# New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterificaton reaction

Frederique R. Abreu[a], Melquizedeque B. Alves[a], Caio C.S. Macêdo[a],
Luiz F. Zara[b], Paulo A.Z. Suarez[a],*

[a] *Instituto de Química, Universidade de Brasília, CP 4478, 70919-970 Brasilia, D.F., Brazil*
[b] *Universidade Católica de Brasília, Brasília, D.F., Brazil*

## Abstract

It is reported here about some attempts in order to develop a multi-phase catalytic system active for vegetable oil alcoholysis based upon tin compounds. The immobilization of $Sn(3-hydroxy-2-methyl-4-pyrone)_2(H_2O)_2$ by dissolving it in the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid and supporting it in an ion-exchange resin, as well as the catalytic behavior of tin oxide was studied. By anchoring the tin complex in the ionic liquid, it was observed that its catalytic activity was maintained but it was not possible to reuse the catalytic system due to leaching of the catalyst from the ionic phase during each reaction. On the other hand, it was found that the tin complex lost its catalytic activity when supported in the organic resin. It was also shown that tin oxide was active for soybean oil methanolysis (conversion yields up to 93% in 3 h were achieved) and was also possible to recycle it without any loss in its catalytic activity.
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## 1. Introduction

Depletion of the world petroleum reserves and increasing environmental concerns has stimulated the search for renewable fuels [1]. Biodiesel is an interesting alternative due to the fact that its properties are similar to those of diesel [2].

Different methods of synthesizing biodiesel have been proposed [3–5]. The most common is the catalytic transesterification reaction of vegetable oils with a short-chain alcohol, usually methanol. Also known as methanolysis, this reaction is well studied and established for soybean, sunflower and rapeseed, using acids or alkalies as catalysts [6,7].

Unfortunately, these traditional catalytic systems are associated with corrosion and difficulties in the process due to emulsion formation [8]. In order to minimize these problems, attempts to use heterogeneous catalyst systems in alcoholysis of triglycerides have been made [8–10]. The use of heterogeneous catalysts makes separation of the product easier and achieves conversions higher than 95% in systems using high molecular weight alcohols where neither alkali nor acid catalysts work [11]. However, these catalytic systems have very low reaction velocities when compared with the traditional ones [8–11].

We have recently shown that metal compounds of the type $M(3-hydroxy-2-methyl-4-pyrone)_2(H_2O)_2$, where $M = Sn$, Pb or Zn, used as catalysts are active for vegetable oil transesterification in homogeneous conditions [12,13]. Sn and Zn complexes were much more active than the traditional NaOH and $H_2SO_4$ catalysts under the same conditions. It is worth mentioning that these catalystic systems are active for the transesterification of different vegetable oils and several alcohols, including the high molecular ones [13], with the tin complex always showing the highest catalytic activity. However, as long as these catalytic systems remain dissolved in the reaction medium, it is difficult to recover and reuse them. For

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* Corresponding author. Tel.: +55 61 307 2162; fax: +55 61 273 4149.
  *E-mail address:* psuarez@unb.br (P.A.Z. Suarez).

this reason, immobilization of the tin complex was attempted in order to obtain similar catalytic activity allied with the advantages of an heterogenous system. To achieve this goal, two different strategies were followed: (i) anchoring the tin complex to ionic liquids (biphasic catalysis) and (ii) supporting it in an organic solid phase. Tin oxide was also prepared and tested as catalyst for the methanolysis reaction.

## 2. Experimental

### 2.1. Reagents

All reagents were obtained from commercial sources and used without further purification. Reagent grade tin(II) chloride, 3-hydroxy-2-methyl-4-pyrone, acetylacetone, sodium hydroxide and Dowex 50WX8-100 ion-exchange resin were obtained from Aldrich (Milwaukee, WI). Refined soybean oil was obtained from Bunge (Gaspar-Santa Catarina State, Brazil). Dimethylsiloxane (DMSO) and methanol (MeOH) were analytical grade and obtained from Merck. Methylimidazole, butylchloride and potassium hexafluorophosphate were obtained, in analytical grade, from Acros.

### 2.2. Preparation of catalysts

#### 2.2.1. Materials

The $BMI(PF_6)$ ionic liquid was prepared according to methods previously described [14]. A 2 L, three-necked, round-bottomed flask, equipped with a heating oil bath, a nitrogen inlet adapter, an overhead mechanical stirrer and a reflux condenser, was flushed with nitrogen. Then, the flask was charged with 151.5 g (1.85 mol, 1 equiv.) of freshly distillated $N$-methylimidazol, 100 mL of acetonitrile and 220 g (2.4 mol, 1.3 equiv.) of $n$-chlorobutane, and kept under gentle reflux (75–80 °C internal temperature) for 48 h and then cooled to room temperature. The volatiles were removed from the resulting yellow solution under reduced pressure and the remaining light-yellow oil was re-dissolved in dry acetonitrile (250 mL). The obtained solution was added dropwise via cannula to a well-stirred, 1000 mL of dry ethyl acetate placed in a 2-L round-bottomed flask, equipped with a nitrogen inlet adapter and an overhead mechanical stirrer. The imidazolium salt crystallized exothermically almost immediately and after the addition of the acetonitrile solution was completed, the flask was placed at −30 °C for 2 h. The supernatant solution was removed via filtration through a filter-cannula and the resulting white solid was dried under reduced pressure (0.1 mbar) at 30 °C for 6 h affording 1-$n$-butyl-3-methylimidazolium chloride 309.2 g (96%). Then, a one-necked round-bottomed flask was charged with 65.6 g (0.37 mol, 1 equiv.) of the 1-$n$-butyl-3-methylimidazolium chloride so prepared, 69.3 g (0.37 mol, 1 equiv.) of potassium hexafluorophosphate, used as received from commercial sources, and 70 mL of distilled water. The reaction mixture was stirred at room temperature for 2 h affording a two-

phase system. The organic phase was washed three times with 50 mL of distilled water. Then, 100 mL of dichloromethane and 35 g of anhydrous magnesium sulfate were added. After 1 h, the suspension was filtered and the volatiles eliminated under reduced pressure (0.1 mbar) at 30 °C for 2 h, affording 97.5 g (0.34 mol, 91%) of 1-$n$-butyl-3-methylimidazolium hexafluorophosphate as a light yellow viscous liquid.

The $Sn(3\text{-hydroxy-2-methyl-4-pyrone})_2(H_2O)_2$ complex was prepared according to methods previously described [15]. In 20 mL of distilled water 0.2 mmol of ligand (3-hydroxy-2-methyl-4-pyrone) and 2 mmol of sodium hydroxide were dissolved. To this solution 0.1 mmol chloride salts of metals dissolved in 20 mL of water were added slowly under continuous magnetic stirring. The mixture was left stirring at 323 K for 30 min and then was kept in a refrigerator overnight and the resulting precipitate was isolated by filtration, washed several times with distilled water and dried in a vacuum desiccator over silica gel. 158.63 mg (0.43 mmol, 43%) of $Sn(C_6H_5O_3)_2 \cdot 2H_2O$ were obtained.

#### 2.2.2. Anchoring Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ to BMI(PF$_6$) (1)

The $Sn(3\text{-hydroxy-2-methyl-4-pyrone})_2(H_2O)_2$ (0.036 g) was mixed at room temperature in $BMI(PF_6)$ (2 mL) until its complete dissolution.

#### 2.2.3. Supporting Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ in Dowex 50WX8-100 ion-exchange resin (2)

The $Sn(3\text{-hydroxy-2-methyl-4-pyrone})_2(H_2O)_2$ (0.200 g) was dissolved in DMSO (9 mL) and then impregnated in an acid ion-exchange resin (4 g) at 60 °C for 72 h. The resulting product 2 was isolated by filtration, washed with distilled water, and dried in a vacuum desiccator over silica gel.

#### 2.2.4. Preparation of SnO (3)

A water solution (20 mL) containing acetylacetone (0.2 g, 2 mmol) and sodium hydroxide (0.079 g, 2 mmol) was slowly added, under magnetic stirring, to a water solution (20 mL) of tin(II) chloride (0.551 g, 2 mmol). The mixture was left under stirring at 40 °C for 30 min and then kept in a refrigerator overnight. The resulting precipitate was isolated by filtration, washed several times with distilled water and dried in a vacuum desiccator over silica gel. The resulting complex was calcined at 500 °C for 24 h.

### 2.3. Characterization of catalysts

#### 2.3.1. ICP emission spectroscopy

The amount of Sn adsorbed on the surface of the catalyst 2 and present in the catalyst 3 were determined by ICP emission spectroscopy using a Varian Liberty RL Series II inductively coupled plasma-optical emission spectrometer (ICP-OES).

### 2.3.2. Surface area (BET)

The surface area of the catalyst **3** was obtained by the BET method using a 'MICROMERITICS' analyzer model ASAP-2010. The isotherms were obtained through adsorption of $N_2$ at 77.30 K.

### 2.4. Catalytic experiments

The vegetable oil (10 g) was transesterified in the presence of methanol (1.5 g) using 2 mL of **1** or 0.5 g of **2** or **3** as catalysts. The reaction mixtures were kept in a 50 mL batch reactor under gentle reflux (approximately 60 °C) and magnetic stirring for the desired time. The product obtained was washed three times with distilled water. The recovered esters were analyzed by gas chromatography on a Shimadzu GC-17A chromatograph with FID detector, equipped with a poly-dimethylsiloxane column (CBPI PONA-M50-042, 30 m, 0.25 mm i.d. and film thickness of 0.2 μm), at temperatures varying from 80 to 180 °C, with a heating rate of 10 °C/min. Ethyl acetate (0.1 g) was used as internal standard.

## 3. Results and discussion

### 3.1. Biphasic catalysis

In the last decade, ionic liquids have received attention as solvents for two-phase catalysis. These compounds, especially those derived from the combination of quaternary ammonium salts and weakly coordinating anions, have proved to be ideal immobilizing agents for various 'classical' transition-metal catalyst precursors in reactions ranging from those of the Ziegler–Natta type to the hydroformylation of olefins [16] and references therein.

Thus, the first attempt to immobilize the Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ catalyst was by anchoring it to BMI(PF$_6$). A two-phase system, obtained by mixing a solution of the tin complex in ionic liquid, methanol and soybean oil, was kept in reflux for 1 h. Then, water was added to the reaction mixture and a three-phase system was obtained as illustrated in Fig. 1. Note that the upper layer contained the fatty acid methyl esters, the middle one was composed of water and hydroxyl compounds, and the bottom layer contained the ionic liquid, all separable by simple decantation. The ionic liquid, which was supposed to contain the tin complex, was reused up to four times and the results are shown in Fig. 2. It became clear from this figure that by anchoring the tin complex in the ionic liquid, the catalytic activity of the catalyst was maintained. Indeed, in 1-h reactions, yield up to 55% was achieved. However, as can be depicted from the picture, the reactions' yield drastically decreased with each new substrate charge, dropping from 58% in the first charge to almost zero in the last one. This behavior is probably caused by leaching of the catalyst from the ionic phase during each reaction. Due to this fact, it was concluded that it is not fea-
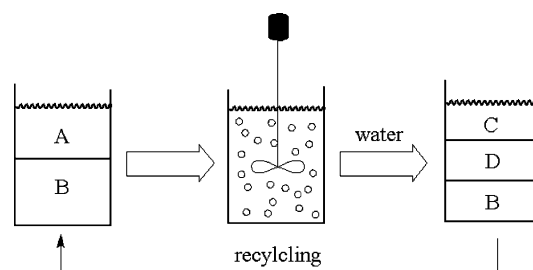


Fig. 1. Illustration of the soybean oil methanolysis reaction using the tin complex (**1**) immobilized in the ionic liquid. (A) Soybean oil/methanol; (B) methanol/ionic liquid/**1**; (C) fatty-acid compounds; (D) water/glycerine. Note that the reaction was carried out under reflux conditions ($T \approx 60$ °C) for 1 h.

sible to use BMI(PF$_6$) to anchor the tin complex to obtain a recyclable catalytic system for the methanolysis of soybean oil.

### 3.2. Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ supported in acid resin

Another attempt to obtain a recyclable catalytic system for the transesterification reaction using the tin complex was made by supporting it in a DOWEX® acid resin. The chemical adhesion of the tin complex to the acid resin was achieved by keeping a DMSO solution of the complex in contact with the resin at 60 °C. The tin complex probably reacts with the sulfonic acid group of the resin, remaining bonded in the resin surface after the elimination of one molecule of the ligand. After 76 h, the resulting solid **2** was isolated and purified and it was observed that 86 mg of tin was retained per gram of **2**.

Since the resin is acid, it was tested as a catalyst for soybean methanolysis using the same reaction conditions of the other catalytic systems. One percentage of the reaction yield was obtained after 1 h. Then, the mixture of **2**, soybean oil and methanol was kept under reflux for 1 h. Unfortunately, the observed reaction yield of 0.5% was lower than that obtained using pure resin. This result was particularly unexpected because the amount of tin in the resin used in this reaction is almost the same used in homogeneous conditions ([13], Section 2). This reduction in the reaction yield can be explained
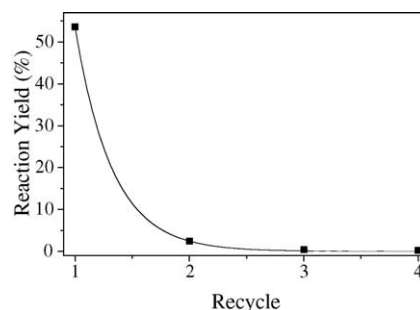


Fig. 2. Reaction yields observed for four soybean oil methanolysis reactions the same ionic phase composed by **1** dissolved in BMI(PF$_6$).

Table 1
Methanolysis of soybean oil using SnO as catalysts

| Entry | Time (h) | Reaction yield (%) | | | |
|---|---|---|---|---|---|
| | | First substrate charge | Second substrate charge | Third substrate charge | Fourth substrate charge |
| 1 | 1 | 56.5 | 56.5 | 57.9 | 55.3 |
| 2 | 3 | 92.6 | | | |
| 3 | 5 | 94.7 | | | |

by assuming that the interaction of the resin with the tin complex probably deactivated the acid sites of both the resin and the complex.

### 3.3. SnO

In a previous paper, it was found that the catalytic activity for soybean methanolysis decreased in the order $Sn^{2+} \gg Zn^{2+} > Pb^{2+} \cong Hg^{2+}$ [13]. Since both attempts at heterogenization of the tin complex failed, a new heterogeneous catalyst was prepared using tin. According to the literature, alkaline earth-metal and zinc oxides are active in the alcoholysis reaction of esters [17,18]. Thus, tin oxide was tested as a catalyst for the alcoholysis of vegetable oils.

Tin oxide **3** was prepared by calcination of tin(II) acetylacetonate at 500 °C for 24 h, as depicted in Scheme 1. By ICP–IOS analysis, it was verified that tin oxide so prepared **3** had 87.9% of tin, and was in excellent agreement with the theoretical composition of SnO (88.12%). The surface area of this solid was determined by the BET method to be approximately 35 m$^2$/g.

Solid tin oxide was tested as a catalyst for the soybean oil transesterification reaction. The results are shown in Table 1 and Fig. 3. It is worth mentioning that no emulsion formation was observed at the end of the reaction. After 1 h, a conver-

sion of up to 56% was obtained (entry 1). Catalyst recycling was achieved by simple filtration of the mixture at the end of the reaction. The recovered solid was used three more times, under the same reaction conditions. It is important to highlight that catalytic activity was totally conserved. When the reaction mixture was kept under reflux for longer periods of time, higher conversions were achieved, as illustrated in the Fig. 3.

## 4. Conclusions

Due to the good results obtained by using the complex Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ as catalyst for vegetable oil alcoholysis, attempts were made to immobilize it. Unfortunately, it was not possible to obtain a recyclable multi-phase system anchoring the tin complex to an ionic liquid or to a solid phase.
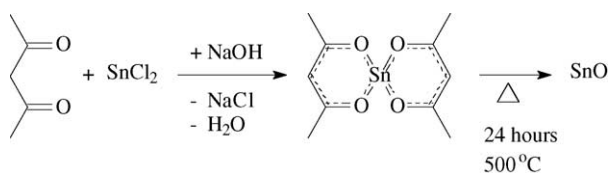
On the other hand, it was shown that tin oxide is active for soybean oil methanolysis in a heterogeneous system, with the advantage of no emulsion formation at the end of the reaction. It was observed that, by using this catalyst, not only high conversion yields were achieved (up to 93% in 3 h), but it was also possible to recycle it without any loss in catalytic activity.

Scheme 1.



Fig. 3. Methyl ester production in soybean oil transesterification in the presence of **3** as catalysts.

## References

[1] E.G. Shay, Biomass Bioenergy 4 (1993) 227.
[2] E.H. Pryde, J. Am. Oil Chem. Soc. 60 (1983) 1557.
[3] M.J. Nye, T.W. Williamson, S. Deshpande, J.H. Schrader, W.H. Snively, T.P. Yurkewich, C.Z. French, J. Am. Oil Chem. Soc. 60 (1983) 1598.
[4] M.J. Haas, S. Bloomer, K. Scott, J. Am. Oil Chem. Soc. 77 (2000) 373.
[5] C.M. Murrieta, B.W. Hess, D.C. Rule, Meat Sci. 65 (2003) 523.
[6] F. Ma, M.A. Hanna, Biores. Technol. 70 (1999) 1.
[7] S. Bhattacharyya, C.S. Reddy, J. Agric. Eng. Res. 54 (1994) 157.

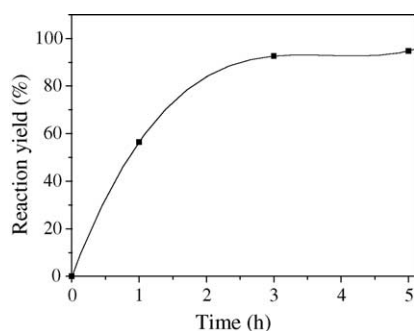[8] R. Stern, G. Hillion, J. Rouxel, S. Leporq, US Patent 5,908,946 (1999).

[9] G.R. Peterson, W.P. Scarrah, J. Am. Oil Chem. Soc. 61 (1984) 1593.

[10] S. Gryglewicz, Biores. Technol. 70 (1999) 249.

[11] G.J. Suppes, K. Bockwinkel, S. Lucas, J.B. Bots, M.H. Mason, J.A. Heppert, J. Am. Oil Chem. Soc. 78 (2001) 139.

[12] F.R. Abreu, D.G. Lima, E.H. Hamú, S. Einloft, J.C. Rubim, P.A.Z. Suarez, J. Am. Oil Chem. Soc. 80 (2003) 601.

[13] F.R. Abreu, D.G. Lima, E.H. Hamú, C. Wolf, J. Mol. Catal. A: Chem. 209 (2004) 29.

[14] P.A.Z. Suarez, S. Einloft, J.E.L. Dullius, R.F. de Souza, J. Dupont, J. Chim. Phys. PCB 95 (1998) 1626.

[15] A.B. De Oliveira, I.F. Jorge, N.R. De, S. Basso, Polym. Bull. 45 (2000) 341.

[16] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.

[17] S. Gryglewicz, Appl. Catal. A: Gen. 192 (2000) 23.

[18] G.J. Suppes, M.A. Dasari, E.J. Doskocil, P.J. Mankidy, M.J. Goff, Appl. Catal. A: Gen. 257 (2004) 213.