Utilization of metal complexes as catalysts in the transesterification of Brazilian vegetable oils with different alcohols

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Abstract

This article reports the use of Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**1**), Pb(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**2**), and Zn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**3**) as catalysts in the transesterification reaction of different alkyl-chain triglycerides and alcohols. The methanolysis of native oils from Brazilian's Savannah and Amazonian regions, such as Andiroba (*Carapa guianensis*), Babassu (*Orbignia sp.*), Cumaru (*Dipteryx odorata*), Palm tree (*Elaeis sp.*), Piqui (*Caryocar sp.*), and Soybean oil as well as the alcoholysis of Soybean oil with several alcohols (ethanol, propanol, *iso*-propanol, *n*-butanol, *terc*-butanol and *cyclo*-hexanol) was studied. Activities of the tin and lead pyrone complexes were observed in all the alcohol studies. For linear alcohols, the reaction activities decrease with increasing carbonic chain length. It was also shown that the catalytic activities are higher when vegetable oil with short chain fatty acids or with a high unsaturated degree and short and linear chain alcohols are used.
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1. Introduction

The increasing demand for energy and environmental awareness has prompted a lot of research to produce alternative fuels from renewable resources that are environmentally more acceptable [1]. Biodiesel is an interesting alternative because it shows a decrease in the emission of CO$_2$, SO$_X$ and unburned hydrocarbons during the combustion process when compared with fossil fuels [2].

Normally produced by a catalytic transesterification reaction of vegetal oils with short chain alcohols, having glycerin as a subprocuct, biodiesel is a mixture of fatty acid esters of low alkyl-chain alcohols. Its production is well studied and established, especially using acids or alkyl catalysts, like alkyl metal hydroxides or alkoxides and sulfuric acid [3–5]. However, these catalytic systems have some technological problems, being the acid system associated with corrosion and the basic one with emulsification. In fact, the soaps formed when using basic catalysis are known to emulsify

the biodiesel with glycerin, specially if ethanol is used. Besides, these catalytic systems are less active or completely inactive for ethanol and high molecular weight alcohols [6].

In order to minimize these problems, attempts to use heterogeneous catalyst systems in alcoholysis of triglycerides have been made [7–9]. These heterogeneous systems are active for high molecular weight alcohols, achieving conversions higher than 95% in systems where neither alkyl nor acid catalysts work [8], and produce neither corrosion nor emulsion, making it easier to separate the products obtained. Moreover, these catalysts present very low methanolysis and ethanolysis activities when compared with the traditional acid and basic ones.

On the other hand, homogeneous metal catalysts have not been studied in vegetable oil alcoholysis. We have recently communicated that metal compounds of the type M(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$, where M = Sn, Zn, Pb and Hg, are active for Soybean oil methanolysis under homogeneous conditions [10]. We have found that the catalytic activity decreases in the order Sn^{+2} ≫ Zn^{+2} > Pb^{+2} ≅ Hg^{+2}. It is worth mentioning that the complexes of

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Sn and Zn showed great activities for this reaction, achieving a reaction yield of up to 90 and 40%, respectively, in 3 h using molar ratio 400:100:1 (methanol:oil:catalyst), with no emulsion formations at the end. Note that this activities are much higher than those observed using the traditional NaOH and H_2SO_4 catalysts under the studied conditions.

The aim of this work was to investigate the catalyst behavior of the Sn, Pb and Zn complexes when different alkyl-chains are present in both triglyceride and alcohol. For this reason, a wide selection of triglyceride sources was used to obtain significative changes in fatty acid composition. The methanolysis of native oils of Brazilian's Savannah and Amazonian regions, such as Andiroba (*Carapa guianensis*), Babassu (*Orbignia sp.*), Cumaru (*Dipteryx odorata*), Palm tree (*Elaeis sp.*) and Piqui (*Caryocar sp.*), as well as Soybean oil were investigated. The alcoholysis of Soybean oil with several alcohols (ethanol, propanol, *iso*-propanol, *n*-butanol, *terc*-butanol and *cyclo*-hexanol) was also studied.

2. Experimental

2.1. General procedures

Reagent grade tin(II) chloride, lead(II) chloride, zinc(II) chloride, 3-hydroxy-2-methyl-4-pyrone, dimethylformamide (DMF), methanol (MeOH), ethanol (EtOH), *n*-propanol (*n*-PropOH), *iso*-propanol (*i*-PropOH), *n*-butanol (*n*-ButOH), *terc*-butanol (*t*-ButOH), *cyclo*-hexanol (*c*-HexOH) and H_2SO_4 of analytical grade were obtained from commercial sources and used without further purification. All vegetable oils were obtained from commercial sources and used as received.

2.2. Preparation of the catalysts

The catalysts Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**1**), Pb(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**2**) and Zn (3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**3**) were prepared according to the methods described in the literature [10,11].

2.3. Characterization of the vegetable oils

Vegetable oils (0.3 g) were methanolized using 6 ml of a 0.5N NaOH methanol solution. The reaction mixtures were kept in a 50 ml batch reactor under gentle reflux (approximately 60 °C) and magnetic stirring for 30 min. Then, methanol (10 ml) and concentrated H_2SO_4 (1 ml) were added and the reaction mixture was kept again under gentle reflux for 120 min. The product obtained was washed three times with brine and then analyzed by gas chromatography on a Varian 3400CX chromatograph with FID detector, equipped with a polar polyethyleneglycol column (DBWax, 30 m, 0.32 mm i.d. and film thickness of 0.25 μm). Oven temperature ranged from 150 to 220 °C, using a heating rate of 12 °C/min.

2.4. Catalytic experiments

All catalytic experiments were carried out using the same molar ratio 400:100:1 for alcohol, vegetable oil and catalyst, respectively. The vegetable oils (0.01 mol) were transesterified in the presence of alcohol (0.04 mol) using 0.1 mmol H_2SO_4, (**1**), (**2**) or (**3**) as catalysts. Before the reaction, the metal catalyst precursors were solubilized in 0.5 ml dimethylformamide (DMF). The reaction mixtures were kept in a 50 ml batch reactor under gentle reflux (approximately 60 °C) and magnetic stirring for 60 min. 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 polydimethylsiloxane column (CBPI PONA-M50-042, 30 m, 0.25 mm i.d. and film thickness of 0.2 μm), working between 80 and 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. Characterization of the vegetable oils

The fatty acid compositions determined for the different vegetable oils used in this work are shown in Table 1. As can be seen, except for Babassu oil, although the nature of the fatty acid present does not varies significantly among the vegetable oil sources, great variations in their proportions, and thus their unsaturation degree, are noted. It is important to point out that Babassu oil has the highest concentration of short chain fatty acids.

3.2. Influence of triglyceride alkyl chain in vegetable oil transesterification

The different vegetable oils were methanolyzed using the catalytic precursors (**1**), (**2**), (**3**) and H_2SO_4, in similar reaction conditions, and the main results are shown in Table 2. Note that, since Table 2 presents the reaction yield of all catalytic systems for the same period of time (1 h) using the same conditions, it is possible to compare their activities directly from this parameter. It is worth mentioning that these conditions are not optimized for highest reaction yield; however, they provide a way to compare the catalytic activities of the catalysts. It can be noted that, using the same vegetable oil, the catalytic systems formed by the tin complex, under those conditions, always presents higher conversion than the others, confirming previous results obtained for Soybean oil [10]. It also became clear from Table 2 that, independent of the catalyst, the reaction activities are strongly influenced by the nature of the vegetable oil. Comparing Palm tree and Soybean fatty acid compositions (see Table 1), it is clear that the sizes of the carbonic chains are similar but the oils have different saturation degrees. Since all catalytic systems

Table 1
Fatty acid composition of the vegetable oils

Vegetable oil	Fatty acid (wt.%)							
	C12:0	C14:0	C16:0	C16:1 ($n = 7$)	C18:0	C18:1 ($n = 9$)	C18:2	Others
Andiroba	–	–	27	1	7	49	16	–
Babassu	48	16	10	–	2	14	5	5
Cumaru	–	–	23	–	7	37	29	4
Palm tree	–	–	35	–	7	44	14	–
Piqui	–	–	40	–	2	47	4	7
Soybean	–	–	14	–	4	24	52	6

were more active when Soybean oil was the substrate (compare entries 1–4 with 17–20 of Table 2), it can be assumed that the methanolysis reaction is favored by the presence of unsaturations in the carbonic chain. This hypothesis is corroborated by the behavior of Piqui oil (entries 21–24 of Table 2), which shows a saturation degree slightly superior to those of Palm tree oil (see Table 1), and presented lower activity. On the other hand, when the results obtained for the Babassu oil (entries 9–12 of Table 2) and those obtained for Palm tree and Piqui oils, which are the three essentially saturated oils with differences in their alkyl-chain length, are compared it can be assumed that activity increases for shorter chains. It is important to highlight that, among all the substrates used, Babassu and Soybean oils presented the best activities, probably indicating that both saturation degree and alkyl-chain length are determinant factors in the catalytic activity.

The alcoholysis of Soybean oil using different alkyl-chain alcohols was carried out using the catalytic precursors (**1**), (**2**), (**3**) and H_2SO_4, in similar reaction conditions, and the main results obtained are shown in Table 3. The same considerations about the reaction conditions and the relationship between activity and reaction yield can be made. As can be depicted from Table 3, the catalytic activities are strongly dependent on the nature of the alcohol. It is worth mentioning that only the systems formed by Sn and Pb complexes were active for all reactions (see Table 3), independent of the alcohol used, and that the Sn systems present reaction

Table 2
Methanolysis of different vegetable oils catalyzed by (**1**), (**2**), (**3**) and H_2SO_4, using the same alcohol/vegetable oil/catalyst molar ration (400:100:1)

Entry	Vegetable oil	Catalyst	Yield (%)[a]	Fatty acid composition	
				Unsaturated (%)	Chain size $\leq$ 16C (%)
1[b]	Soybean	H_2SO_4	1.4	76	14
2[b]		(**1**)	37.1		
3[b]		(**2**)	4.2		
4[b]		(**3**)	15.5		
5	Andiroba	H_2SO_4	3.8	66	28
6		(**1**)	23.3		
7		(**2**)	5.2		
8		(**3**)	11.2		
9	Babassu	H_2SO_4	12.5	19	74
10		(**1**)	35.6		
11		(**2**)	17.0		
12		(**3**)	26.2		
13	Cumaru	H_2SO_4	0.6	66	23
14		(**1**)	10.3		
15		(**2**)	1.4		
16		(**3**)	7.2		
17	Palm tree	H_2SO_4	8.5	58	35
18		(**1**)	16.2		
19		(**2**)	5.4		
20		(**3**)	11.3		
21	Piqui	H_2SO_4	3.9	51	40
22		(**1**)	9.6		
23		(**2**)	4.6		
24		(**3**)	6.3		

[a] Percentage of the recovered methyl esters after 1 h of transesterification per initial mass of vegetable oil.
[b] Extracted from ref. [10].

Table 3
Alcoholysis of Soybean oil using different alcohols catalyzed by (**1**), (**2**), (**3**) and H_2SO_4, using the same alcohol/vegetable oil/catalyst molar ration (400:100:1)

Entry	Alcohol	Catalyst	Yield (%)[a]
1[b]	Methanol	H_2SO_4	1.4
2[b]		(**1**)	37.1
3[b]		(**2**)	4.2
4[b]		(**3**)	15.5
25	Ethanol	H_2SO_4	1.0
26		(**1**)	8.3
27		(**2**)	3.4
28		(**3**)	3.2
29	*n*-Propanol	H_2SO_4	–
30		(**1**)	4.2
31		(**2**)	3.8
32		(**3**)	4.4
33	*iso*-Propanol	H_2SO_4	–
34		(**1**)	0.2
35		(**2**)	0.3
36		(**3**)	0.2
37	*n*-Butanol	H_2SO_4	–
38		(**1**)	1.1
39		(**2**)	2.9
40		(**3**)	0.2
41	*terc*-Butanol	H_2SO_4	–
42		(**1**)	0.3
43		(**2**)	0.3
44		(**3**)	–
45	*cyclo*-Hexanol	H_2SO_4	–
46		(**1**)	4.3
47		(**2**)	3.0
48		(**3**)	2.3

[a] Percentage of the recovered short-chain alcohol esters after 1 h of transesterification per initial mass of vegetable oil.
[b] Extracted from ref. [10].

conversions higher than Pb ones. Note that, when the alcohol carbonic chain is linear, independent of the catalyst used, the reaction activities decrease with increasing carbonic chain length (for example, compare entries 2, 26, 30 and 38 of Table 3). Also note that the activity decreased drastically in all reaction systems when branched alcohols were used (for example, compare entries 39 and 43 of Table 3). These results strongly suggest that a steric effect is controlling the catalytic activity.

3.3. Mechanism aspects

Studies of urethane formation catalyzed by tin and iron complexes pointed to an alkoxide complex with a vacant site as the catalytic active specie [12,13]. Indeed, it was proposed that a bivalent iron complex of a bidentate oxygenated ligand reacts with alcohol to form an alkoxide complex, after the elimination of one molecule of the ligand [12]. We believe that similar active specie, probably formed as proposed in Scheme 1, could be responsible for the transesterification reaction. In a previous work [14], we have shown that the catalytic activity of tin(II) complexes of bidentate di-oxygenated ligand precursors in the polyesterification reaction depends on the nature of the ligand, which seems to corroborate the fact that, in the active specie, one bidentate ligand remains coordinated.

The mechanism for the transesterification reaction assisted by divalent metal complexes was largely studied for polyesterification and these complexes are believed to act in these reactions as Lewis acids [15]. As was proposed [16], the ester carbonyl coordinates at a vacant site in the catalytic active specie. This coordination increases the carbonyl's normal polarization thus enhancing the alcohol's nucleofilic attack, which probably occurs via a four-member ring transition state [15]. Since the order of activity obtained for divalent metal pyrone complexes for Soybean oil methanolysis ($Sn^{+2} \gg Zn^{+2} > Pb^{+2} \cong Hg^{+2}$) [10] is in very good agreement with the reported activities for many other complexes for polyesterification using different ligands [15], it is plausible to assume that a similar Lewis acid mechanism is taking place. In fact, we think that, for vegetable oil alcoholysis using pyrone divalent metal complexes, a similar mechanism may be proposed, as suggested in Scheme 2.
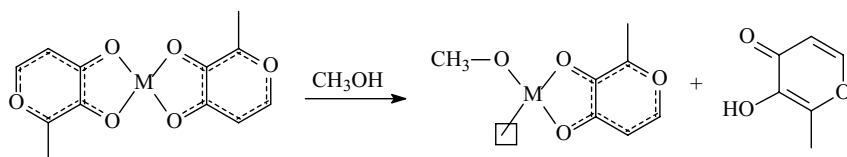
Scheme 1.
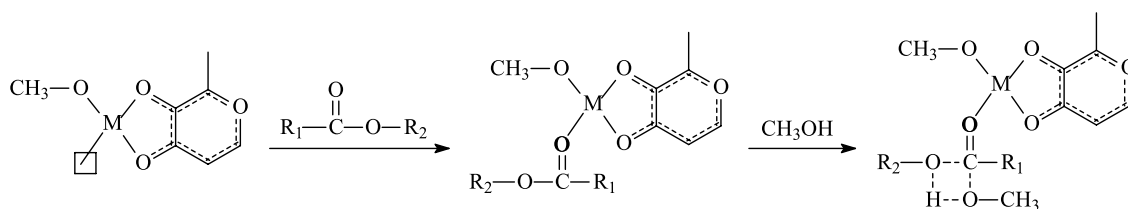
Scheme 2.

After breaking and making C–O and O–H bonds to produce free glycerin and biodiesel, the dissociation of the ester carbonyl completes the cycle.

4. Conclusions

In summary, we have shown that pyrone complexes of different metals are active for different vegetable oil transesterification reactions using different alcohols. Particularly, under the reaction conditions studied, the tin and lead complexes presented activities for all the alcohols used, even for branched ones, when the other catalyst failed. It was also shown that the catalytic activities are higher when vegetable oil with short chain fatty acids or with a high unsaturated degree and short and linear chain alcohols are used.

This study is interesting from both an academic point of view and a technological approach. As has already been pointed out, this is the first example of homogeneous metal complexes as catalyst precursors for vegetable oil alcoholysis. Also there are very few examples of active systems for high molecular weight alcohols. The comparative study of alcoholysis activity, using different catalysts, of several vegetable oil sources, with varying fatty acid compositions, is particularly important for Brazil, and possibly for other tropical countries as well, due to its diversity of native vegetable oil sources.

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