

Short communication

Hydrolysis of triacylglycerides in the presence of tin(IV) catalysts



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ABSTRACT

Tin(IV)-based compounds (mono-*n*-butyltin hydroxide oxide (**a**), di-*n*-butyl-oxo-stannane (**b**), di-*n*-butyl tin dilaurate (**c**) and tin oxide (**d**)) were used as catalysts in the hydrolysis of triacylglycerides (TGs). The effects of the nature and amount of the catalysts, the nature of the TGs, the temperature and reaction time were evaluated. Compared with the usual industrial processes, these systems showed excellent activities at mild temperatures and pressures, and low amounts of catalyst (ca. 0.3% w/w_{oil}). Fatty acid (FA) conversions of ca. 97% were obtained at 180 °C, 4 h at oil:water:catalyst a molar ratio of 1:24:0.01 and, using soybean oil.

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1. Introduction

Triacylglycerides (TGs) and their derivatives, present in oils and fats from animal or vegetal origin, are renewable sources that can produce several useful products. They are strong candidates to replace fuels and chemicals obtained from fossil sources. The chemical structure of these species allows a diversity of reactions, such as transesterifications, esterifications, oxidative polymerization and hydrolysis [1,2].

In the oleochemical industry, the hydrolysis is very important because, via this reaction, highly pure fatty acids (FAs) and glycerol, which have important applications in the production of soaps, surfactants, lubricants, cosmetics, foods, pharmaceuticals, plasticizers, paints, biofuels, etc., are commonly produced [3,4].

Conventionally, the hydrolysis of an ester (mono-, di- or triacylglycerides abbreviated as MGs, DGs and TGs, respectively) may occur in the presence of basic or acid Bronsted catalysts or even enzymes. Independent of the nature of the catalyst used, the hydrolysis of TGs is based on three consecutive steps: TGs are converted to DGs that are converted to MGs and finally to glycerol, resulting in three FA molecules (individually formed in each step) – see Figure S1 in Supporting Information [2,5–7].

Due to the immiscibility of vegetable oils (or fats) in water, it is often necessary to operate the hydrolysis process at high temperatures or pressures to increase the compatibility of such components [3,4,7–9]. Consequently, the industrial processes are based on high energy consumption and high costs due the use of a considerable amount of water vapor overheated and use of large reactors made of materials resistant to corrosion, which are associated at the poor quality of the

obtained products (FAs and glycerol) and require additional purification steps [9].

Therefore, the investigation of alternative chemical or enzymatic catalytic systems that help overcome the problems discussed above is very important. Indeed, many proposals have been presented and discussed in the scientific and technical literature, including the use of Lewis acid species [3,9–12]. In terms of the hydrolysis mechanism, it is possible to adopt the same considerations to transesterification and esterification reactions catalyzed by Lewis acids [12,13]. These reactions involve the formation of a Lewis acid–base complex through an interaction between the acylglycerides (TG, DG, and MG) at the metal center via the oxygen of the carbonyl group.

There are some examples of use of tin(IV)-based homogeneous or heterogeneous catalytic systems in esterification, transesterification and polycondensation reactions to produce polymeric and intermediate materials [14–16]. Recently, we reported the potential use of this family of catalysts for fatty acid alkyl ester production [17–20].

However, to the best of our knowledge, no information is available about the performance of tin(IV) compounds as catalysts for acylglyceride hydrolysis. In this context, mono-*n*-butyltin hydroxide oxide (**a**), di-*n*-butyl-oxo-stannane (**b**), di-*n*-butyl tin dilaurate (**c**) and tin oxide (**d**) were used, as examples of tin(IV) compounds, to evaluate their potential as catalysts for the production of FAs from TGs.

2. Experimental

2.1. Materials

All of the chemicals were used as received without further purification. Mono-*n*-butyltin hydroxide oxide (**a**), di-*n*-butyl-oxo-stannane (**b**), di-*n*-butyl tin dilaurate (**c**), and tin oxide (**d**) were purchased

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from Sigma-Aldrich (MO, USA). Soybean oil (commercial grade) was supplied by Bunge Alimentos (Brazil), coconut oil was purchased from Sococo (Brazil), and castor oil was acquired at a local market. All of the oils were used as received and were analyzed (viscosity and acidity) using standard methods described by the Association of Official Analytical Chemists (AOAC, reapproved 1997) [21]. The fatty acid compositions of the oils were determined via gas chromatography (GC) using the official AOCS methods Ce 1-62 and Ce 2-26 (A.O.C.S., 1998) [21].

2.2. Hydrolysis reactions

Hydrolysis reactions were performed in a 100-mL batch stainless steel reactor coupled to a manometer, temperature probe and a mechanic stirrer operated at 1000 rpm. All of the reactions were carried out using an oil:water:catalyst molar ratio of 1:x:y ($x = 3, 6, 12,$ or 36 and $y = 0.01, 0.02$ or 0.03) at different temperatures ($140, 160$ or 180 °C) for 0.25 to 8 h. The endogenous pressure, observed during the experiments, was ca. of 3 bar at 140 °C, 4 bar at 160 °C and 5 bar at 180 °C. After the appropriate reaction time, the obtained product was analyzed by titration, and the reaction conversion was calculated based on the increase in the acid index for the products in relation to acid index for the initial content of TGs, according to the AOCS Cd3d63 standard method [21]. For that, 0.5 g of sample was diluted in 10 mL of diethyl ether:ethanol and alcohol ($2:1$ v:v) solution and 0.2 mL of phenolphthalein was added. This solution was titrate, under stirring, with the potassium hydroxide solution (0.01 mol.L⁻¹) until pink color, which must persist for at least 10 s. This determination is done in triplicate.

For the samples characterized by HPLC, a Shimadzu chromatograph (CTO-20A) equipped with a UV detector ($\lambda = 205$ nm) and a reverse phase column (Shim-pack VP-ODS C18, 250 mm \times 4.6 mm, 5 mm) at 40 °C. The injection volume was 10 μ L, and the flow rate was 1 mLmin⁻¹ using methanol and a 2-propanol:*n*-hexane solution ($5:4$ v:v) with a composition gradient in the mobile phase: 100% methanol at 0 min, 50% methanol and 50% of the 2-propanol:*n*-hexane solution at 10 min, and isocratic elution for 10 min. The chromatograms were analyzed using LabSolutions software.

In order to investigate the Sn concentration presents in the reaction medium in the case of solid catalysts, reactions using **a** and **b** were investigated using oil:water:catalyst molar ratio of $1:24:0.01$ at 180 °C for 4 h. After the appropriate reaction time, the oil and water phase were separated, and filtered through a 0.45 μ m Millipore filter. After this procedure, the Sn content (mg/kg) was investigated in the two phases, by radial view Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) using Spectro Arcos equipment.

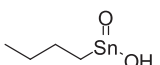
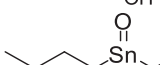
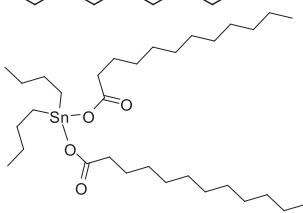
Catalysts **a** and **b** were characterized using: (i) TM3000 TableTop SEM with a magnification of $1000\times$ and SwiftED 3000 X-Ray software (Oxford Instruments, USA); (ii) FTIR spectra for evaluated pyridine adsorption at 100 °C, 150 °C and 200 °C on a Shimadzu infrared spectrophotometer (model Prestige-21) and (iii) isotherms were investigated (specific surface areas and pores diameter) at 77 K with a Nova 2200e instrument (Quantachrome Instruments).

3. Results and discussion

In this work, catalysts based on tin(IV) compounds, presented in Table 1, were employed as catalysts in the hydrolysis of TGs. The catalytic performance of these chemical species and the influence of several reaction parameters in the reaction yields were investigated.

Three different natural sources of TG were used (soybean, coconut and castor oils), and these three oils exhibited different characteristics in terms of their FA compositions (Table S1 in Supporting Information). Complementarily, the viscosity and acidity were also determined (Table S2 in Supporting Information). The acidity values were suitable for use in hydrolysis.

Table 1
Nomenclature and formulas of the catalysts.

Nomenclature	General formula ^a
a Mono- <i>n</i> -butyl tin hydroxide oxide	
b Di- <i>n</i> -butyl-oxo-stannane	
c Di- <i>n</i> -butyl tin dilaurate	
d Tin oxide	SnO ₂

^a Schematic representation of the chemical species because these species are more likely to displaying intramolecular coordination or intermolecular association leading to dimers, oligomers, or polymers [13].

3.1. Influence of the catalyst nature, temperature and reaction time

The catalysts **a**, **b**, **c** and **d** were used in the hydrolysis of soybean oil at 140 and 160 °C and at several reaction times, employing the molar ratio of oil:water:catalyst of $1:24:0.01$. Fig. 1 presents the results for both temperatures in comparison with the reaction in the absence of catalyst.

The catalyst **d** showed the same behavior observed in the reactions run in the absence of catalyst, indicating that this compound did not act as a catalyst in this type of reaction, regardless of the temperature or reaction time considered.

When the catalysts **a**, **b** and **c** were used, significant conversions were attained, especially at 160 °C, demonstrating the positive influence of the temperature on the reaction conversion of TGs to FAs. When analyzing the evolution in relation to the reaction time, the conversions were enhanced with as the reaction time increased.

The best conversion results were obtained with catalyst **a** at 160 °C, which could be justified by the better access to the reaction site, according to the mechanism mentioned in the introduction. The results observed in the presence of **b** and **c** were comparable but lower than that obtained for **a** due the presence of two butyl substituents (in **b**) and two butyl and two carboxylate substituents (in **c**).

Additionally, since the catalysts **a** and **b** are solids, the Sn content (mg/kg) was investigated on the filtrated oil and water phase, after reaction (oil:water:catalyst molar ratio of $1:24:0.01$ at 180 °C for 4 h). Considering the amount of catalyst employed, if the whole catalyst is in the aqueous phase the concentration of Sn expected is 2749 mg/kg. On the contrary, if the totality of catalyst stays in the oily phase, the estimated Sn concentration will be 1361 mg/kg. In the aqueous phase, it was detected <0.010 mg/kg of Sn, for both catalysts. In the oily phase, 40 mg/kg and 69 mg/kg of Sn were detected for **a** and **b**, respectively. From these results, it is possible to assume that the catalysts **a** and **b**, are really solids with low solubility, since just a small amount of catalyst can be found, either in the aqueous or in the oily phases.

Furthermore, a reaction at oil:water molar ratio of $1:24$ at 180 °C (1 to 4 h) was studied, using the amount of Sn detected for **a** (40 mg/kg), after the procedure described above (see Figure S3 in Supporting Information). The results, if compared those obtained at oil:water:catalyst molar ratio of $1:24:0.01$, show proportional conversions with the catalyst amount. It is important to mention that it is not possible to dismiss that this Sn amount, detected by ICP in the oily phase, can be associated to solid catalyst, since the minor particles of **a** and **b** can permeate through the filter.

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