

Greener Epoxidation Reaction of Macaw Palm Oil Using Metal Oxides and Niobium Phosphate as Catalysts

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The present work focused on the screening process of different inorganic oxides and different temperatures for the epoxidation reaction of macaw palm vegetable oil without using solvent, a promising Brazilian biomass that can substitute other vegetable oils (e.g., soybean oil) in technological applications. This oil has an iodine value of 108.48 g of I₂ per 100 g being categorized as a semi-dry oil. The epoxidized vegetable oil can be applied in manifold areas in polymer science. The epoxidation reaction here presented avoided organic solvents and organic acids and aimed to produce a greener route using metal oxides or niobium phosphate as a peroxide-activating catalyst. The experimental parameters were maintained as 10 mol% of catalyst loading and a time of 24 h; however, the temperature for some catalysts was changed to improve the epoxide conversion. Experiments were measured by proton nuclear magnetic resonance (¹H NMR). Experiments using titanium oxide (TiO₂) as a catalyst reached a conversion greater than 84.7%, while experiments using aluminium oxide (Al₂O₃) or lanthanum oxide (La₂O₃) achieved conversions of 22.6 and 30.1%, respectively. Furthermore, it was observed that both niobium compounds instantly react with hydrogen peroxide to form peroxy derivatives.

Keywords: green chemistry, metal oxide, epoxidation, *Acrocomia aculeata*, renewable monomer

Introduction

Epoxidized vegetable oils are widely used as monomers which can be applied in different systems such as 3D printers, biomaterials, coatings (paints and waterproof vanishers), adhesives/glues, lubricants and plasticizers.¹⁻⁹ The thermal and mechanical properties of the final polymer can be improved with greater cross-linking and reduced time to achieve the gel point, which is related to the epoxy content.¹⁰⁻¹²

To be applied as a potential monomer, the vegetable oil (triacylglyceride) should be categorized as a semi-dry or dry oil. This property is determined by its iodine value (IV), which is a parameter used to quantify the unsaturation degree per 100 g of sample. Samples with IV between 90 and 130 are semi-dry oils (e.g., soybean oil,

grapeseed oil and sunflower oil) and samples with IV higher than 130 are dry oils (e.g., linseed oil, tung oil and safflower oil).¹³ In this regard, the macaw palm oil (MPO) was selected for epoxidation, being a promising renewable compound from Brazilian biomass. The MPO is categorized as a semi-dry oil constituted by oleic chain (32.9%), linoleic chain (46.6%) and saturated fatty chains (20.5%) and is extracted from the fruit of a palm tree (*Acrocomia aculeata*).¹⁴ The macaw palm tree has a high production of vegetable oil per hectare of the crop, which reaches a value of 4,000 L of oil; this value is far superior to soybean which produces only 500 L per hectare.¹⁵ Our research group has already reported¹⁶⁻¹⁹ the use of epoxidized macaw palm oil for polyacrylate, polyesters and poly-hidroxyurethanes synthesis, which shows its potential for application in the polymer field.

The most common epoxidation process is via the Prilezhaev reaction, where the organic peracid is formed

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in situ using hydrogen peroxide, the most commonly used organic acid is formic or acetic acid in the presence of a catalyst (inorganic acids, amberlite™ IR-120, enzymes and so on).²⁰ Thereafter, the peracid attacks the alkene by electrophilic oxidation, forming the epoxide ring, thus regenerating the organic acid. Although this reaction is effective, some concerns about the process residue have been shown in the literature, and its purification process demands plenty of water. The neutralization process removes the organic acid as sodium acetate/formate, though the sodium salt is not a toxic residue it should be reduced. Sodium hydroxide or sodium carbonate are usually used in the neutralization process, both should be used with care to avoid the ester hydrolysis and soap formation.

In this sense, a greener process can be executed in the absence of organic acids but using inorganic compounds as peroxide-activating catalysts. For instance, manganese complexes with *N,N'*-bis(2-picolyl)-2,2'-bispyrrolidine or salen ligands presented a promising use in epoxidation reactions and after filtration, it can be used multiple times; however, for both catalysts, organics solvents were used to assist the reaction.^{21,22} La Garza *et al.*,²³ in 2017, reported an amphiphilic dipyrindinium-phosphotungstate catalyst for epoxidation of methyl oleate, the reaction just took 4 h using water as solvent. Although these peroxide-activating catalysts are promising, the main idea is to use catalysts that do not take much time to be synthesized or generate waste in their synthesis process. Looking for a solution, metal oxides can be used in this purpose. They are relatively inexpensive; some are by-products of industrial processes and are used in neat form. Oxides of titanium (TiO₂), niobium (Nb₂O₅), molybdenum (MoO₂), copper (CuO), and aluminium (Al₂O₃) have been reported as peroxide-activating catalysts for epoxidation of vegetable oils and fatty acid methyl/ethyl esters in an organic solvent medium.²⁴

Therefore, the present work aims for an evaluation of the epoxidation of macaw palm oils without using organic solvents, applying metal oxides as catalysts that are sustainable in the view of endangered elements, avoiding byproduct formation and the use of large amounts of water in the purification step.²⁵ In this sense, the screening provides a green way for the epoxidation reaction.

Experimental

Macaw palm oil (batch code: MAO073/18; leaking data: 03/2019) was purchased from Mundo dos Óleos (Brasília, Brazil). The hydrogen peroxide (H₂O₂, 30.0%) was provided by Exodo (Sumaré, Brazil). Aluminium oxide-Al₂O₃ (≥ 99.5%), titanium oxide-TiO₂ (≥ 99.0%), niobium oxide-Nb₂O₅ (99.9%), and lanthanum oxide-La₂O₃

(99.9%) were provided by Sigma-Aldrich (Cotia, Brazil). The niobium phosphate-Nb₃O₂₀P₅ was kindly provided by Companhia Brasileira de Metalurgia e Mineração (CBMM, Araxá, Brazil). All chemicals were used as received.

Epoxidation reaction of macaw vegetable oil

The MPO has an IV equal to 108.48 g of I₂ per 100 g of oil, calculated by proton nuclear magnetic resonance (¹H NMR). The IV can be converted to mol of carbon double bond (C=C), resulting in 0.4274 mol per 100 g.

Epoxidation reaction was executed without solvent following a molar ratio of 1:5 (C=C:H₂O₂). First, 10.0 g of MPO, 23.01 g of hydrogen peroxide solution (H₂O₂) and 10 mol% of catalyst (Al₂O₃, La₂O₃, Nb₂O₅, TiO₂ or Nb₃O₂₀P₅) in relation to carbon double bond were added into a round-bottomed flask with a magnetic bar. The reaction was maintained at 80 °C for 24 h under reflux. After 24 h, the product was filtered to remove the catalyst and then settled in a separatory funnel, then the water layer was removed. The organic layer was washed twice with 20 mL of distilled water, and then, with brine (1×) to completely remove the added hydrogen peroxide. The organic layer was then dried using MgSO₄. Consequently, the organic layer was filtered and the epoxidized product was obtained.

The same procedure was used for each catalyst and depending on the catalyst, the temperature was also changed (25, 50, 80, or 100 °C). A blank reaction was executed using MPO and H₂O₂ in the absence of catalyst at 80 °C. All samples were characterized by ¹H NMR.

¹H NMR analysis

¹H NMR analyses were performed using an Agilent 400 MHz Premium Shield spectrometer (Santa Clara, United States). Samples were solubilized in deuterated chloroform (CDCl₃, 99.8% D) from Sigma-Aldrich (Cotia, Brazil).

The IV of each sample was calculated via ¹H NMR analysis, using the integrations of the vinyl hydrogens (K) at 5.3 ppm and equation 1.¹⁴ To integrate these areas correctly, it was necessary to relate these environments to a normalized area such as the methylene hydrogens of the α-carbonyl in the acyl chain at 2.3 ppm (six hydrogens).

$$IV = 12691 \times K / (120 + 701.3 + 6.006 \times K) \quad (1)$$

Results and Discussion

Table 1 summarizes all experiments regarding the IV, double bond content and epoxide conversion.

Table 1. Conversion value of carbon double bonds (C=C) into epoxy in the macaw palm oil after 24 h of reaction and using different catalysts

entry	Catalyst ^a	Temperature / °C	K ^b	IV / (g of I ₂ per 100 g)	C=C / (mol per 100 g)	Epoxy conversion / %
1 ^c	–	–	7.40	108.48	0.4274	0
2	–	80	5.66	83.98	0.3309	20.1
3	Al ₂ O ₃	80	5.85	86.69	0.3415	22.6
4	La ₂ O ₃	80	5.09	75.83	0.2988	30.1
5	Nb ₂ O ₅	80	3.25	49.00	0.1933	54.8
6	Nb ₂ O ₅	50	2.71	41.06	0.1618	62.1
7	Nb ₂ O ₅	25	6.87	101.08	0.3983	6.8
8	TiO ₂	80	1.08	16.56	0.0652	84.7
9	TiO ₂	100	0.79	12.14	0.0478	88.8
10	Nb ₃ O ₂₀ P ₅	25	3.91	58.74	0.2314	45.8
11	Nb ₃ O ₂₀ P ₅	50	3.20	48.32	0.1904	55.5
12	Nb ₃ O ₂₀ P ₅	100	3.21	48.46	0.1909	55.3

^aThe catalyst loading was 10 mol% in relation of C=C. ^bThe value of K was obtained by integration at 5.3 ppm. ^cThe result is related to raw macaw palm oil. K: integration constant; IV: iodine value; –: not used or undefined.

The MPO has an IV = 108.48 g of I₂ per 100 g of oil and a double bond content equal to 0.4274 mol per 100 g (entry 1). The principal ¹H NMR signals for MPO are related to the vinyl hydrogens at 5.3 ppm (multiplet) and vicinity hydrogens between two alkenes (triplet) at 2.7 ppm. As expected, these signals must diminish with the epoxidation process; and new signals related to epoxide hydrogens appear as a multiplet between 1.4 and 3.1 ppm.¹⁴

A blank experiment (entry 2) was performed in the absence of catalyst. After 24 h, a conversion of 20.1% was reached. The blank experiment is important to prove the influence of catalysts in the system.

Sepulveda *et al.*²⁶ described a conversion of 100% using Al₂O₃ as catalyst at 80 °C after 24 h using fatty esters as substrate. Van Vliet *et al.*²⁷ studied the epoxidation process in terpenes, using Al₂O₃ and anhydrous or aqueous H₂O₂, achieving good conversions. However, the present system used a triacylglyceride as substrate, achieving a conversion of 22.6% (entry 3). Although Al₂O₃ reacts with H₂O₂ to form a hydroperoxide derivative (Al–OOH), the catalyst has low dispersion in the organic phase causing a slow reaction rate. Therefore, the stirring process is not sufficient to reach an efficient homogeneity.²⁴ Furthermore, internal epoxides show lower conversion, due to steric hindrance effect when compared to external epoxides. The reaction using La₂O₃ (entry 4) in the same parameters resulted in a low conversion of 30.1% after 24 h. A poor dispersion in organic phase was also observed for the lanthanum oxide.

Nb₂O₅ is a white powder that reacts exothermically with H₂O₂ to form niobium hydroperoxide, a light-yellow compound. In this reaction, the release of O₂ is also observed due to hydrogen peroxide decomposition.²⁸ Catalyst of SiO₂ containing Nb(V) was used in epoxidation reaction

of methyl fatty esters and rapeseed oil, which occurred at 90 °C and using acetonitrile as solvent, resulted in a conversion of 44.0% after 4 h (rapeseed oil).²⁹ The reaction performed at 80 °C (entry 5) was vigorous, releasing a huge amount of O₂ (parallel reaction) due to niobium hydroperoxide decomposition, reducing the epoxidation reaction; therefore, a conversion of 54.8% was obtained. To avoid the uncontrolled O₂ releasing, a second reaction was performed but at 50 °C (entry 6). Consequently, it was not observed the release of O₂ and the conversion reached 62.1%. Furthermore, the Nb₂O₅ presents a homogeneous dispersion in organic phase. A third reaction using the same catalyst was performed at room temperature (entry 7) and the O₂ releasing was not observed, however, the conversion was not appreciable (6.8%). Therefore, a temperature between 50 and 70 °C should be used to obtain a reasonable conversion and to prevent parallel decomposition.

TiO₂ is a white compound that can form two different species in hydrogen peroxide solution (peroxide or hydroperoxide). In both cases, the titanium valence remains as IV and the color does not change. The peroxide derivative may react with alkenes in three different ways: by electrophilic oxidation, metallacycle intermediate or radical epoxidation.³⁰ The epoxidation reactions for TiO₂ are presented in Figure 1. The TiO₂ has a highly catalytic activity for the epoxidation of fatty methyl esters in the presence of organic solvents; however, its activity in triacylglycerol system is not reported.³⁰

The TiO₂ showed the best dispersion in organic phase, reaching a conversion of 84.7% after 24 h at 80 °C (entry 8). Thereafter, for improvement, a new experiment was executed increasing the temperature to 100 °C (entry 9); it was not observed decomposition of hydrogen peroxide by

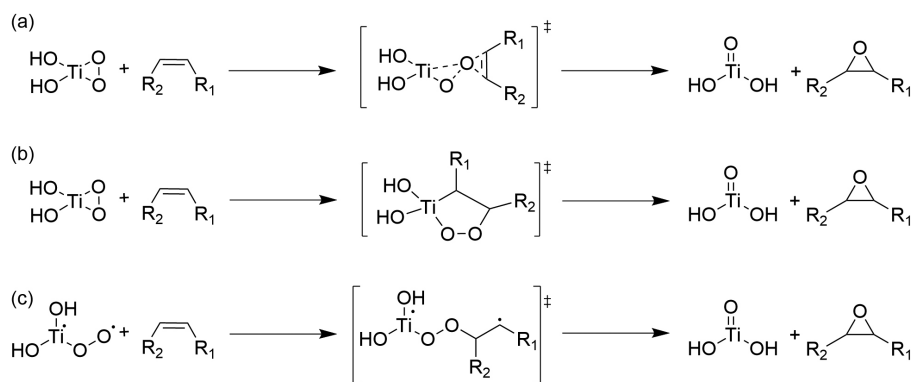


Figure 1. Epoxidation reactions using TiO_2 as catalyst by (a) electrophilic oxidation, (b) metallacycle intermediate, and (c) radical (adapted from reference 30).

releasing O_2 . As expected, this reaction achieved a higher conversion than entry 8 with 88.8%. This aspect proves the efficiency of TiO_2 in the epoxidation process of internal alkenes in MPO.

The niobium phosphate ($\text{Nb}_3\text{O}_{20}\text{P}_5$) was also evaluated as a peroxide-activating catalyst. It is a white compound that instantly reacts with hydrogen peroxide forming a peroxy-phosphate derivative, which has a bright intense yellow colour.³¹ The epoxidation reaction does not present the decomposition of hydrogen peroxide at 25, 80 or 100 °C. The peroxy-phosphate derivative is stable and can be manipulated without further problems after drying and exhibits dispersion in the organic phase (vegetable oil). The first reaction using niobium phosphate was executed at 25 °C (entry 10), achieving a conversion of 45.8%. In the second reaction, the temperature was increased to 80 °C (entry 11), reaching a conversion of 55.5%, which is similar to niobium oxide in

the same condition (entry 5); however, without showing the hydrogen peroxide decomposition. The last reaction was performed at 100 °C (entry 12) and presented a conversion of 55.3%, which is similar to the previous experiment. The resulted conversion close to 55.0% for each experiment using niobium phosphate can be explained by the high stability of peroxy-phosphate derivative that probably does not react with alkenes in an effective way.

The ^1H NMR for each experiment is found in the Supplementary Information section (Figures S1 to S12). Figure 2 displays the ^1H NMR spectra for MPO and experiments executed at 80 °C for each catalyst.

Conclusions

The epoxidation reactions of macaw palm oil using hydrogen peroxide and metal oxides or niobium

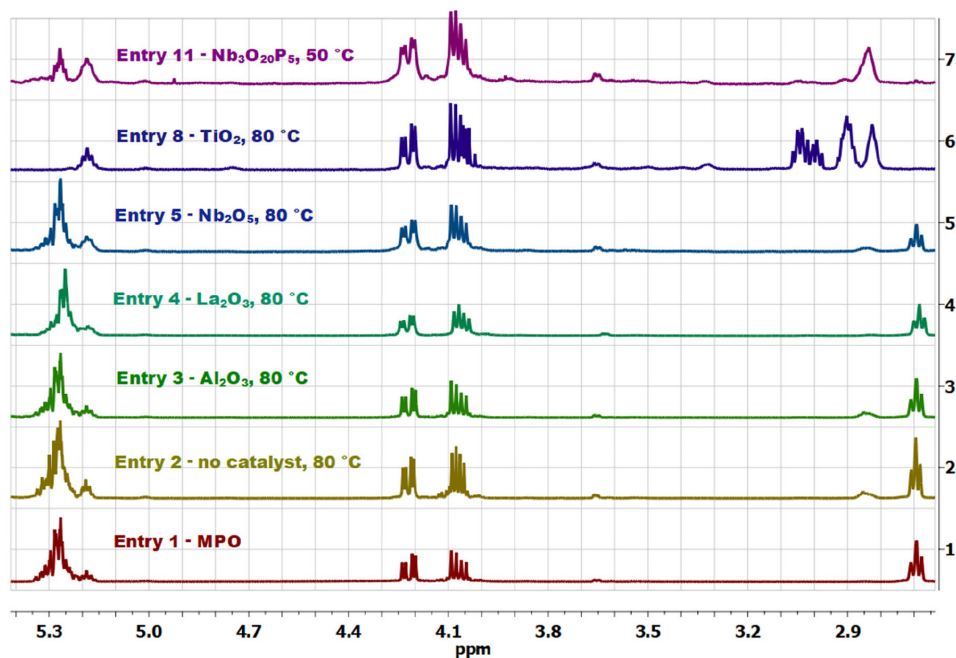


Figure 2. ^1H NMR spectra (400 MHz, CDCl_3 , 99.8% D) for epoxidized MPO performed at 80 °C with different catalysts. MPO is the entry 1.

phosphate were performed in 24 h without organic solvents. The aluminium oxide (Al_2O_3) and lanthanum oxide (La_2O_3) showed conversions of epoxides, similar to the blank reaction. The niobium oxide (Nb_2O_5) presented an exothermic reaction with releasing of O_2 , which spoils the evolution of the epoxidation reaction. Niobium phosphate ($\text{Nb}_3\text{O}_{20}\text{P}_5$) presented a similar conversion independent of the studied temperature (between 45.8 and 55.5%). Titanium oxide (TiO_2) is a promising peroxide-activating catalyst, achieving values greater than 84.5% of epoxide conversion in both studied temperatures (80 and 100 °C). Moreover, ^1H NMR analysis is very accurate, reliable and sensitive, which can provide the IV value, total conversion of alkene into epoxy rings and other types of conversion or monitoring processes, which is an alternative to titrimetric methods. Further studies should be executed to achieve higher conversions at lower times for the TiO_2 system. Green organic solvent during the synthesis could assist the homogeneity of Al_2O_3 and La_2O_3 systems, which may result in high conversion values. Furthermore, the process presented in this work should be tested on other vegetable oils with higher iodine values and different reactive groups.

Supplementary Information

Supplementary data (Figures S1-S12) are available free of charge at <http://jbcbs.sbq.org.br> as PDF file.

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Author Contributions

Rafael T. Alarcon for conceptualization, investigation, methodology, formal analysis, resources, writing original draft; Gilbert Bannach for supervision, funding acquisition, writing review and editing; Éder T. G. Cavalheiro for supervision, data curation, project administration, funding acquisition, writing review and editing.

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