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ORIGINAL PAPER

p-Sulfonic acid calix[*n*]arenes as organocatalysts for the transesterification reaction of *Passiflora* seed oil

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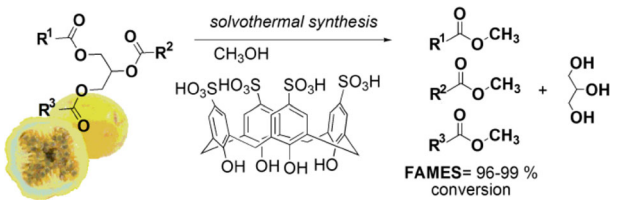
Abstract The catalytic activity of *p*-sulfonic acid calix[4]arene was studied in the transesterification reactions of *Passiflora* seed oil with methanol or ethanol. Calix[*n*]arenes are highly versatile organocatalysts and conversion rates >98 % were obtained for the transformation of *Passiflora* seed oil to its methyl or ethyl esters after 5 h of reaction in the presence of *p*-sulfonic acid calix[4]-arene (3.52 mol % in ethanol; 5.28 mol % in methanol). Moreover, the organocatalyst was recovered and reused in two subsequent cycles without a significant decrease in the activity or selectivity. The use of a non-corrosive and reusable organocatalyst is the positive aspect of this process.

Graphical abstract



Keywords Seed oil · Calix[*n*]arenes · Catalysis · Biodiesel · Fatty acids

Introduction

Recently, a tremendous interest in the utilization of biomass as feedstock to produce renewable fuels and chemicals has been observed worldwide. The biodiesel production from biomass is usually carried out by the esterification and transesterification of vegetable oils with methanol or ethanol, producing glycerine and methyl or ethyl esters (biodiesel). It is a highlighted industrial process which has gained an increasing importance, since vegetable oils are an interesting green energy resource as a renewable, biodegradable, and non-toxic material [1–5].

The most common method used for the production of biodiesel is the transesterification of vegetable oils with methanol or ethanol under homogeneous alkaline catalysis conditions, sodium and potassium hydroxides or methoxides being the most employed catalysts [6]. Despite of the low cost of those chemicals and the high yields of ester obtained, these processes have significant drawbacks [7].

Besides the high corrosion caused by the alkaline catalysts, there are great difficulties in removing them from the reaction medium. The necessity of neutralization at the end of the reaction results in the production of a large amount of effluents and residues, unfriendly to the environment.

The high cost of raw material has led to the search for inexpensive feedstocks to produce biodiesel. However, these raw materials frequently contain high levels of free fatty acids (FFA) and their alkaline esterification leads to the formation of soaps or emulsions, hampering even more the recovery and purification of the esters.

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In the last years, a great number of studies have been conducted to search for new efficient catalysts. Heterogeneous alkaline catalysts have been developed to answer this demand [8, 9]. Nevertheless, they are unable to catalyze the transesterification of raw materials such as non-edible oils or industrial oil-chemistry residues. For these reasons, solid acid catalysts have occupied a highlighted position and their use for the biodiesel production from these feedstocks has been intensively explored [10–12]. Although significant advances have been achieved, the leaching of solid catalysts caused by the highly polar medium results in their deactivation and in the contamination of the products with metal, remaining thus a challenge to be overcome [13, 14].

Recyclable organocatalysts are still little explored alternatives and may promote the esterification and transesterification reactions, with potential cost and energy savings, operational simplicity, lower toxicity, and greater water tolerance than conventional catalysts [15]. Recently, the application of calix[*n*]arenes as organocatalysts in several organic transformations has been described [16–19]. Calix[*n*]arenes are macrocyclic compounds obtained via the condensation of *p*-substituted phenols with formaldehyde [20–22]. They are recyclable catalysts and their main advantage is that they avoid the contamination of the products with metal.

We previously reported excellent results for the esterification of carboxylic acids catalyzed by calix[*n*]arenes [23–25]. The present work describes the first use of *p*-sulfonic acid calix[4]arene as a reusable organocatalyst in a simple and efficient method for the transesterification of a vegetable oil with methanol or ethanol. *Passiflora* oil, obtained by the extraction the fruit seeds, a juice processing industry residue, was chosen as a potential feedstock for the production of biodiesel [26].

Results and discussion

Characterization of the *Passiflora* oil

The content and the composition in terms of FFA and triglycerides are key aspects of the transesterification reactions because these compounds have different chemical reactivity caused by the presence of double bonds and by the different carbon chain length of fatty acids. *Passiflora* oil was analyzed according to AOCS official methods [27, 28] and the main results are summarized in Table 1.

The results show that the *Passiflora* oil sample used in the transesterification reactions had only ca. 0.2 % of FFA (acidity value) and consequently, a high triglycerides amount (ca. 99.8 %, esterification value). Palmitic and oleic acids ($C_{16:0}$ and $C_{18:1}$) were present in almost equal amounts (ca. 21.6 and 21.9 %, respectively). Linoleic acid

Table 1 *Passiflora* oil analysis [12, 13]

Physicochemical analysis					
Density/g cm^{-3}	SV/mg KOH/g	IV (I_2/100 g)	PV/meq/1000 g	AV/meq/1000 g	EV/%
0.92	173.4	236.8	3.69	0.2	99.8
Fatty acid composition/%					
$C_{16:0}$		$C_{18:1}$		$C_{18:2}$	
21.6		21.9		56.5	

SV saponification value, *IV* iodine value, *PV* peroxide value, *AV* acidity value, *EV* esterification value

($C_{18:2}$) was the major component (ca. 56.5 %). Although the presence of $C_{18:0}$ and $C_{18:3}$ (2.2–3.1 and 0.3–0.4 %) has been described in *Passiflora* species [29], they were not detected in the present work.

p-Sulfonic acid calix[4]arene-catalyzed *Passiflora* oil transesterification with methanol or ethanol: conversion rate determination via ^{1}H NMR spectroscopy results

The triglycerides conversion rate of *Passiflora* oil to fatty esters was calculated from the ^{1}H NMR spectra [30] obtained after the transesterification reactions with ethanol or methanol compared to the one of the starting *Passiflora* oil (Electronic Supplementary Material). No signals from the four methylene hydrogens of the glycerol at 4.2 ppm were observed after the completion of the transesterification reaction indicating that the reaction was complete. The remaining olefinic hydrogens of the unsaturated portions of the aliphatic chains resulted in resonance signal at 5.35 ppm.

To obtain the conversion rate, signal of the hydrogens at 2.28 ppm, corresponding to the two hydrogens of the α-carbonyl moiety of the oil, were integrated (I_1), and related to the signal integration I_2 of the hydrogens at 4.11 ppm (ethyl esters) or 3.64 ppm (methyl esters). The conversion rate C was obtained by the ratios between these areas Eqs. (1) and (2), within 2 % error [31]:

$$\text{Ethyl esters}: C/\% = (I_2/I_1) \times 100 \quad (1)$$

$$\text{Methyl esters}: C/\% = (2I_2/3I_1) \times 100 \quad (2)$$

Reaction selectivity of *p*-sulfonic acid calix[4]arene-catalyzed *Passiflora* oil transesterification with methanol determined by GC analysis

The reaction selectivity was assessed by GC analysis of samples collected at the end of the reaction, which were compared with authentic standard samples. In general, after

p-sulfonic acid calix[4]arene-catalyzed transesterification reactions only monoalkyl esters (i.e., FAMEs or FAEEs when methanol or ethanol was used, respectively) were formed. However, the reaction selectivity was almost equal, regardless of the alcohol employed. The transesterification of *Passiflora* oil gave alkyl palmitate (ca. 22 %), alkyl myristate (ca. 6 %), alky oleate (ca. 20 %), alkyl linoleate (ca. 31 %), and non-identified alkyl ester (ca. 21 %).

Influence of the heating method

Three different methods to heat the reaction were used (i.e., conventional, microwave radiation, and Teflon autoclave heating). All the reactions were carried out with *p*-sulfonic acid calix[4]arene catalyst (ca. 20 % w/w; 23.5 mol %) in an excess of ethanol (5 cm^3). The results are detailed in Table 2.

No reaction progress was observed performing the reactions in a microwave reactor during 8 h. Conversely, by the use of conventional heating (ca. reflux temperature) or of an autoclave working under autogenic pressure the reactions reached an almost total conversion. However, the required time was noticeably dependent on the heating process. When carried out during an equal time interval (ca. 8 h), the reaction performed in an autoclave reactor proceeded faster than that performed under reflux conditions. This different behavior may be related to the phase equilibrium established inside the reactor, affecting the methanol concentration in the reaction solution [32]. Meneghetti et al. have estimated that heating to high temperatures (ca. 150 °C), the alcohol concentration at liquid phase is, in average, threefold higher than those observed using reflux reactor [33]. Since an excess of alcohol is desirable to shift the equilibrium towards products, the reaction carried out under autogenic pressure achieved higher conversion.

The reactions proceeded more slowly under conventional heating (ca. 28 h) than the ones carried out in an autoclave reactor, where triglycerides were completely converted to fatty ethyl esters (FAEE) after 5 h of reaction. This fact may be also explained by the higher temperature (ca. 180 °C against 78 °C), besides the high internal pressure reached in the autoclave, that increases the ethanol concentration in the liquid phase.

Noticeably, the heating procedure had a crucial role on *p*-sulfonic acid calix[4]arene-catalyzed transesterification reaction. At the same temperature (ca. 78 °C, reflux temperature of ethanol), the conversion rise from 5 to 98 %, when the microwave heating was replaced by conventional heating or autoclave heating. An increase of the temperature (78–180 °C) resulted in the reduction of the time to complete reaction, from 28 to 5 h. It is important to note that in the absence of catalyst the reaction conversion was lower than 5 %.

Effect of the catalyst concentration in the transesterification of *Passiflora* oil with methanol or ethanol

Since the reactions reached high conversions when performed in an autoclave reactor, this methodology was selected to carry out the other investigations with ethanol or methanol, in order to evaluate the effects of *p*-sulfonic acid calix[4]arene concentration (Fig. 1). The catalyst load varied from 0 to 4.5 % w/w (5.28 mol %) in relation to the oil weight, keeping the time and the reaction temperature constant (ca. 5 h and 180 °C).

The *p*-sulfonic acid calix[4]arene catalyst load was a crucial aspect and remarkably affected the conversion rates obtained in the transesterification reactions. The reactions only proceeded significantly when the catalyst concentrations were equal or higher than 3.0 % w/w; 3.52 mol %). Remarkably, the transesterification of *Passiflora* oil with ethanol was more effective than that with methanol [34, 35]. Increasing the catalyst amount to 4.5 % w/w (5.28 mol %), conversions of *Passiflora* oil to ethyl or methyl esters above 98 % was observed.

We find out that employing the catalyst at low concentrations (i.e., 0.5–1.5 wt%), the methanol is more reactive than ethanol. Nevertheless, using catalyst concentrations higher than 1.5 wt% (ca. 1.5–3 wt%), the

Table 2 Effects of the heating method on the *p*-sulfonic acid calix[4]arene-catalyzed *Passiflora* oil transesterification with ethanol (catalyst 20 % w/w) 23.5 mol % molar ratio

Run	Ethanol/cm^3; mmol	Oil/g	Time/h	Temp./°C	Heating mode	Conv./%
1	4.0; 70	0.5	8	78	Microwave radiation[a]	<5
2	4.0; 70	0.5	8	78	Conventional	25
3	4.0; 70	0.5	28	78	Conventional	>98
4	4.0; 70	0.5	8	78	Teflon autoclave reactor	55
5	4.0; 70	0.5	5	180	Teflon autoclave reactor	>98

[a] $P = 150$ Watt

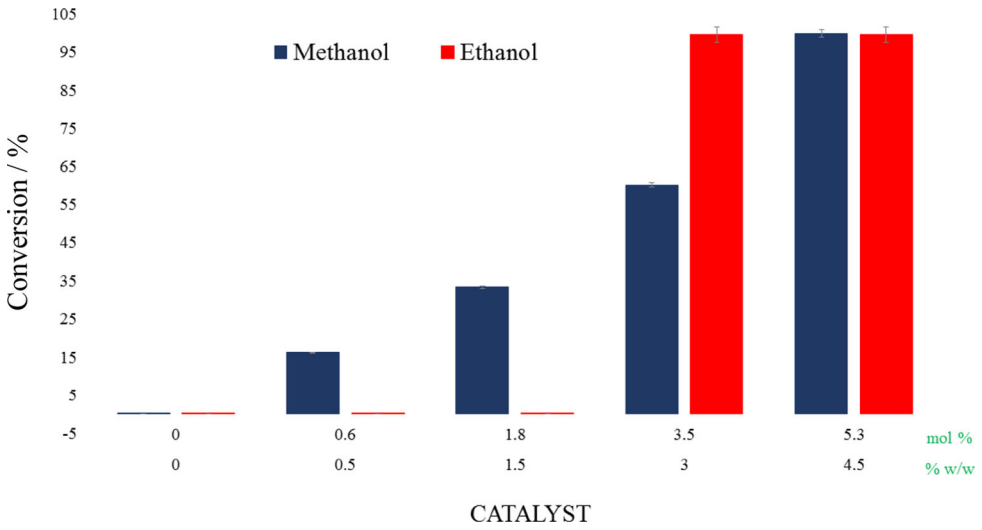


Fig. 1 Effect of the *p*-sulfonic acid calix[4]arene catalyst concentration on the transesterification of *Passiflora* oil. Reactions were carried out in an autoclave reactor under autogenic pressure (reaction conditions: 0.1 g oil, 5 cm^3 alcohol, 180 °C, 5 h)

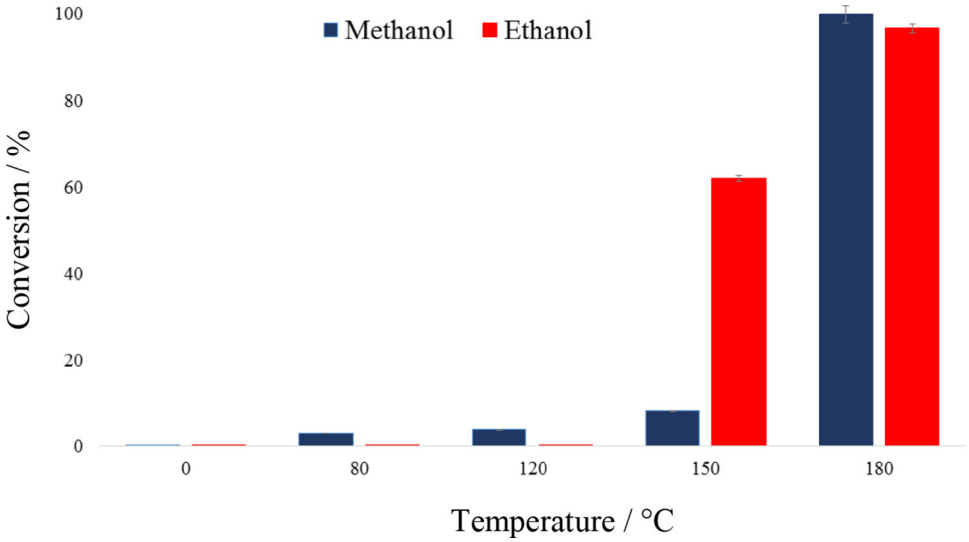


Fig. 2 Effect of temperature on the *p*-sulfonic acid calix[4]arene-catalyzed *Passiflora* oil transesterification reaction. Reactions carried out in an autoclave reactor under autogenic pressure (reaction conditions: 0.1 g oil, 5 cm^3 alcohol, catalyst (4.5 % w/w; 5.25 mol %), 5 h)

reactions with ethanol achieved higher conversion than that with methanol. This fact reinforces the hypothesis that the interactions (i.e., type van der Waals) between ethanol and the catalyst molecules are more favored when these species are in higher concentrations.

Effects of temperature in the *p*-sulfonic acid calix[4]arene-catalyzed *Passiflora* oil transesterification reaction

Regardless of the kind of alcohol, the conversion rate of the transesterification reactions increased with the temperature, reaching almost 100 % after a 5-h reaction when heated to 180 °C (Fig. 2).

However, the alcohols reactivity was notably different. When the reactions were carried out at 150 °C, the ethanol was much more reactive than methanol (ca. 62.0 % against 8.2 % conversion, respectively). A lower conversion rate was achieved, similar to the described in the previous section [34, 35]. These results suggest that when *p*-sulfonic acid calix[4]arene is used, an increase of the alcohol carbon chain may favor the reaction.

Effect of the catalyst nature on the transesterification of Passiflora oil with methanol or ethanol

For comparison, the transesterification of *Passiflora* oil with methanol or ethanol were performed using the monomer *p*-hydroxybenzenesulfonic acid of the calix[*n*]arenes the same hydrogenionic concentration (3.0 % w/w; 3.52 mol % or 4.5 % w/w; 5.28 mol %) of *p*-sulfonic acid calix[4]arene and *p*-hydroxybenzenesulfonic acid at 12.0 or 18.0 % w/w, respectively.

Remarkably, even when the catalyst was employed at the same hydrogenionic concentration, the conversions were significantly different, suggesting that other aspects may be involved in these reactions [24, 25].

Acid-catalyzed transesterification reactions: a comparison with results of the calix[4]arene-catalyzed reactions

The following section describes various Brønsted acid catalysts based methods for the transesterification reaction, which normally requires long reaction times. For instance, Pryde et al. showed that the H_2SO_4-catalyzed methanolysis of soybean oil, in the presence of 1 mol % of catalyst, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (>99 %) [36]. The effects of reaction conditions such as temperature, alcohol-to-oil molar ratio, catalyst load, and type of oil should be taken in account when a comparison is carried out [37].

Table 3 summarizes some results that allow compare calix[4]arene activity and other acid catalysts. As can be seen, the reaction conditions affect the catalytic performance of the transesterification process. However, calix[4]arene was more active than sulfuric acid even when employed at lower load.

Organocatalyst reusability and leaching tests

An important characteristic of the organocatalysts is their reusability in successive reaction cycles, and a high level of catalyst recovery, retaining its activity without further treatment is highly desired.

The solubility of the *p*-sulfonic acid calix[4]arene was observed in the mixture of ethanol and fatty ethyl esters than in the analogues methyl esters, hampering the recovery of the organocatalyst in ethanol. Thus, the recovery and reuse of *p*-sulfonic acid calix[4]arene were only studied for the reactions in methanol.

After 5 h of reaction in an autoclave reactor, the reaction mixture with the fresh organocatalyst was cooled to ambient temperature, and dichloromethane was added to the mixture. The solid catalyst was removed by filtration, dried, and reused in the same conditions of reaction. The operation was repeated for two cycles (Fig. 3).

The relative amount of organocatalyst recovered in the two cycles was similar (54 %). The conversion rate of triglycerides to methyl esters remained almost unchanged in the first cycle (96 %), but a decay was observed in the second one (76 %). However, the ^{1}H NMR and IR spectra of the organocatalyst after the third cycle did not show evidences of drastic chemical decomposition of the structure (Electronic Supplementary Material).

We would point that when the effect of the catalyst concentration was studied it was verified that when 3 wt% the ethanol was used the conversion was almost complete (see Fig. 3). It is corresponding to nearly 35 % of the concentration initially used in the recycle reactions. In the

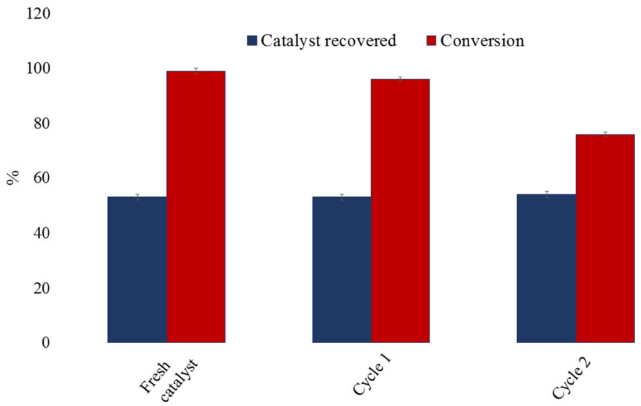


Fig. 3 Conversion rates obtained in the *p*-sulfonic acid calix[4]arene-catalyzed transesterification reactions of *Passiflora* oil with methanol after successive cycles of catalyst recovery/reuse (reaction conditions: autoclave reactor under autogenic pressure; 0.1 g oil, 5 cm^3 alcohol, catalyst (3.0 % w/w; 3.52 mol % or 4.5 % w/w; 5.28 mol % in ethanol, respectively), 180 °C; 5 h)

Table 3 Reaction of transesterification with methanol in presence of different Brønsted acid catalysts[a]

Exp	Catalyst, load/wt%	Methanol-to-oil molar ratio	Time/h	Temp./°C	Conversion/%	References
1	H_2SO_4, 1.3	6:1	3	85	1.5	[38]
2	H_2SO_4, 3.0	6:1	48	60	90	[39]
5	H_2SO_4, 4.0	20:1	20	95	90	[40]
6	H_2SO_4, 41.8	245:1	4	70	99	[41]
2	H_3PO_4, 1.0	6:1	3	85	<5	[38]
5	$H_3PW_{12}O_{40}$, 3.75	70:1 (15 % FFA)	14	65	88	[42]
3	Dehydrated $H_3PW_{12}O_{40}$, 1.6	6:1	3	85	45	[38]
7	H_3PO_4, 1.0	6:1	3	85	<5	[38]
8	Calix[4]arene, 4.5	220:1	5	78	99	[This work]

first step, the recovery percentage of the catalyst was slightly higher than 60 %.

To justify the low rate of recovery of the catalyst, an experiment where *Passiflora* oil, methanol, and catalyst were heated in an autoclave at 180 °C for 1 h was conducted. After this period, the catalyst was removed from the reaction and the mixture was heated during 4 h. The ^{1}H NMR spectra of the reaction mixture were obtained for the samples after 1 and 5 h of reaction, where conversions of 20 and 90 % were obtained, respectively. These results show that the catalyst is soluble in the methyl esters and glycerol mixture thus hindering their recovery.

Proposed mechanism for transesterification

Based on the reports documented in literature and on our observation in the present protocol, a plausible reaction mechanism has been proposed (Scheme 1). The sulfonic groups of the catalyst are completely dissociated in methanol or ethanol [43, 44]. The esterification reaction catalyzed by homogeneous acids proceeds through the following mechanism: in a first step, the carbonyl oxygen is attacked by the acid proton that increases the electrophilicity of the carbon atom. This carbon atom is then more susceptible to the nucleophilic attack of the hydroxyl group of the alcohol, which is the rate determining step. The following steps are the dehydration and deprotonation (transesterification) of the intermediate with the corresponding formation of the new ester and the recovery of the catalyst [45, 46].

Conclusions

In this work, a novel and efficient process based on *p*-sulfonic acid calix[4]arene as a homogeneous and recyclable organocatalyst was developed for the synthesis of esters, which make it a potential catalyst for the production of biodiesel. The *p*-sulfonic acid calix[4]arene catalyst used in this work was able to promote the transesterification of a vegetable oil in high yields of conversion in a short time and free metal conditions.

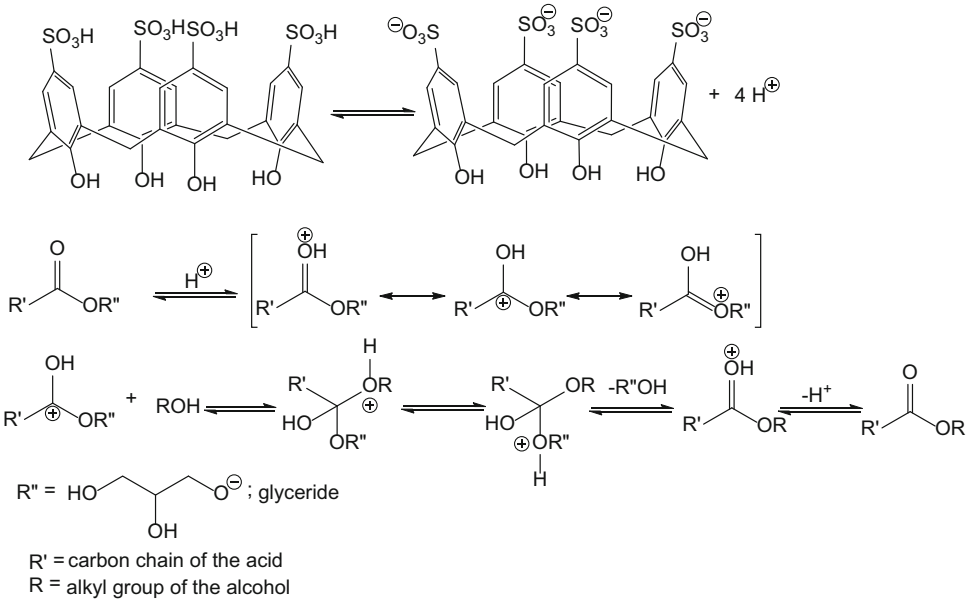
Experimental

Refined passion fruit oil was purchased from Emfal Empresa Fornecedora de Álcool Ltda (Betim, Minas Gerais, Brazil) and analyzed before used. Methanol and ethanol were purchased from VETEC Química Ltda (Rio de Janeiro, Brazil) and used without further purification.

Characterization of the *Passiflora* oil

Passiflora oil physicochemical properties were determined in agreement with AOCS rules [27]. The fatty acid profile was determined as fatty acid methyl esters by gas chromatography–mass spectroscopy [28]. Separation of fatty acid esters was performed on a Shimadzu GC-2010 Gas Chromatograph equipped with a Restek RTX-2330 capillary column (60 m × 0.25 mm × 0.2 mm). The column temperature was programmed at 130 °C for 10 min, then

Scheme 1



increased to 230 °C at 5 °C/min with a final isothermal period of 13 min. Hydrogen was used as carrier gas with constant linear velocity of 25 cm/s. The injector temperature was set at 250 °C, with a split ratio of 1:10. The flame ionization detector temperature was 250 °C. Fatty acid methyl esters (FAMEs) were identified by comparison of retention times with authentic standards (Supelco 37 comp. FAME mix 10 mg/cm^3 in CH_2Cl_2), and quantification was performed by the internal normalization method.

Catalyst synthesis

The *p*-sulfonic acid calix[4]arene was synthesized in our laboratory according to literature procedures [20–22], as described in Scheme 2.

The synthesis of the *p-tert*-butylcalix[4]arene (20.8 g, 77 % yield) was prepared by the condensation of 25.0 g *p-tert*-butylphenol and 16.0 cm^3 formaldehyde solution in a basic medium (NaOH, 0.6 g) and under heating. The product was obtained as a white solid in 77 % yield. The synthesis of calix[4]arene (10.6 g) was carried out using 20.0 g *p-tert*-butilcalix[4]arene, 13.5 g phenol, and 23.0 g anhydrous aluminum chloride in toluene [20]. The system was kept under stirring and nitrogen atmosphere at room temperature for 1 h. The desired product was obtained as a white solid in 81 % yield after recrystallization in methanol–chloroform. The synthesis of *p*-sulfonic acid calix[4]arene (16.0 g) was conducted from 10.0 g calix[4]arene in the presence of 100 cm^3 concentrated sulfuric acid and heated for 4 h [22]. The product was obtained in 75 % yield as a white solid.

Catalytic tests

The catalytic reactions were carried out in a Teflon-lined stainless steel autoclave of 20 cm^3 capacity placed in a digital oven (M.S. Mistura Equipamentos Para Laboratórios, Rio de Janeiro, Brazil) or in a CEM Discover microwave reactor (CEM Corporation, Matthews, NC, USA) or under conventional heating (glass reflux apparatus heated with an oil bath on a magnetic stirrer hotplate).

Typically, a mixture of 0.05–0.34 g oil, 5 cm^3 methanol or ethanol, and *p*-sulfonic acid calix[4]arene (2.15–21.5 % w/w; 23.5 mol %) were heated at 78–180 °C for 3–36 h. All experiments were performed in triplicate.

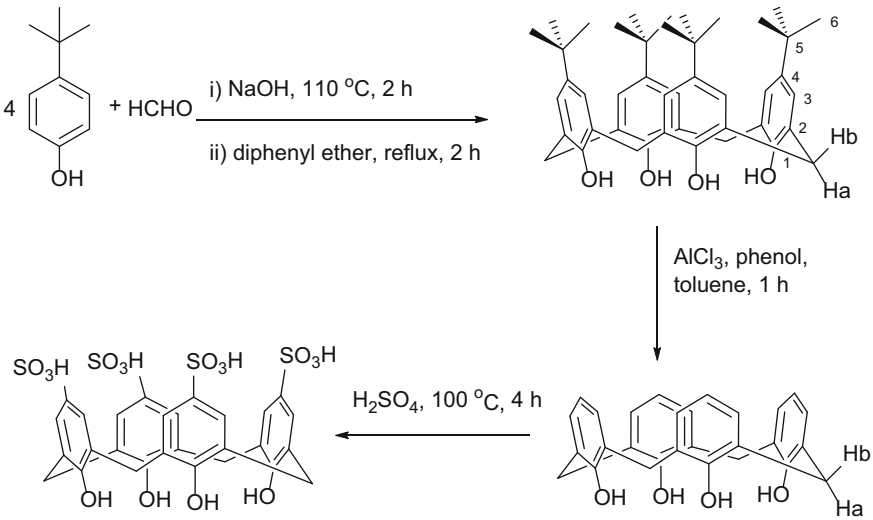
Separation and quantification of the reaction products

The reaction mixtures were cooled to room temperature and dichloromethane was added. The precipitated organocatalyst was then removed by filtration and washed with brine and dichloromethane. The concentrated organic phase was analyzed by ^{1}H NMR spectroscopy to calculate the conversion rate of triglycerides to methyl or ethyl esters. NMR spectra were recorded on a Bruker AVANCE DRX 300 MHz, in deuterated dichloromethane and trimethylsilane as internal reference.

Recovery and reuse of catalyst

The precipitated organocatalyst recovered from the reaction was dried at 50–60 °C, analyzed by ^{1}H NMR, and reused in another catalytic run.

Scheme 2



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