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An unexpected behavior of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ heteropolyacid catalyst on the biphasic hydrolysis of vegetable oils

M. J. Da Silva* and M. G. Teixeira

Fatty acids (FA) are key ingredients in formulating numerous high-value chemicals. In general, catalytic routes for their production require drastic conditions of pressure and temperature or homogeneous catalysts and high water consumption. The novelty of this work is to discover a versatile catalyst for hydrolysis reactions able to migrate from the aqueous phase into the oil phase throughout the process and then back to the initial phase at the end of reaction: the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ heteropolyacid catalyst. We have found that variation in the pH value during the reaction promoted the conversion of $\text{PMo}_{12}\text{O}_{40}^{3-}$ heteropolyanion to a $\text{PMo}_{11}\text{O}_{39}^{7-}$ lacunar anion which was partially soluble in the oil layer, favouring the reaction. $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was compared with other heteropolyacids and also to sulfuric acid. The effects of the main reaction variables such as temperature, water : oil molar ratio, concentration and type of catalyst were assessed. ^1H NMR spectroscopy analysis allowed monitoring the reactions and provided fatty acid yields.

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1. Introduction

Fatty acids (FA) are the main ingredients used in the synthesis of numerous chemicals with high added value, such as pharmaceuticals, cosmetics, surfactants, lubricants, plasticizers, paints, food additives, agricultural and personal care products.^{1,2} The catalytic hydrolysis of triglycerides (TG) present in animal fats or vegetable oils has been important in converting these renewable raw materials to FA.^{3,4}

Traditionally, the non-catalytic hydrolysis of TG has been performed using a fat splitting process, where superheated water reacts with oil under drastic reaction conditions (*i.e.*, 373 to 533 K and 100 to 7000 kPa).⁵ Another industrial route utilized to produce FA is the Twitchell process carried out with stronger Bronsted acid at the boiling temperature of water.⁶ However, the main drawbacks are that homogenous catalysts are not reusable, the reaction time is great and is required a large amount of water.

Concurrent reactions at these conditions such as oxidation, degradation of FAs or interesterification of triglycerides, compromise the reaction selectivity.^{7,8} Enzymatic hydrolysis is more selective; however, it is a long-running operation, requiring 16 h to several days.⁹ Moreover, enzymatic catalysts are more expensive and unstable due to higher sensitivity reaction conditions such as pH variation, high temperature and type of solvent.^{9,10}

Heteropolyacids (HPAs) are versatile solid acid catalysts which have been used on the development of clean technologies in replacement to the mineral acids homogeneous catalysts.¹¹ HPAs are clusters belong to a special class of polyoxometalates, composed of several metals, non-metals and oxygen. Keggin HPAs such as silicotungstic ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$), phosphotungstic ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and phosphomolybdic ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) acids have been widely used as acid catalysts in various reactions to conversion processes of biomass to chemicals or fuels.^{12–15}

Acrocomia aculeata (*i.e.*, known as “macauba”) is a specie of native palm common in tropical and subtropical regions of the Americas.^{16,17} The macauba is considered one of the most conspicuous palm species abundant in the Brazil, it is easily adapted to the different ecosystems like degraded or intact areas.^{18–20} Macauba is nonedible crop, which cultivation is economically attractive due to its high oil yield (*i.e.*, 6.2 tons of oil per ha, 16 times greater than soybean).^{21–23} This accredits the macauba oil as the major raw material to manufacturing biodiesel.

In this work, we have evaluated the catalytic activity of HPAs on the hydrolysis reaction of macauba oil under mild conditions of reaction (*ca.* 413 K temperature, autogenic pressure). The effects of main reaction variables such as temperature, oil : water molar ratio, nature and type of catalyst were assessed. Insights on the reaction mechanism to explain the different behavior of acid catalysts were proposed. ^1H NMR spectroscopy was employed to determine the FA yields. The stability of HPAs throughout reaction was investigated.

Chemistry Department, Federal University of Viçosa, Avenida Peter Henry Rolfs, s/n, Viçosa, Minas Gerais, MG, Brazil, 36570-900. E-mail: silvamj2003@ufv.br; Fax: +55-31-3899-3065; Tel: +55-31-3899-3210



2. Experimental

2.1 Chemicals

All reagents and solvents were obtained from commercial sources and used without further purification. The crude macauba oil used in this work was provided by the company Agrotech Sementes Ltd. (Viçosa, Minas Gerais, Brazil). Sulfuric acid (98% wt) and methanol (99% wt) were Merck. Heteropolyacids $H_3PMO_{12}O_{40}$, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were purchased from Sigma-Aldrich (99.5% wt). Chloroform-*d* (99.8% wt) from Sigma Aldrich was used as a solvent for 1H NMR sample preparation.

2.2 Characterization of vegetal oil

To obtain the chemical composition of macauba oil it was transesterified with methanol and converted to methyl fatty acid esters (FAMES), which were analyzed in a gas chromatography with mass spectrometer detector (Shimadzu 2010 GC-MS equipment).

Typically, macauba oil (*ca.* 1.0 g) reacted with CH_3OH in presence of KOH catalyst (*ca.* 3% wt) for 2 h. At the end of the reaction, FAMES were extracted with hexane, resulting in an organic phase that was dried with Na_2SO_4 and analyzed by GC-MS technique.

$$AMW = \frac{\sum [(A_i) \times (MW_i)]}{\sum (A_i)} \quad (1)$$

where A_i = percentage of ester i ; MW_i = molar weight of ester i ($g \text{ mol}^{-1}$).

$$MW = [(3 \times AMW) - 4] \quad (2)$$

2.3 General procedure of HPA-catalyzed hydrolysis

Hydrolysis of vegetable oils was carried out adding an adequate acid catalyst (*i.e.*, H_2SO_4 , $H_3PW_{12}O_{40}$, $H_3PMO_{12}O_{40}$ or $H_4SiW_{12}O_{40}$) in powdered form (*ca.* 15–35 mol% of H^+) to a known quantity of vegetable oil (*ca.* 2.5 g) and water (molar ratio of oil : water = 1 : 30 to 1 : 50) in a sealed tube (*ca.* 35 mL).

The mixture of reaction was heated to temperature ranging from 413 to 453 K during a period of 8 h. At the end of the reaction, the sealed tube was cooled to 298 K. The reaction produced two layers; an upper oily layer, consisting of free fatty acids, mono-, di and triglycerides, and an aqueous layer, containing water and glycerol. These layers were separated by decantation. A small amount of the upper phase was collected and analyzed by 1H NMR spectroscopy.

2.4 1H NMR analysis of samples resulting of acid-catalyzed hydrolysis reactions of macauba oil

Ratnasamy *et al.* have developed a methodology based on NMR spectroscopy to quantify FA and presence of TG.²⁴ They have calculated the FA, the average molar weight (AMW) of methyl esters, and the molar weight (MW) of vegetal oil through eqn (1)–(3), respectively.

$$FA (\%) = \frac{4 \times \text{area of unmerged peak of } \alpha\text{-CH}_2 \text{ of FFA}}{\text{total area of } \alpha\text{-CH}_2 \text{ of both FA and ester}} \times 100 \quad (3)$$

To performing the measurements, an adequate amount of the sample collected at the end of the reaction (*ca.* 20–25 mg) was dissolved in $CDCl_3$ (*ca.* 0.6 mL) and the 1H NMR spectrum was recorded at 298 K on a Mercury-300 MHz Varian Spectrometer; 30 scans for each sample were taken during the analysis. An acquisition time of 3.9 s, relaxation delay of 1 s, flip angle of 30° , and sweep width of 4.139 kHz were employed in the spectral measurements.

3. Results and discussion

3.1 1H NMR spectroscopy analysis of TG and FA

Quantification of the FA and glycerides in the vegetable oil through 1H NMR spectroscopy is based on the fact that $\alpha\text{-CH}_2$ peaks of FA appear at higher values than those of glycerides. This difference on the chemical shift is due to the lower shielding effect of the carboxylic acid group compared to the ester group.²⁴

Due to this shift, the most unshielded peak of the triplet referring to the hydrogen atoms of $\alpha\text{-CH}_2$ of the FA (2.38 ppm) lies outside the $\alpha\text{-CH}_2$ region of the ester, whereas the other two peaks (2.34 and 2.30 ppm, respectively) that are merged with those two of the glycerides at 2.35 and 2.31 ppm, respectively (Fig. 1).

The 1H NMR spectrum of a sample containing FA and glyceride reveals that in the $\alpha\text{-CH}_2$ region there is a signal with quartet pattern, with the intensity of the peaks depending on the relative concentrations of FA and glyceride (Fig. 1). The unmerged triplet peak of FA, appearing around 2.38 ppm (*i.e.*, a triplet signal more outside than glycerides triplet signal); thus it can be used to determine the FA amount in the vegetable oil.

Therefore, it is necessary to multiply the area of glycerides triplet peak four times to having the total area corresponding to the triplet FA; this because the triplet peak appears with an intensity ratio of 1 : 2 : 1. The total area corresponding to $\alpha\text{-CH}_2$ of both FA and glyceride can be determined by integrating the spectral region from 2.27 to 2.40 ppm. The equation used for

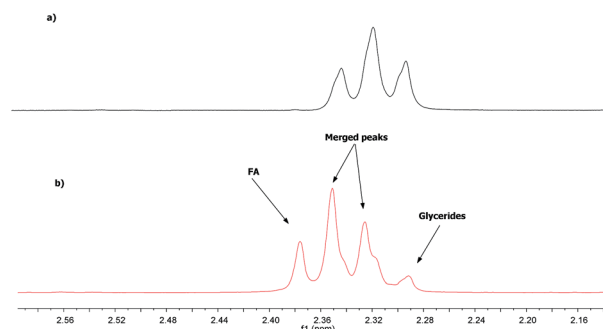


Fig. 1 1H NMR spectra in $\alpha\text{-CH}_2$ region: (a) macauba oil and (b) mixture of FA and macauba oil.



the calculation of the fatty acid content is described in Section 2.4.

3.2 FA profile of macauba oil

Fig. 2 shows the FA profile of macauba oil used in this work. Oleic acid predominates, followed by myristic, palmitic and lauric acids. These data are similar to the FA profiles of others macauba oils reported in the literature.¹⁶

Using the chemical composition of macauba oil and eqn (1) and (2) (Section 2.2), it was possible calculate the average molar weight (AMW) of methyl esters (*ca.* 262 g mol⁻¹) and molar weight (MW) of macauba oil (*ca.* 780 g mol⁻¹).

Hydrolysis of triglycerides is a reversible reaction that occurs in consecutive three-steps. In the first step, the triglyceride (TG) is converted into diglyceride (DG), which is then converted to a monoglyceride (MG). Thus, the stoichiometry between oil and water to convert one mole of triglyceride to 3 mol of FA and one of glycerol is 1 : 3 (Scheme 1).

3.3 Conventional mechanism for acid-catalyzed hydrolysis of triglycerides

Before considering yields of acid-catalyzed triglycerides hydrolysis reactions, seems profitable discuss the role of catalyst on these reactions. It is known that esters are slowly hydrolyzed because the water is a poor nucleophile. Moreover, esters are very basic leaving groups. Thus, the role of acid catalyst is protonating the oxygen atom of ester carbonyl group to promote this step. In the Scheme 2, we have described a mechanism involving steps commonly reported in literature.²⁵ To simplify, only the formation of the first molecule of FA and the diglyceride are depict. We hope that this mechanism may be useful to rationalizing the results of reaction on the next sections.

The first step (I) of the mechanism for acid-catalyzed ester hydrolysis is protonation of the carbonyl oxygen by the proton provided by the catalyst acid. In the step II of the mechanism, the nucleophile (H₂O) attacks the protonated carbonyl group, which is more susceptible to this attack than non-protonated carbonyl groups. It can be explained because the positively charged oxygen atom is more electron withdrawing than a neutral oxygen atom.

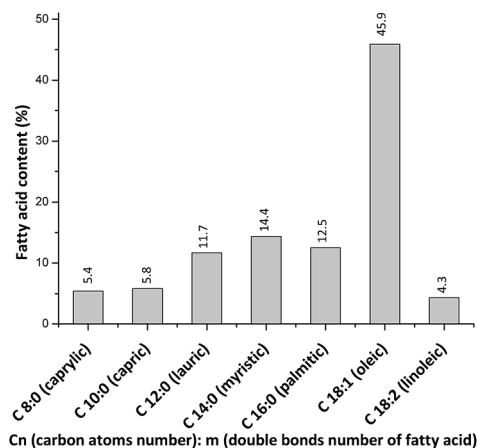
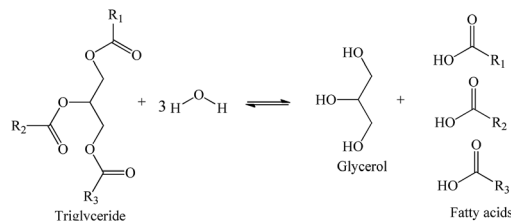


Fig. 2 Fatty acids profile of macauba oil.



Scheme 1 Hydrolysis reaction of TG present in the vegetable oils.

The resulting protonated tetrahedral intermediate is in equilibrium with its non-protonated form (step III). In the step IV, the oxygen atom of ester group of TG is then protonated. The equilibriums showed in the steps III and IV describes an intermolecular rearrangement of proton (*i.e.*, prototropism). On the last step, the tetrahedral intermediate collapses regenerating the H⁺ cation and resulting in the formation of the FA and diglyceride molecules.

Afterwards, the hydrolysis reaction proceeds through the same pathway; the diglyceride react with water resulting in the formation of FA and monoglyceride and, finally, this last one react with another water molecule generating the glycerol and FA molecules.

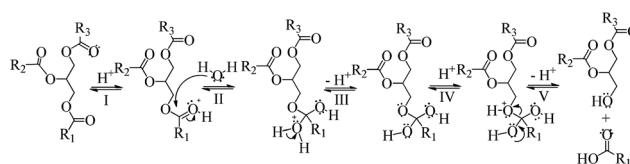
3.4 Assessing the acidity strength of catalysts

In almost of cases, the activity of acid catalysts is straight linked to acidic strength. Keggin heteropolyacids possess strong Brønsted acidity, higher than other solid acids such as zeolites, alumina or liquid mineral acids such as sulfuric acid.^{26,27} We have measured the acidity strength of catalysts in CH₃CN through potentiometric titration with *n*-butylamine (Fig. 3).

The initial electrode potential (E_i) allows to distinguish the acidity strength of protons as follow; $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ (weak sites) and $E_i < -100$ mV (very weak sites).²⁸ So, the values of (E_i) in Fig. 4 demonstrate that all the catalysts have very strong acidity. The measurement of the acid strength of catalysts in acetonitrile through titration with *n*-butylamine provided the following tendency: H₃PW₁₂O₄₀ > H₃PMO₁₂O₄₀ > H₄SiW₁₂O₄₀ > H₂SO₄ (Fig. 3). This result is in agreement with literature.^{26,29}

3.5 Effect of catalyst nature on the acid-catalyzed hydrolysis of macauba oil

The hydrolysis reactions of macauba oil were carried with or without catalyst with oil : water molar ratio of 1 : 35, heating the reactor to 423 K temperature during 8 h of reaction. All the



Scheme 2 Mechanism proposed for the Brønsted acid-catalyzed ester hydrolysis (adapted from ref. 25).



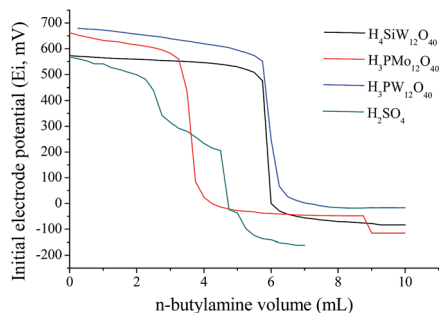


Fig. 3 Potentiometric titration with *n*-butylamine of the HPAs and H_2SO_4 catalysts in CH_3CN .

catalysts were used at *ca.* 25 mol% of H^+ cations concentration. To calculating the FA yields, we performed ^1H NMR spectroscopy analyses of samples collected at the end of reaction (Fig. 4).

An excess of water could have shifted the reaction equilibrium toward products, however, this did not occurred because the catalyst-free reactions achieved only a poor FA yield (*ca.* 1.8%). When we analyzed the FA yields displayed in the Fig. 4, we realize that among catalysts assessed, the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ have a remarkable activity, achieving highest FA yield (*ca.* 39.4%), while the others acidic catalysts had a behavior comparable reaching low FA yield; *ca.* 6.7% ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) and 10.8%, ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$).

Based on the acidity strength of catalysts, we may hope that the activity of the catalysts on the hydrolysis reactions should follow a similar trend to that displayed in the Fig. 3 (*i.e.*, $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_2\text{SO}_4$). Nevertheless, since E_i values were not very different, it was expected only a little difference on the reaction yields.

Possibly, it could be true if the reactions happen in the oil phase. However, the hydrolysis occurs in a biphasic system (*i.e.* water/oil).

Therefore, there is another key aspect; the presence of the water results in a leveling effect on the acidic strength of catalysts. Indeed, in aqueous solutions all the protons of the HPAs catalysts and too the first one of sulfuric acid are completely dissociated and they should provide an equal H^+ cations concentration.³⁰ So, it is not guarantee that the catalysts performance will be too equal in a biphasic system.

As show in the Fig. 4, in the absence of acid the reaction virtually no occurs. On the other hand, the presence of catalyst the FA yield was greater, mainly for $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed reaction. The highest catalytic activity of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ can be reasonably explained by visual observation done during the experiments. We found out that in the aqueous phase of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis reaction of macauba oil, there was a noticeable change of coloration. The initial color of the solution changed of intense yellow at reaction beginning to a blue-green tonality. Moreover, the oil phase also assumed a dark green coloration. It is noteworthy that this apparent solubility of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ on the oil phase only occurred at temperatures higher than 100 degrees.

The mechanism proposed in the Scheme 2, show that the role of catalyst consists in protonating the carbonyl group of TG,

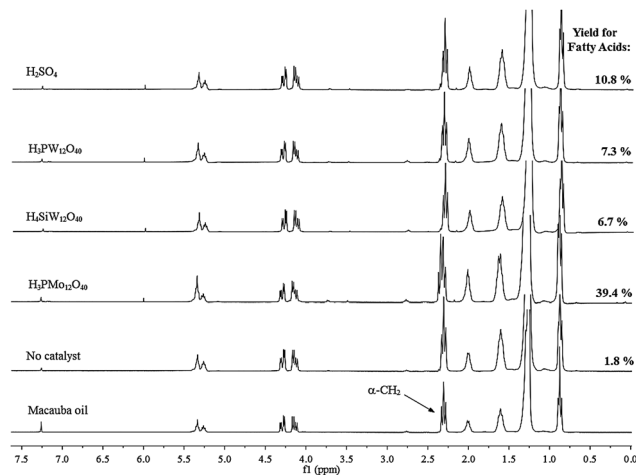


Fig. 4 ^1H NMR spectra (300 MHz, in CDCl_3) of non-polar phase containing FA and unreacted macauba oil, and identification of signals used to calculating FA yield.^a Reaction conditions: macauba oil (*ca.* 1.27 g), oil : water molar ratio (*ca.* 1 : 35), catalyst concentration (*ca.* 25 mol% of H^+ cations), temperature (*ca.* 423 K), reaction time (*ca.* 8 hour).

which is present on the non-polar layer. Therefore, seems reasonable to accept that the main steps of reaction should occur on the interface region between water and oil. Certainly, if the concentration of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ or others acid species containing molybdenum is high throughout reaction on non-polar layer, as denoted by green coloration of oil phase, the hydrolysis reaction should be favored. So, the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis achieved the highest FA yield.

Although it may be inconvenient that the catalyst is soluble in the phase oil which contains the FA produced, we easily recovered the molybdenum HPA catalyst from oil phase when we cooled the system to room temperature. Immediately, it is precipitate in the bottom side of flask, or, if the aqueous layer is present, it migrates to the solution. This easy recovery of catalyst makes this biphasic reaction an environmentally friendly process.³¹

The high activity of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in the reactions performed in biphasic systems was previously reported by us, when we have investigated reactions of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed oxidative desulfurization in a biphasic system CH_3CN /isooctane.³² On that system, we carried out the oxidation of thiophene to sulfone with hydrogen peroxide and verified that though in the absence of phase transfer catalyst, the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and its salt $\text{AlPMo}_{12}\text{O}_{40}$ were much more active than tungsten heteropolyacids.

3.6 Assessing the stability of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst throughout the hydrolysis of macauba oil

It was known that many HPAs degrade to a mixture of polyoxometalates anions in aqueous solution when the pH value is increased. It was demonstrated that the hydrolytic stability of HPAs depends on the structure and composition of the anion, and of the pH values of the solution.^{33,34} To investigate if the acidity variation might is affecting the behavior of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$



during the reaction of hydrolysis, we measured the pH values of aqueous layer of reaction and their components before, during and after of the hydrolysis (Table 1).

We have found that heating the aqueous solution of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ to 423 K resulted in the formation of white solid. The FT-IR spectrum of this solid displayed characteristic stretching band of ion phosphate (*ca.* 900 cm^{-1}) and molybdate (*ca.* 600 and 1000 cm^{-1}) anions suggesting that part or all the heteropolyanion was decomposed (Fig. 5a).³⁵

Indeed, a comparison of finger print region of Keggin anion FT-IR spectrum (Fig. 5b) confirm that the main bands are absent (Fig. 5a).

It is noteworthy that the thermal stability of the Keggin heteropolyacids is very higher when they are solid than in the solution. The literature have demonstrated that the Keggin heteropolyanions begin to be decomposed at 673 K.^{27,29}

The pH values of aqueous solutions of others HPAs catalysts were measured and revealed that no significance change was observed. Indeed, the literature describe that even that pH values had changed, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ are stable until values of pH equal to 5.³⁶

Conversely, the change of coloration was an indicative that the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was being decomposed throughout the macauba oil hydrolysis reaction. This phenomenon may have been triggered by high reaction temperature of reaction, as demonstrated by comparison of entries 1 and 2, Table 2. Nonetheless, the variation on the pH values could also initiate the hydrolysis and the consequent decomposition of heteropolyanion.³⁷

Holclajtner-Antunovi *et al.* studied the stability of silico-tungstic and phosphomolybdic acids in water at different pH values.³⁶ They concluded that different of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, that was stable between pH values of 1 to 7, the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ underwent decomposition at pH values higher than 1.0. Those authors visually followed the change of the color of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ solutions, *i.e.*, from the intense yellow through green to light blue at $\text{pH} > 5.0$. They have attributed the change of color to the hydrolytic decomposition of molybdenum. FT-IR, UV-Vis and ³¹P NMR spectroscopy analyses allowed identify all the species formed at different pH values.³⁶

Thus, we suppose that the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst was being converted into lacunar specie throughout the reaction, because the pH value measured was 1.1 after the end of reaction (Table 2).

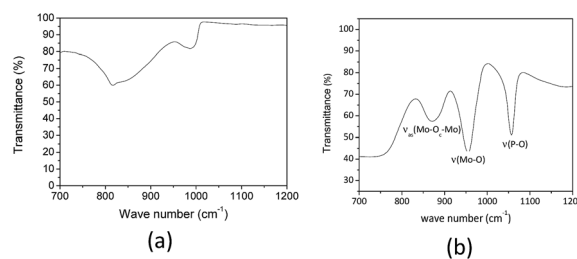


Fig. 5 FT-IR of white solid obtained after heating the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ aqueous solution to 423 K by 8 h and FT-IR of solid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$.

The high hydrolytic trend of $\text{PMo}_{12}\text{O}_{40}^{3-}$ compared to the others Keggin anion may be attributed the magnitude of charge on terminal oxygen atoms, which is higher when tungsten is the metal atom, and the lower binding energy between terminal oxygen atoms and molybdenum atom.³⁸

To verify if the Keggin anion of the HPAs are present in the oil phase, we carried out FT-IR spectroscopy analyses of samples collected at the end of the reactions, aiming identify the characteristics stretching bands of anions. The spectra are displayed in Fig. 6.

In general, the FT-IR spectra of type-Keggin HPAs have noticeable absorption bands at region of wavenumber between 700 and 1200 cm^{-1} . For instance, the more stronger stretching bands of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ are as follow: $\nu_{\text{as}}(\text{P-O}) = 1055 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{Mo=O}) = 955 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{Mo-O-Mo}) = 890 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{Mo-O-Mo}) = 760 \text{ cm}^{-1}$ (Fig. 5b).^{36,37}

The Fig. 6 shows that finger print region of HPAs infrared spectra did not provided any information about the presence of Keggin anion. The FT-IR spectra of the mixture containing macauba oil after reaction with all the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ or $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ displayed only one band at region of wavenumber 1750 cm^{-1} , corresponding to asymmetric stretching of carbonyl group belonging to TG. Obviously, this band also was present in the pure oil layer.

On the other hand, the spectrum of the sample collected from $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis reaction of macauba oil has two bands at this region; the same band present in the others spectra (*i.e.*, $\nu_{\text{as}}(\text{C=O}) = 1750 \text{ cm}^{-1}$) and a strong and well defined band around 1720 cm^{-1} due to asymmetric stretching of double bond of the carbonyl group of FA.

Table 1 Values of pH for components of the reaction of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis of the macauba oil^a

Entry	Composition of the system	pH values of aqueous phase ^b	Visual aspect of aqueous solution
1	$\text{H}_3\text{PMo}_{12}\text{O}_{40}(\text{aq})$	0.56	Intense yellow
2	$\text{H}_3\text{PMo}_{12}\text{O}_{40}(\text{aq})$ after heating to 423 K/30 min	0.57	Light green and formation of white solid
3	Macauba oil + $\text{H}_3\text{PMo}_{12}\text{O}_{40}(\text{aq})$ before reaction	0.56	Intense yellow
4	Macauba oil + $\text{H}_3\text{PMo}_{12}\text{O}_{40}(\text{aq})$ after the reaction/30 min	0.74	Dark green
5	Macauba oil + $\text{H}_3\text{PMo}_{12}\text{O}_{40}(\text{aq})$ after the reaction/8 h	1.1	Dark green
6	Macauba oil + $\text{H}_3\text{PW}_{12}\text{O}_{40}(\text{aq})$ before/and after the 8 h reaction	0.8/0.7	Colorless
7	Macauba oil + $\text{H}_4\text{SiW}_{12}\text{O}_{40}(\text{aq})$ before/and after the 8 h reaction	0.8/0.9	Colorless

^a Reaction conditions: macauba oil (*ca.* 1.27 g), oil : water molar ratio (*ca.* 1 : 35), catalyst concentration (*ca.* 25 mol% of H^+ cations), temperature (*ca.* 423 K). ^b The measurements of pH values were done at room temperature.



Table 2 Effect of reaction temperature on the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis of macauba oil^a

Entry	Temperature (K)	Yield for fatty acids ^b (%)	
		4 h	8 h
1	413	11.0	35.2
2	423	12.0	39.4
3	433	39.0	54.2
4	443	49.0	68.2
5	453	43.0	63.5

^a Reaction conditions: macauba oil (ca. 1.27 g), oil : water molar ratio (ca. 1 : 35), catalyst concentration (ca. 25 mol% of H^+ cations).

^b Determined by ^1H NMR spectroscopy analysis.

The macauba oil infrared spectrum display stronger absorption band at region of 1500 to 1000 cm^{-1} wave number, and another at 1750 cm^{-1} , which might has overlapped the possible absorption bands of HPAs. Nonetheless, a thorough analysis of spectra reveals the absence of the bands at region around of 955 and 890 cm^{-1} , which are typical stretching bands of Keggin anion. Therefore, their absence suggests that there are no Keggin anions in the oil phase after the reaction end. It was confirmed by change on the coloration of oil at the end of reaction, which return from green (*i.e.*, during the reaction) to the initial color typical of oil (*i.e.*, yellow). This change of color may be an indicative that molybdenum is being partially reduced.^{36–39}

We believe that the formation of lacunar Keggin anion, which has a higher charge than anion Keggin present at the reaction beginning (*i.e.*, conversion of $\text{PMo}_{12}\text{O}_{40}^{3-}$ to lacunar anion $\text{PMo}_{11}\text{O}_{39}^{7-}$) (Fig. 7), could explain the partial solubility of molybdenum catalyst in the oil layer, evidenced by the change of color of oil phase during reaction (*i.e.*, yellow to green, Table 1).

So, these molybdenum heteropolyanion species with high negative charge may be more soluble in the interface oil/water, favoring the reaction of hydrolysis. Several reports have described that an increasing on the charge of Keggin anion may contribute to higher stabilization of positively charged

intermediates due to increase on softness of anionic species.^{26,30,41} As depicted in the mechanism proposed in Scheme 2, in the course of the hydrolysis reaction there is the formation of various protonated intermediates, which could then react be stabilized by Keggin lacunar anion.

3.7 Effects of temperature on the acid-catalyzed hydrolysis of macauba oil

The hydrolysis of vegetable oils has been mainly difficult by the low solubility of oils in water. Thus, an alternative to minimize this limitation is to conduct such reaction at elevated temperatures. Nonetheless, it is always important that the catalyst should be stable and active at these temperatures. An increasing on reaction temperature might improve the water solubility in the oil layer and also favor the kinetics of the process. To assess this effect, we have performed the reactions with temperatures ranging of 413 to 443 K (Table 2).

The FA yield improved with an increasing on the reaction temperature from 413 to 443 K . Notwithstanding, for temperatures higher than 443 K , no enhancement was observed. Contrariwise, there was a decrease on the FA yield on hydrolysis reactions carried out at 453 K temperature (entry 5, Table 2). This decreasing may be attributed the reverse esterification reaction of FA with glycerol could be too more significant at this temperature.

In general, in almost of TG hydrolysis reactions the FAs are the major goal and solid acids have been widely used. For instance, Satyarathi *et al.* assessed the hydrolysis of edible and nonedible vegetable oils over solid Fe–Zn double-metal cyanide complexes catalysts, and the yield of FAs were 9% wt, at temperature of 433 K and soybean oil : water molar ratio equal to 1 : 30.⁴² Those authors achieved high FA yield (ca. 60–90%) only when worked at temperatures 463 K .

In homogeneous phase, Meneghetti *et al.* have assessed the activity of tin(IV)-based compounds on hydrolysis of different vegetal oils.⁴³ They found out that by using of reactions conditions conversions of ca. 97% to FA were obtained at 453 K , 4 h at oil : water : Sn(IV) catalyst a molar ratio of 1 : 24 : 0.01 and, using soybean oil.

3.8 Effects of water : oil molar ratio on the acid-catalyzed hydrolysis of macauba oil

Another essential parameter for the hydrolysis of oils is the stoichiometric proportion between reactants (*i.e.*, oil and

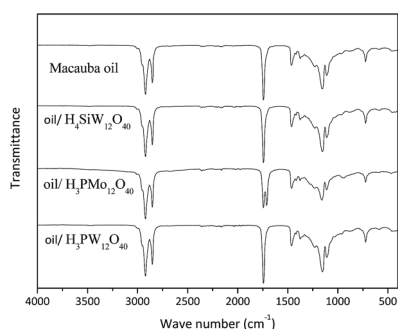


Fig. 6 FT-IR spectra of non-polar phase containing unreacted macauba oil and/or FA after reaction.^{a,b} ^aReaction conditions: macauba oil (ca. 1.27 g), oil : water molar ratio (ca. 1 : 35), catalyst concentration (ca. 25 mol% of H^+ cations), temperature (ca. 423 K), reaction time (ca. 8 hour). ^bThe sample of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed reaction was collected after decantation of oil phase.

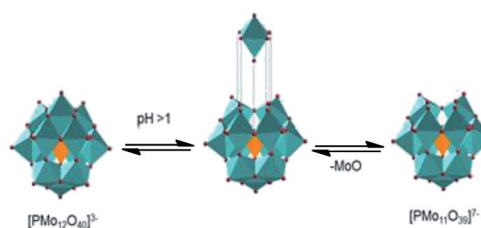


Fig. 7 Hydrolytic decomposition of Keggin anion of $\text{PMo}_{12}\text{O}_{40}^{3-}$ to lacunar anion $\text{PMo}_{11}\text{O}_{39}^{7-}$ (adapted from ref. 40).



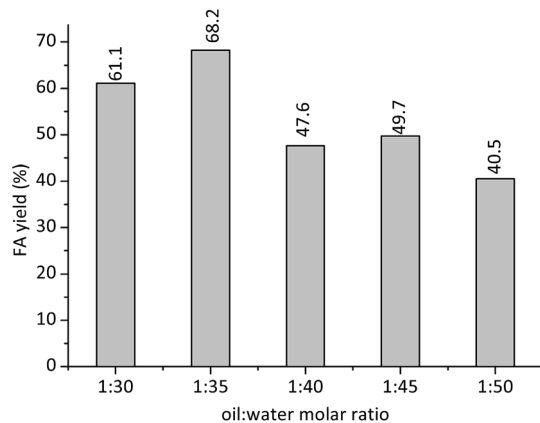


Fig. 8 Effect of reactants stoichiometry on the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis of the macauba oil.^a Reaction conditions: macauba oil (ca. 1.27 g), catalyst concentration (ca. 25 mol% of H^+ cations), temperature (ca. 423 K), reaction time (8 h).

water). Probably, the main reaction steps might occur in the interface between the water and oil. The greatest problem is that an increasing on water amount may be insufficient to shift the reaction equilibrium toward products. Therefore, the FA yield may be not proportional to the increasing on the water : oil molar ratio. The Fig. 8 presents the FA yields obtained in the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed reaction of macauba oil at different oil : water stoichiometric proportions.

For proportions of water : oil higher than 1 : 35, the water excess may have reduced the efficiency of H^+ cations in the protonation steps of TG. Consequently, the FA yields were lower at these reaction conditions.

Reactions of hydrolysis carried out over solid Fe–Zn complexes catalysts (10 mol%) achieved a FA yield of 67% wt, with soybean oil : water molar ratio equal to 1 : 20. However, those authors carried out the reaction to 463 K.⁴²

3.9 Effects of catalyst concentration on the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis of macauba oil

Although reactions yield that reach equilibrium are not affected by the variation on the catalyst concentration, it always important know what the lowest catalyst concentration provide the highest conversion at the shortest reaction time.

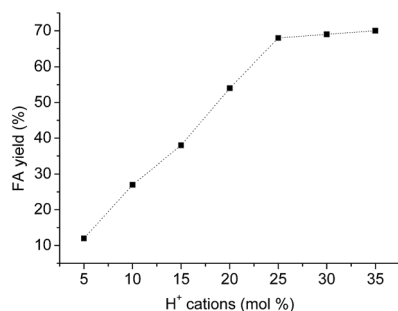


Fig. 9 Effect of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ concentration on the acid-catalyzed hydrolysis of macauba oil.^a Reaction conditions: macauba oil (ca. 1.27 g), temperature (ca. 423 K), time (8 h).

The highest FA yield was reached at the 8 h of reaction when the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst was used at H^+ cation concentration equal or higher than to 25 mol%. So, no increasing on FA yield was achieved when the reaction was carried with higher catalysts loads within this period (Fig. 9).

Satyarthi performed the hydrolysis of soybean oil (1 : 20 molar ratio) in presence of sulfuric acid 100 mol%, and found that 92% of FA yields after 8 h of reaction to 463 K temperature.⁴² It is an evidence that superior performance of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst over mineral acids.

4. Conclusions

Hydrolysis of macauba oil has been investigated over different heteropolyacid catalysts, in addition to the sulfuric acid. $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -catalyzed hydrolysis reactions exhibited the highest fatty acid yield. The largest novelty of this work is that we have finding that $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ heteropolyacid is a versatile catalyst able to migrating from the aqueous phase to the oil phase throughout the hydrolysis and then back to the initial phase at the end of reaction. Measurements of pH performed during the reaction showed that the pH achieve values able to hydrolyze the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, converting it to a lacunar specie (*i.e.* $\text{PMo}_{11}\text{O}_{39}^{7-}$). This specie is this way more soluble that $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ itself, a fact seen by changes of coloration of oil phase. So, the interaction between protonate TG intermediate formed during the reaction and lacunar anion favor the FA yield. The same was not found to the other HPAs, which are more stable at reaction conditions studied.

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