New Metal Catalysts for Soybean Oil Transesterification

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ABSTRACT: We report here the synthesis, characterization, and use of tin (3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$, lead (3-hydroxy-2-methyl-4-pyrone)$_2$ (H$_2$O)$_2$, mercury (3-hydroxy-2-methyl-4-pyrone)$_2$-(H$_2$O)$_2$, and zinc (3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ as catalysts in the transesterification reaction of soybean oil with methanol. All complexes are active in this reaction, with the following decreasing activities: $Sn^{2+} \gg Zn^{2+} > Pb^{2+} \approx Hg^{2+}$. The catalytic activities of these complexes were also compared with classical alkali and acid transesterification catalysis (with NaOH and H$_2$SO$_4$).

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KEY WORDS: Biodiesel, catalytic soybean transesterification, lead complex, maltol, mercury complex, tin complex, zinc complex.

Biodiesel, a renewable fuel, is normally produced by a catalytic transesterification reaction of vegetable oils with a short-chain alcohol. When compared with fossils fuels, biodiesel shows a decrease in the emission of CO$_2$, SO$_x$, NO$_x$, and unburned hydrocarbons during the combustion process (1). For these reasons, biodiesel is an elegant alternative solution to meet an increasing energy demand in an environmentally aware manner (2).

Transesterification reactions of different oils are reported in the literature (3) and some reviews are available (4,5). The use of methanol combined with soybean oil or rapeseed oil as a precursor for biodiesel production is commonly observed. These reactions are usually carried out using acids or alkalis such as sulfuric acid or sodium hydroxide as catalysts (6–8). Moreover, these catalytic systems are associated with corrosion and are not active for long-chain alcohols (9). Enzymatic catalysts such as lipase and immobilized lipase are also known as methanolysis promoters (10,11).

Some attempts have been made to use heterogeneous catalytic systems in the alcoholysis of TG. Indeed, hydroxides, carbonates, oxides, and alkoxides of several main metals of groups 1, 2, 12, 13, 14, and 15 have already been used as typical heterogeneous catalysts in transesterification reactions (12–14). In most of the reports, the reaction proceeded at a relatively slow rate compared to those conducted with alkali or acid catalysts. These slow reaction rates are due to diffusion problems since these heterogeneous media behave as a three-phase system (oil/methanol/catalysts). In spite of this, the use of heterogeneous catalysts is advantageous because of their easy separation from the product and because they are often still active for high-M.W. alcohols (12–14). Indeed, these catalysts achieve conversions higher than 95% in systems where neither alkali nor acid catalysts work (13).

On the other hand, homogeneous metal catalysts have not been studied extensively and few examples are reported. It has recently been shown that tin (3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**1**) is as active as the industrially useful bis(tri-*n*-butyltin)oxide complex for the polyesterification reaction of terephthalic acid, neopentyl glycol, and trimethylolpropane, with the advantages of being cheaper and easier to handle than the organotin compound (15,16).

We show in this work that complexes **1**, lead (3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**2**), mercury (3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**3**), and zinc (3-hydroxy-2-methyl-4-pyrone)$_2$-(H$_2$O)$_2$ (**4**) are viable catalysts for the transesterification reaction of soybean oil with methanol. In this report we also present a study on the performance of these catalysts as compared to those of the traditional ones (NaOH and H$_2$SO$_4$). Indeed, we have chosen fixed molar proportions of methanol/oil/catalyst (400:100:1) to compare the activities of the metal complexes with the usual H$_2$SO$_4$ and NaOH catalysts. We also report on the synthesis of **2**, **3**, and **4** and their characterization by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopies.

MATERIALS AND METHODS

General procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX300 300 MHz spectrometer. Chemical shifts were measured in ppm relative to tetramethylsilane as the external standard. FTIR spectra were obtained on a Bruker Equinox 55. The FTIR spectra correspond to the sum of 64 scans at a 4 cm^{-1} spectral resolution.

The catalytic reaction products were analyzed by GC on a Shimadzu GC-17A chromatograph equipped with an FID detector and a polydimethylsiloxane column (CBPI PONA-M50-042; Shimadzu, Kyoto, Japan) 30 m, 0.25 mm i.d., and film thickness of 0.2 μm, working between 80 and 180°C at a heating rate of 10°C/min, using ethyl acetate as internal standard.

Reagent grade tin(II) chloride, lead(II) chloride, zinc(II) chloride, mercury(II) chloride, 3-hydroxy-2-methyl-4-pyrone, and sodium hydroxide were obtained from commercial sources (Aldrich, Milwaukee, WI) and were used as received without

further purification. Refined soybean oil was obtained from commercial sources (Bunge, Gaspar, Santa Catarina, Brazil) and used as received. The DMSO, dimethylformamide (DMF), and methanol (MeOH) were of analytical grade, commercially obtained (Merck), and used as received.

Preparation of catalysts. (i) *Sn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$* (**1**). The Sn(C$_6$H$_5$O$_3$)$_2$(H$_2$O)$_2$ was prepared according to a method described in the literature (15) using reagents obtained from commercial sources.

^{1}H NMR (DMSO): 8.21 ppm (*s*, 1H, H-5); 6.69 ppm (*s*, 1H, H-6); 2.26 ppm (*s*, 3H, H-7). ^{13}C-{^{1}H} NMR (DMSO): 177.3 ppm (C-4); 155.1 ppm (C-3); 153.3 ppm (C-5); 151.0 ppm (C-6); 111.2 ppm (C-2); 14.7 ppm (C-7).

(ii) Pb(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (2). A water solution (20 mL) containing 3-hydroxy-2-methyl-4-pyrone (0.504 g, 4 mmol) and sodium hydroxide (0.159 g, 4 mmol) was slowly added under magnetic stirring to a water solution of lead(II) chloride (0.556 g, 2 mmol). The mixture was left stirring at 50°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 yellow pearls of Pb(C$_6$H$_5$O$_3$)$_2$(H$_2$O)$_2$ obtained (0.668 g, 1.35 mmol, 68%) were soluble in DMSO and DMF.

IR (KBr pellets): 1602 cm^{-1} (*s*, νC=O), 1570 cm^{-1} (*vs*, νC=C), 1505 cm^{-1} (*s*, ν$_{ring}$), 1451 cm^{-1} (*vs*, δ CH$_3$). Calculated for Pb(C$_6$H$_5$O$_3$)$_2$(H$_2$O)$_2$: C, 29.21%; H, 2.86%. Found: C, 29.05%; H, 2.93%. ^{1}H NMR (DMSO): 7.99 ppm (*d*, 1H, $^3J_{HH}$ = 5.0 Hz, H-5); 6.35 ppm (*d*, 1H, $^3J_{HH}$ = 5.0 Hz, H-6); 2.24 ppm (*s*, 3H, H-7).

(iii) Hg(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**3**). The complex was prepared using a procedure similar to that described for **2** using an aqueous solution of mercury(II) chloride (0.543 g, 2 mmol), 3-hydroxy-2-methyl-4-pyrone (0.504 g, 4 mmol), and sodium hydroxide (0.159 g, 4 mmol). The resulting pale-yellow Hg(C$_6$H$_5$O$_3$)$_2$(H$_2$O)$_2$ obtained (0.578 g, 1.18 mmol, 59%) was soluble in DMSO and DMF.

IR (KBr pellets): 1610 cm^{-1} (*s*, νC=O), 1570 cm^{-1} (*ms*, νC=C), 1508 cm^{-1} (*m*, ν$_{ring}$), 1455 cm^{-1} (*w*, δ CH$_3$). Calculated for Hg(C$_6$H$_5$O$_3$)$_2$(H$_2$O)$_2$: C, 29.61%; H, 2.90%. Found: C, 29.51%; H, 2.94%. ^{1}H NMR (DMSO): 8.06 ppm (*d*, 1H, H-5); 6.42 ppm (*d*, 1H, H-6); 2.35 ppm (*s*, 3H, H-7).

(iv) Zn(3-hydroxy-2-methyl-4-pyrone)$_2$(H$_2$O)$_2$ (**4**). The complex was prepared using a procedure similar to that described for **2** by using an aqueous solution of zinc(II) chloride (0.272 g, 2 mmol), 3-hydroxy-2-methyl-4-pyrone (0.504 g, 4 mmol) and sodium hydroxide (0.159 g, 4 mmol). The white Zn(C$_6$H$_5$O$_3$)$_2$(H$_2$O)$_2$ obtained (0.425 g, 1.21 mmol, 60%) was soluble in DMSO and DMF.

IR (KBr pellets): 1615 cm^{-1} (*vs*, νC=O), 1578 cm^{-1} (*vs*, νC=C), 1516 cm^{-1} (*vs*, ν$_{ring}$), 1459 cm^{-1} (*vs*, δ CH$_3$). Calculated for Zn(C$_6$H$_5$O$_3$)$_2$(H$_2$O)$_2$: C, 40.99%; H, 4.01%. Found: C, 40.96%; H, 4.02%. ^{1}H NMR (DMSO): 8.08 ppm (*d*, 1H, $^3J_{HH}$ = 3.0 Hz, H-5); 6.51 ppm (*d*, 1H, $^3J_{HH}$ = 3.0 Hz, H-6); 2.31 ppm (*s*, 3H, H-7). ^{13}C-{^{1}H} NMR (DMSO): 177.6 ppm (C-4); 153.6 ppm (C-3); 151.7 ppm (C-5); 146.8 ppm (C-6); 109.8 ppm (C-2); 14.7 ppm (C-7).

Catalytic experiments. Catalytic experiments were carried out using different catalysts at the same MeOH/oil/catalyst ratios (400:100:1). Soybean oil (8.724 g, 0.01 mol) was transesterified in methanol (1.282 g, 0.04 mol) using 0.1 mmol of NaOH, H$_2$SO$_4$, and **1**, **2**, **3**, or **4** as catalysts. Metal catalysts were previously dissolved in 0.5 mL DMF. The reaction mixtures were kept in a 50-mL batch reactor under gentle reflux (approximately 60°C) with magnetic stirring for a desired time. The product obtained was washed three times with distilled water, and the methyl esters were analyzed by GC using ethyl acetate (0.1 g) as the internal standard.

RESULTS AND DISCUSSION

Metal complex preparation. Reaction of a metal chloride with 3-hydroxy-2-methyl-4-pyrone (maltol) in the presence of sodium hydroxide and water at 50°C leads to the precipitation of a pyrone metal complex in high yields, as depicted in Figure 1.

The coordination of the pyrone ligand to the different metals in the metal complexes was investigated using FTIR spectroscopy. The most remarkable differences between the ligand spectrum and those of the complexes were the disappearance of the OH stretching mode at 3262 cm^{-1} and the shift of C=O stretching from 1656 cm^{-1} in the maltol to *ca.* 1610 cm^{-1} in the maltolato complexes. These results strongly suggest that complexation of the ligand occurs by the α-hydroxyquinone deprotonated fragment.

The pyrone ligand and its complexes were also characterized by ^{1}H and ^{13}C NMR spectroscopy. For complexes **2** and **3**, the ^{13}C NMR spectra presented a very poor resolution, probably due to their high relaxation times. Table 1 summarizes the chemical shifts for the nuclei of hydrogen. In all the complexes investigated, no ^{1}H NMR signal attributable to the maltol O-H fragment was observed, in accordance with the FTIR results. As can be seen, the chemical shifts of all hydrogens bonded to the carbons of the ring were deshielded compared to those of the pure pyrone ligand, suggesting an enhancement of the electron ring resonance.

Soybean oil transesterification. To study the catalytic performance of the metal complexes (**1**, **2**, **3**, and **4**) for soybean methanolysis, we also ran experiments using two traditional catalysts, NaOH and H$_2$SO$_4$, to compare their performance with the new catalytic systems. To make direct comparisons, the same molar ratio of 400:100:1 (methanol/oil/catalyst) was used for each catalyst in all experiments. These conditions did not represent the optimal conditions necessary to obtain the highest reaction yields; however, they did provide a way to compare catalytic activities among catalysts.

Some results of these reactions are summarized in Table 2. As Table 2 shows, complex **3** (entries 27 to 30) reached conversions of *ca.* 5% (after 10 h), and it had almost the same activity
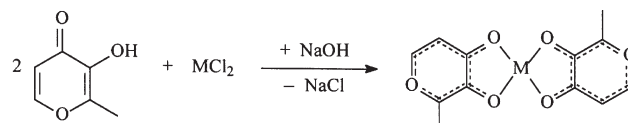

FIG. 1. Synthesis of pyrone metal complexes **1** (M = Sn), **2** (M = Pb), **3** (M = Hg), and **4** (M = Zn).

TABLE 1
^{1}H NMR Results for the Pyrone Ligand and Its Complexes

Hydrogen	Pure pyrone	Metal complexes			
		Sn	Pb	Hg	Zn
H5	7.97	8.21	7.99	8.06	8.08
H6	6.31	6.69	6.35	6.42	6.51
H7	2.22	2.26	2.24	2.35	2.31
H8	8.73	—	—	—	—

as that observed when using NaOH (entries 1–4) and H_2SO_4 (entries 5–8). A better catalytic activity was achieved using complex **2** (entries 19–22), which obtained conversions up to 20%.

The most active systems were obtained when using complex **4** (entries 23–26) and complex **1** (entries 9–18). Conversions of up to 30 and 90% for **4** and **1**, respectively, were reached after just 3 h. Between 3 and 6 h, these reaction systems achieved the maximum yield. After 6 h, a continuous decrease in reaction yields was observed, and after 10 h the conversions decreased to 5% for **4** and 20% for **1** (see Fig. 2). This behavior, illustrated in Figure 2, can be explained by the reversibility of this reaction. During the methanolysis of soybean oil, methyl esters and glycerin are produced, affording a two-phase system. For all metal catalyst systems, we observed that the glycerin layer was colored, suggesting that significant amounts of the metal complexes were driven to this phase. Based on the way the conversion yields are expressed, i.e., the percentage of mass of recovered ester per initial mass of soybean oil, a decrease in this value means a decrease in the ester concentration. Since the catalyst is driven to the polar phase, a
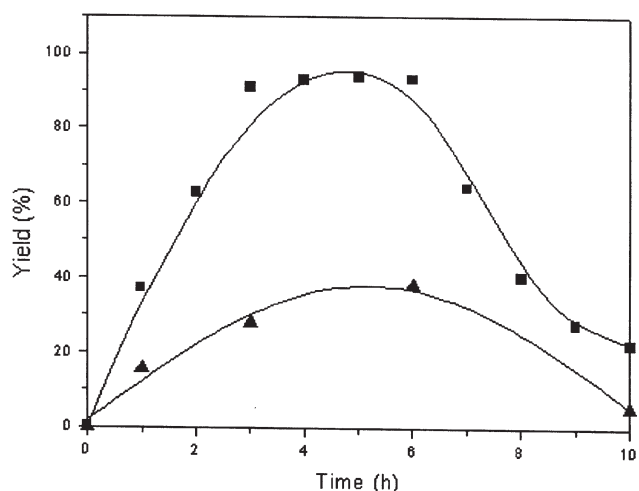

FIG. 2. Methyl ester production in soybean oil transesterification in the presence of complexes **1** (■) and **4** (▲). For structures of **1** and **4** see Figure 1.

large excess of glycerin in the vicinity of the catalyst promotes methyl ester consumption in a reverse reaction.

The activity order obtained ($Sn^{2+} >> Zn^{2+} > Pb^{2+} \cong Hg^{2+}$) was in accordance with that observed in polyesterification reactions for many other complexes with the same metals and different ligands. This observation suggests that the soybean methanolysis reaction possibly occurs *via* the same Lewis acid catalysis mechanism accepted for polyesterification (17). It is worth mentioning that the catalyst activities followed their metal acid strength as described in the literature (18). The stronger Lewis acidity of complex **1** explains its higher efficiency in the catalytic transesterification of soybean oil.

In summary, we have shown that pyrone complexes of different metals are active for soybean transesterification re-

TABLE 2
Main Results for Soybean Oil Methanolysis with Different Catalysts^a

Entry	Catalyst^b	Time (h)	Yield (%)^c	Entry	Catalyst^b	Time (h)	Yield (%)^c
1	NaOH	1	0.173	16	**1**	8	40.213
2	NaOH	3	5.135	17	**1**	9	27.451
3	NaOH	6	6.912	18	**1**	10	22.125
4	NaOH	10	9.904	19	**2**	1	4.195
5	H_2SO_4	1	1.364	20	**2**	3	15.177
6	H_2SO_4	3	2.201	21	**2**	6	19.183
7	H_2SO_4	6	4.700	22	**2**	10	24.054
8	H_2SO_4	10	6.992	23	**4**	1	15.541
9	**1**	1	37.139	24	**4**	3	28.038
10	**1**	2	62.840	25	**4**	6	37.926
11	**1**	3	91.116	26	**4**	10	5.181
12	**1**	4	92.935	27	**3**	1	1.347
13	**1**	5	93.872	28	**3**	3	2.157
14	**1**	6	93.180	29	**3**	6	3.142
15	**1**	7	64.153	30	**3**	10	4.149

^{a}Molar proportions of methanol/oil/catalyst (400:100:1) were fixed for all experiments.
^{b}**1**, tin (3-hydroxy-2-methyl-4-pyrone), $(H_2O)_2$; **2**, lead (3-hydroxy-2-methyl-4-pyrone)$_2$ $(H_2O)_2$; **3**, mercury (3-hydroxy-2-methyl-4-pyrone)$_2$ (H_2O); **4** zinc (3-hydroxy-2-methyl-4-pyrone)$_2$ $(H_2O)_2$.
^{c}Percent of mass of recovered ester per initial mass of soybean oil.

actions. In particular, the tin complex presents the strongest activity compared to the other complexes and to the traditional sodium hydroxide and sulfuric acid catalysts at the same conditions.

ACKNOWLEDGMENTS

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