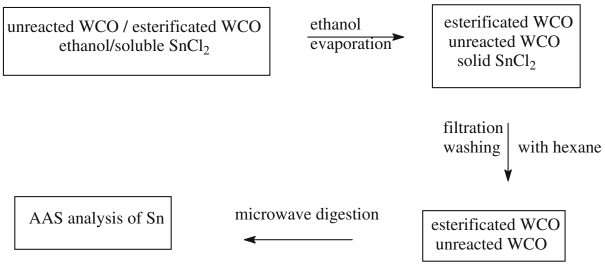

Fig. 1 Procedure for determination of the residual Sn in the biodiesel layer

Results and Discussion

General Aspects

The acid value of an oil sample suggests the number of acidic functional groups (FFA) present, and may be determined in terms of the quantity of KOH consumed for their neutralization. However, some experimental errors such as those provoked by the indicator used, in addition to side-reactions such as hydrolysis, can compromise the precision of the method. Herein, the FFA content of the WCO sample was determined by volumetric titration and via GC analyses of their respective ethyl esters. To assure the efficiency of the latter process, three samples of refined soybean oil containing 10% w/w of oleic acid previously added (sample 1, Table 1) were also reacted with ethanol in the presence of sulfuric acid (2% w/w) and analyzed by the same protocol. Despite requiring a laborious procedure, it was possible to provide a comparison of the FFA content obtained by two different standard methods which are currently used. Taking into account the several steps involved in the process (saponification, extraction, esterification), and considering that the FFA esterification reactions are reversible and do not reach 100% conversion, an acceptable agreement between the expected results (ca. 10.00% w/w) and those obtained by GC analysis of FAEE was achieved (ca. 9.80% w/w, Table 1). Although hydrolysis of the FAEE may take place in volumetric titration reactions, it was verified that the results were satisfactorily reproducible and were in agreement with those obtained by GC analysis (Table 1).

Table 1 Comparison of results for determination of the FFA content in WCO samples by GC analysis versus volumetric titration

Samples[a]	FFA GC analyses (%)[b]	FFA titration analysis (%)	Deviation (%)[c]
1	9.80	9.95	1.5
2	10.75	10.90	1.4
3	10.45	10.60	1.4
4	10.50	10.70	1.9

The results presented here are the averages of triplicates; the standard deviation of the measurements obtained indicates experimental error

[a] Sample 1 is refined soybean oil containing 10% w/w oleic acid previously added, which was esterified with ethanol as in Fig. 1. Samples 2–4 are WCO samples prepared as described in the experimental section and similarly esterified

[b] The FFA content was determined based on the calibration curve of the ethyl oleate standard

[c] The deviation (in %) was calculated in relation to the higher value

Kinetic Investigations of FFA Esterification in WCO Samples Catalyzed by Brønsted or Lewis Acids: $SnCl_2$ Versus pTSA

Initially, reaction kinetics were investigated without the addition of water. No significant conversion was reached after 4-h runs in the absence of catalyst (ca. <5%), despite the high molar ratio of ethanol to WCO. In contrast, in the presence of $SnCl_2$ catalyst, high conversions were reached (ca. 90%) after a 2-h reaction (Fig. 2). However, under the conditions studied, pTSA was less effective than the $SnCl_2$ catalyst, achieving a conversion of only 80% during the same reaction period. Note that the conversion into ethyl esters increases steadily and reaches maximum values (ca. 95%) after a reaction time of 4 h. These values remain almost invariable afterwards, as observed experimentally following the reaction for longer times (data not shown). Furthermore, the two acidic catalysts, despite having such different structures, displayed quite similar activities, as can be confirmed by the attainment of comparable conversion after a reaction time of 4 h (Fig. 2). It should also be highlighted that under mild reaction conditions, i.e. reflux temperature (ca. 78 °C), the transesterification reaction is negligible and consequently conversion was based only on consumed FFA.

To obtain the reaction order in relation to the FFA concentration, plots of ln FFA concentration versus time (not shown) were constructed for each tin-catalyzed reaction. Large molar excess of ethanol was used to assure that its concentration would remain essentially unaltered during the reaction. Table 2 shows that the resulting linear equations were found to have high correlation coefficients, thus indicating that the FFA reaction is of first order.

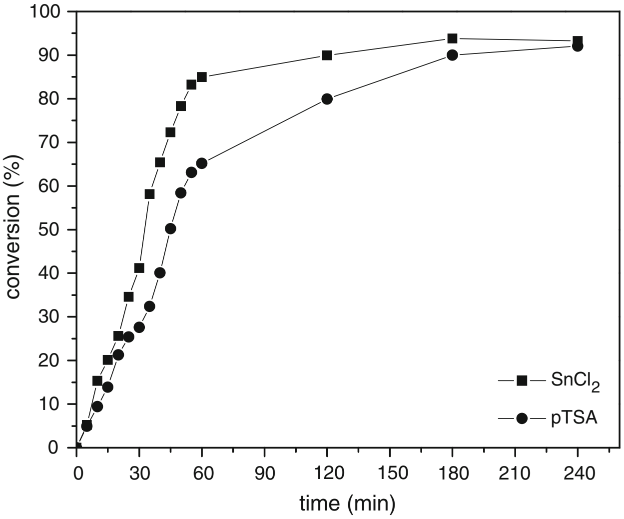

Fig. 2 Acid-catalyzed ethanolysis of FFA in WCO samples Reaction conditions: ethanol (380.0 mmol, 21.8 mL); WCO (13.0 g, 13.2 mL); $SnCl_2{\cdot}2H_2O$ (0.30 mmol); pTSA (1.20 mmol)

Table 2 Values of K (s^{-1}) obtained from linear equations (ln[FFA] as a function of time), with the respective correlation coefficients (R^2) constructed with data from Fig. 1

Catalyst	Values of K (s^{-1})	$t_{1/2}$ (min)	R^2
$SnCl_2$	2.93481×10^{-4}	33.3	0.98394
pTSA	1.89914×10^{-4}	44.8	0.98653

Kinetic data obtained for the first 30 min of reaction

From angular coefficients of these equations, the rate constants (k) and then half-life times ($t_{1/2} = k/0.693$) for each process were obtained. The results for the half-life times, as displayed in Table 2, indicate that during the first hour of reaction, the $SnCl_2$ catalyst activity was higher than that of pTSA and a higher initial rate was measured in the tin chloride-catalyzed reaction (see Fig. 2). It should be mentioned that a direct comparison between the catalytic efficiency of Lewis ad Brønsted acids is difficult, because these catalysts have different action mechanisms. However, under equal reaction conditions, the $SnCl_2$ Lewis acid was more effective than pTSA Brønsted acid. Since the $SnCl_2$ catalyst is less corrosive than Brønsted acid catalysts and can be more efficiently reused ("Efficiency of the $SnCl_2$ Catalyst after Successive Recovery/Reutilization Cycles and the Determination of Tin in Biodiesel"), its advantages are quite noticeable.

Effect of Water on FFA Esterification in WCO Samples

The effect of water in esterification reactions is crucial because H_2O is continuously produced as a byproduct. Certainly, the presence of water promotes the reverse reaction; however, the effect of water on catalyst activity is even more critical, as has been previously shown by Lotero and coworkers, for H_2SO_4-catalyzed esterification of acetic acid [22]. Herein, the inhibitory effect of water on ester formation was investigated and the results involving the pTSA or $SnCl_2$-catalyzed esterification of FFA in WCO samples are shown in Figs. 2 and 3. As expected, the presence of water drives the esterification equilibrium (Eq. 1) towards the reconstitution of the reactants, thus causing a reduction in the ester formation in both Lewis or Brønsted-catalyzed reactions (Figs. 3, 4). In the absence or in low water concentration (ca. 0.1% w/w), a minimal impact was observed on FFA conversion for the two different catalysts.

$$RCOOH + CH_3CH_2OH \rightleftharpoons RCOOCH_2CH_3 + H_2O \qquad (1)$$

The impact of water on FFA ethanolysis seem be more drastic on pTSA catalyzed-reactions, especially at higher concentrations (ca. 1.0–5.0% w/w water).

For instance, after 4 h of reaction, the initial addition of high water content (ca. 5% w/w) resulted in a remarkable decreases in conversion (ca. 90–52%) (Fig. 3). However, under the same reaction conditions when catalyzed by $SnCl_2$, a significantly lower reduction was observed (ca. 92–72%) (Fig. 4). Moreover, after comparing the initial rates for any catalytic run in the presence of significant amounts of water (ca. 1.0–5.0% w/w), much better conversions were achieved in reactions catalyzed by tin chloride (Figs. 3, 4). It is reasonable to state that in Brønsted acid-catalyzed reactions, the smaller number of protons available could also cause the decline in the conversion of FFA into FAEE. These protons should be coordinated to water molecules and therefore this effect may be more noticeable. Contrarily, in the studied experimental conditions, protons are probably not involved in tin-catalyzed reactions. It should be mentioned that the hydrolysis of $SnCl_2$ results in the formation of Sn(OH)Cl, a highly insoluble basic salt, and HCl (Eq. 2), which in turn, may be involved in steps of FFA protonation.

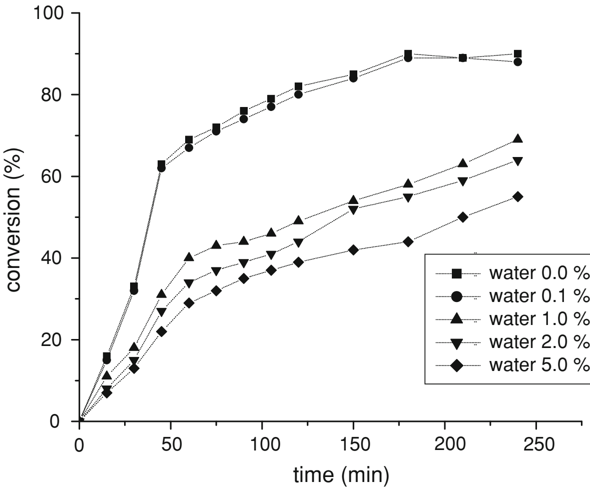

Fig. 3 Effect water on ethanolysis WCO samples catalyzed by pTSA. Reaction conditions: ethanol (380.0 mmol, 21.8 mL); WCO (13.0 g, 13.2 mL); pTSA (1.20 mmol); water initially added (0.0–5.0% w/w)

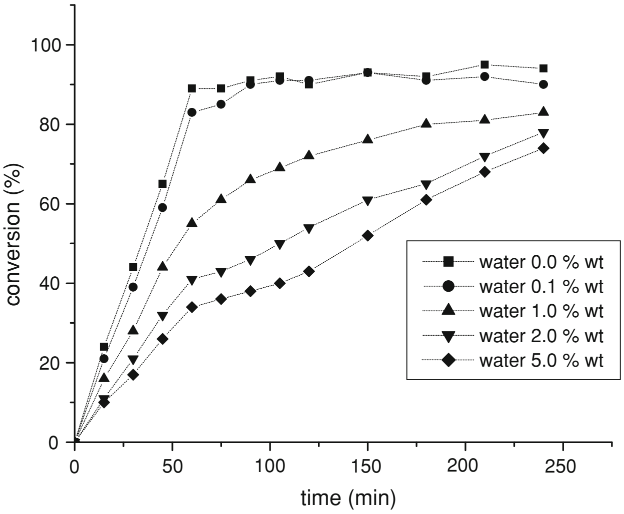

Fig. 4 Effect water on ethanolysis WCO samples catalyzed by $SnCl_2$. Reaction conditions: ethanol (380.0 mmol, 21.8 mL); WCO (13.0 g, 13.2 mL); $SnCl_2$ (0.30 mmol); water initially added (0.0–5.0 w/w %)

$$SnCl_2 + H_2O \rightleftharpoons HCl + Sn(OH)Cl_{(S)} \quad (2)$$

However, the formation of solid was not observed in the reactions for the defined amounts of water (ca. 0.10–5.0% w/w). Only in greater water concentrations was the solid formed (see "Effect of Water on FFA Esterification in WCO Samples").

Thus, it is believed that the main action mechanism of $SnCl_2$ on FFA occurs via polarization of its carbonyl group which favors nucleophilic attack by ethanol. This fact is corroborated by Figs. 2 and 3, which reveal that the effect of water was less pronounced in tin-catalyzed reactions than Brønsted acid-catalyzed ones.

Aiming to minimize the effect of water, acid-catalyzed esterification reactions were carried out in the presence of adsorbent agents (molecular sieves, sodium sulfate) and with water initially added (ca. 1.0 and 2.0% w/w). However, the results obtained show that under the reactions conditions studied (ethanol excess, reflux temperature), these adsorbents were not effective and do not promote any increase in FFA conversion for reactions catalyzed by $SnCl_2$ or pTSA (Table 3).

Efficiency of the $SnCl_2$ Catalyst After Successive Recovery/Reutilization Cycles and the Determination of Tin in Biodiesel

Initially, the effectiveness of aqueous extraction of the tin catalyst from the reaction medium was investigated. However, in the presence of large amounts of water, the hydrolysis of $SnCl_2$ occurs as expected, resulting in a solid white precipitate, probably Sn(OH)Cl. Thus, as described in previous work [21], $SnCl_2$ catalyst was recovered at the end of the reaction via evaporation of the solvent followed by filtration, washing with hexane, and finally drying. This reuse protocol was repeated five times (Fig. 5).

Note that very high $SnCl_2$ recovery yields were achieved upon its extraction from the reaction medium. Additionally, a remarkable result was that the $SnCl_2$ catalytic activity remained almost unaltered even after five recovery/reutilization cycles.

The residual content of Sn in biodiesel samples was quantified via AAS analysis [21]. The method of standard addition was used due to the low levels of tin expected. Furthermore, it was verified that the Sn content in a

Table 3 Lewis or Brønsted acid-catalyzed esterification reactions in the presence of adsorbent agents

Entries	Catalyst	Initial water content (% w/w)	FAEE Conversion without water adsorbent (%)	FAEE Conversion with water adsorbent (%)
Reactions in presence of sodium sulfate				
1	$SnCl_2$	1	93	94
2	pTSA	1	82	83
3	$SnCl_2$	2	72	73
4	pTSA	2	52	51
Reactions in presence of molecular sieves (3 Å)				
5	$SnCl_2$	1	93	95
6	pTSA	1	83	82
7	$SnCl_2$	2	72	74
8	pTSA	2	52	53

Reaction conditions: ethanol (380.0 mmol, 21.8 mL); WCO (13.0 g, 13.2 mL); $SnCl_2{\cdot}2H_2O$ (0.30 mmol); PTSA (1.20 mmol). (1.0 and 2.0% w/w)

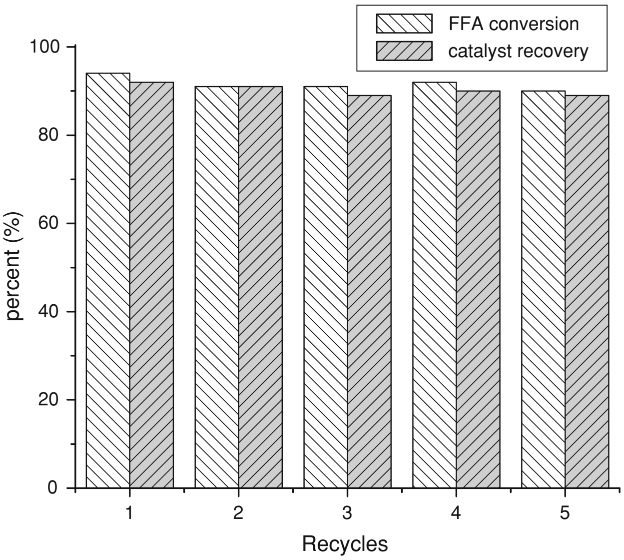

Fig. 5 Recovery and successive reuse of the $SnCl_2$ catalyst in FFA ethanolysis

biodiesel sample prepared via the $SnCl_2$-catalyzed esterification of WCO, was lower than 0.5 ppm of Sn per g of sample (average of three measurements). This result indicates that the content of soluble tin species appears to stay at an acceptably low level in the final product, taking in account that other metals such as Na and K, or Ca and Mg, have maximum limits of 5 ppm (EN 14214). No standards have yet been defined for the maximum content of Sn in biodiesel.

This work evaluated the efficiency of $SnCl_2$ catalyst on FFA esterification with ethanol in WCO samples containing high initial water concentrations. Compared to pTSA (*p*-toluenesulfonic-acid), $SnCl_2$ catalyst efficiently promoted FFA ethanolysis even in the presence of high water concentrations (ca. 5.0% w/w). Remarkably, the tin chloride catalyst was more water tolerant than pTSA, reaching high conversions of FFA into FAEE in almost all catalytic runs. Moreover, despite $SnCl_2$ being a homogeneous catalyst, it may be easily recovered and reused successively without activity loss via a simple and efficient recycle protocol. It was also demonstrated that the Sn concentration in the final product was found to be at an acceptably low level (ca. <0.5 ppm). Additionally, a comparison of kinetic parameters in reactions catalyzed by Lewis ($SnCl_2$) or Brønsted (pTSA) acids was also performed, revealing a first order dependence in relation to FFA concentration for both catalysts. Attractive aspects of this catalyst are easy work-up and reduction of acidic waste, which are crucial from economical and environmental standpoints. In addition, highlights of the $SnCl_2$ catalyst is that it is a low cost Lewis acid, easily manipulated, more water tolerant and reusable. Therefore, where the use of solid acid catalysts is hampered by leaching problems and deactivation, the $SnCl_2$ catalyst may be an interesting alternative for biodiesel manufacture from low cost raw material. It should be mentioned that specifications for elements such as tin will be established in biodiesel standards; thus, this catalyst may find commercial use.

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