Article

Synthesis of Polyols from *Mabea fistulifera* Mart. (Euphorbiaceae) Oil

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Mabea fistulifera Mart. (Euphorbiaceae) é uma planta arbórea com altura variando de 5 a 14 m, típica da vegetação secundária de terrenos arenosos, principalmente de savana. No Brasil, é encontrada nos estados do Rio de Janeiro, Minas Gerais e São Paulo. O processo de extração Soxhlet das sementes desta espécie vegetal com hexano produziu um óleo rico em triacilglicerídeos dos ácidos linolênico e linoléico e que apresenta índice de iodo igual a 182,15 g de I_2 *per* 100 g de óleo. Descreve-se neste trabalho a produção de um biopoliol a partir do óleo de *M. fistulifera* Mart., empregando-se um processo de hidroxilação *in situ*. Ensaios univariados permitiram determinar o tempo ótimo de reação como sendo 720 min. Além disso, realizou-se ainda um planejamento fatorial 2^2 composto central (CCD) contendo 12 ensaios experimentais que permitiram investigar diferentes razões molares dos reagentes empregados na síntese do biopoliol, bem como avaliar sua aplicabilidade como matéria-prima na síntese de poliuretanos com característica rígida.

Mabea fistulifera Mart. (Euphorbiaceae) is an arboreal plant with height varying from 5 to 14 m, typical of secondary vegetation of sandy lands, mainly savannah. In Brazil, it is found in the Rio de Janeiro, Minas Gerais and São Paulo States. Soxhlet extraction of *M. fistulifera* seeds with hexane provided an oil rich in tryacylglycerides of linolenic and linoleic acids, presenting iodine index of 182.15 g of I_2 *per* 100 g of oil. In this study, the synthesis of polyols from *M. fistulifera* oil using an *in situ* hydroxylation procedure is described. Univariate assays were applied to determine the optimal reaction time of 720 min. In addition, a 2^2 factorial central composite design was carried out containing 12 experimental assays that allowed the investigation of different molar ratios of the reagents used in polyol synthesis, as well as the applicability of polyols for the preparation of rigid polyurethanes.

Keywords: *Mabea fistulifera* Mart, polyol, univariate assays, hydroxylation

Introduction

Oil reserve depletion and increasing market prices have led researchers worldwide to seek renewable resources to replace petrochemical derivatives.[1] Vegetable oils such as soybean,[2,3] rape[4] and peanut[5,6] are promising petrochemical alternatives since they are relatively inexpensive and renewable sources.[7]

Mabea (Euphorbiaceae) is a neo-tropical genus composed of 50 species,[8] including *Mabea fistulifera* Mart. (commonly known as "canudo-de-pito"), an arboreal plant with height varying from 5 to 14 m, typical of secondary vegetation of sandy lands, mainly savannah (Figure 1). In Brazil, *M. fistulifera* is found in the Rio de Janeiro,

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Figure 1. The plant species *Mabea fistulifera* Mart.

Minas Gerais and São Paulo States.[9] It is usually found aggregated on forest edges and areas with strong anthropogenic impact. The flowering occurs from February to June, peaking between April and May, corresponding to the onset of the dry season. Since it occurs during periods of food scarcity, many animals such as monkeys, bats, skunks, birds and insects use its abundantly produced pollen and nectar as alternative feed sources.[10]

Soxhlet extraction of *M. fistulifera* seeds with hexane provides oil percentages varying from 35 to 40% in relation to the weight of dried seeds.[11] *M. fistulifera* oil is mainly composed of tryacylglycerides from unsaturated fatty acids.

Plant oils are an excellent renewable source of raw material for the synthesis of polyols, which can be used in the preparation of polymeric materials, such as polyesters and polyurethanes.[7] Polyol production from vegetable matrices is obtained by replacing the unsaturated bonds of the oil constituents by hydroxyl groups.[12] Different methodologies, such as ring opening of epoxides with alcohols,[13,14] ozonolysis, followed by hydrogenation[15] and *in situ* hydroxylation reactions,[12,16] have been used for the preparation of polyols from triacylglycerides contained in vegetable oils. *In situ* hydroxylation of fatty acids is carried out by reacting the oil with hydrogen peroxide/formic acid[17-19] or hydrogen peroxide/glacial acetic acid.[20,21] In these cases, performic acid or peracetic acid is generated, promoting epoxidation of the double bonds present in the oil molecules. An excess of formic acid or acetic acid is used to open the epoxide thus formed. The net result is an *in situ* hydroxylation of the unsaturated molecules present in the oil. Depending on the experimental conditions adopted, the mono and polyfunctional alcohols obtained may present different hydroxyl indices, making polyol a versatile product for the synthesis of polyurethane resins with diverse properties and applications.

In this study, the results obtained from polyol synthesis from *M. fistulifera* oil using *in situ* hydroxylation reaction are described. In addition, a 2^2 factorial central composite design was carried out containing 12 experimental assays investigating several molar ratios of the reagents used in polyol synthesis, as well as the applicability of polyols for the preparation of rigid polyurethanes. To the best of our knowledge, there are no reports on the application of *M. fistulifera* oil for the production of polyols.

Experimental

General methodology

All reagents used were PA grade. Glacial acetic acid, formic acid, hydrogen peroxide solution, sulfuric acid, sodium bisulfite, sodium carbonate and anhydrous sodium sulfate were purchased from Vetec (Rio de Janeiro, Brazil). Toluene and hexane were purchased from Merck.

Infrared (IR) spectra were obtained in KBr pellets containing 1% (m/m) of the compound, using a Perkin Elmer 1000 spectrometer scanning from 500 to 4000 cm^{-1}. Hydrogen nuclear magnetic resonance (^{1}H NMR, 300 MHz) spectra were obtained using Varian Mercury 300 spectrometer. Deuterated chloroform (CDCl$_3$) was used as solvent with tetramethylsilane (TMS) as an internal standard ($\delta = 0$).

Plant material

M. fistulifera Mart. seeds were collected before reaching their maturation period, in early October 2010 in Viçosa City (Minas Gerais State, Brazil). The seeds were covered with a screen and sun-dried until dehiscence.

Extraction procedure

Seeds were extracted for 2 h with hexane under reflux in a Soxhlet extractor. The mixture was filtered and washed with hexane. The filtrate obtained was concentrated under reduced pressure in a rotary evaporator, yielding yellowish oil (35%, m/m).

GC-MS analyses

M. fistulifera oil was transesterified using a standard procedure[22] and analyzed by gas chromatography-mass spectrometry (GC-MS). Qualitative analyses were conducted with a Shimadzu (Kyoto, Japan) gas chromatograph-mass spectrometer (QP 5000 and Classs-5000 software, version 1.2) with an auto sampler and workstation. A fused silica column coated with the DB-5 stationary phase (30 m × 0.2 mm internal diameter, film thickness 0.25 μm, J & W Scientific) was used. Initial oven temperature of 60 °C was held for 5 min, programmed to increase at 2 °C min^{-1} to 240 °C, and held at this temperature for 30 min. Injector temperature was 220 °C. Helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. Injection volume was 1 μL (1% solution in CH$_2$Cl$_2$), with a split ratio of 1:10. The column pressure was 100 kPa. Mass detector conditions were as follows: source temperature of 240 °C, electron impact (EI) mode at 70 eV, scan rate of 1 scan s^{-1} and mass acquisition range 29-450 u.

The components were identified by comparing their retention indexes (RI) relative to a linear standard alkane series (C$_9$–C$_{24}$) and by comparing their mass spectra with reference data from the equipment database (Wiley 330 000) and from the literature.[23]

Determination of physicochemical properties of *M. fistulifera* oil

Acid index,[24] hydroxyl index (ASTM D 2849 Method A)[25] and iodine index[26] were determined according to the literature procedures.

Typical procedure for the preparation of *M. fistulifera* polyol

To a round bottom flask, 5.00 g (0.36 mmol of double bounds) of *M. fistulifera* oil, 9.30 mL (0.162 mol) of glacial acetic acid, 20 mL of toluene and 3 drops of concentrated sulfuric acid were added. The reaction mixture was stirred at 30 °C and 5.30 mL of a H_2O_2 aqueous solution (30%, v/v) were slowly added to the mixture at this temperature. The temperature was then raised to 60 °C and the system was connected to a reflux condenser. After 720 min, the heating was interrupted and an aqueous solution of sodium bisulfide (10%, m/v) was added, with stirring continuing for 20 min. The mixture was transferred to a separatory funnel with diethyl ether, and the layers were separated. The organic layer was washed with aqueous sodium carbonate (10%, m/v) until neutral, dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure.

Univariate assays

Influence of the molar ratios of reagents on polyol synthesis from *M. fistulifera* oil

Screening experiments were performed to verify the influence of different molar ratios of the reagents (Table 1) on polyol synthesis. The formulations were constituted of *M. fistulifera* oil, acetic or formic acid, and water. The amounts of all reagents were divided by the amount of oil in mol to obtain a ratio of 1:Z:Y, where 1 is the number of mol of double bonds present in the oil, Z is the number of mols of acetic or formic acid, which varied according to

Table 1. Reaction conditions for univariate studies to evaluate different polyol formulations

	Oil[b] 1	Acetic acid Z	H_2O_2 Y
A	1	–	–
B	1	1.8	4.75
C	1	3.0	1.5
D	1	4.5	1.5
E[a]	1	4.5	1.5

[a]For ratio E, formic acid was used instead of glacial acetic acid; [b]mol of double bonds of oil *per* g of oil.

the experiment, and Y is the number of mol of hydrogen peroxide, which also varied according to the experiment. The reaction time was 720 min and the temperature was adjusted to 60 °C after the addition of hydrogen peroxide aqueous solution (30%, v/v).

Influence of time on polyol synthesis from *M. fistulifera* oil

The optimized reaction time of 720 min mentioned above was based on a univariate study to evaluate the influence of the reaction time on the transformation of *M. fistulifera* oil into polyol. The reaction times investigated were 60, 120, 240, 360, 480 and 720 min. In the univariate study, 5.00 g (0.036 mol) of *M. fistulifera* oil, 9.30 mL (0.162 mol) of glacial acetic acid and 5.30 mL (0.054 mol) of aqueous H_2O_2 (30%, v/v) were used. The temperature of the reaction was adjusted to 60 °C after the addition of hydrogen peroxide aqueous solution.

Optimization of *M. fistulifera* polyol synthesis

After an initial univariate screening of the experimental conditions, the optimization was carried out using a 2^2 factorial central composite design (CCD) aiming to study different molar ratios of the reagents (oil double bonds, glacial acetic acid and hydrogen peroxide). This experiment was conducted in four replications at the center point, totalizing 12 assays. The levels of the variables codified +1, 0, −1 and ±1.41 corresponded to the highest, middle, lower and axial values, respectively. The values codified X_i can be decodified for the experimental values of the levels of the variables to be studied, using equation 1[27]

$$X_i = \frac{C - \overline{C}}{\Delta C/2} \tag{1}$$

where X_i is the variable coded for CCD design (I = 1, 2, 3…), C is the original variable, $\overline{C}$ is the average between the levels (+) and (−) of the original variable, which corresponds to the value at level zero, and ΔC is the difference between the levels (+) and (−) in the original variables.

In this factorial experiment, reactions were performed under the following conditions: 3 drops of concentrated sulfuric acid, 20 mL of toluene, 720 min and temperature adjusted to 60 °C after addition of hydrogen peroxide aqueous solution (30%, v/v). The codified and decodified variables (X_i) of the factorial experiment are shown in Table 2.

After the assays were carried out and the hydroxyl content (mg of KOH g^{-1} of oil) of the products was obtained, the response surface could be generated using the Statistics 7.0 software.

Table 2. 2^2 Factorial central composite design (CCD)

| Assay | Decodified variables[a] reagent ratio | | Codified variables | |
	Acetic acid	Hydrogen peroxide	X_1	X_2
1	3.5	1.0	−1	−1
2	5.5	1.0	1	−1
3	3.5	2.0	−1	1
4	5.5	2.0	1	1
5	3.1	1.5	−1.414	0
6	5.9	1.5	1.414	0
7	4.5	0.8	0	−1.414
8	4.5	2.2	0	1.414
9	4.5	1.5	0	0
10	4.5	1.5	0	0
11	4.5	1.5	0	0
12	4.5	1.5	0	0

[a]The ratio of *M. fistulifera* oil was set at 1 (0.036 mol of double bonds g^{-1} of oil).

Results and Discussion

Characterization of *M. fistulifera* oil

The physicochemical properties of the *M. fistulifera* oil are presented in Table 3. The iodine index of this oil is higher than that of soybean (120-141 g of I_2 *per* 100 g of oil), cotton (103-115 g of I_2 *per* 100 g of oil) and castor (81-91 g of I_2 *per* 100 g of oil) oils.[28] Thus, the *M. fistulifera* oil is rich in polyunsaturated fatty acids, an essential characteristic for polyol production. The acidity index was higher than that reported for soybean oil (0.20 mg of KOH g^{-1} of oil).[29] This fact is related to the increased percentage of free fatty acids likely due to oil deterioration during storage or processing, enzyme action, moisture or high temperatures.[30]

Table 3. Physicochemical properties of *M. fistulifera* oil experimentally determined

Physicochemical property	Experimental value
AI mg of KOH g^{-1} of oil	2.22
II g of I_2 *per* 100 g of oil	182.15
I_{OH} mg of KOH g^{-1} of oil	2.18

AI: acidity index; II: iodine index; I_{OH}: hydroxyl index.

The GC-MS analysis showed that the major component of the *M. fistulifera* oil is tryacylglyceride of linolenic acid, followed by tryacylglyceride of linoleic acid (Table 4). These fatty acids have three and two double bonds,

Table 4. Compounds identified in *M. fistulifera* oil by GC-MS

Substance	Formula	mass%
Methyl (2*E*, 4*Z*)-deca-2,4-dienoate	$C_{11}H_{18}O_2$	1.10
Methyl palmitate	$C_{17}H_{34}O_2$	4.90
Pentadecane	$C_{15}H_{32}$	0.40
Methyl linoleate	$C_{19}H_{34}O_2$	18.30
Methyl linolenate	$C_{19}H_{32}O_2$	69.00
Methyl stearate	$C_{19}H_{38}O_2$	4.20
Heptadecane	$C_{17}H_{36}$	0.60
Icosane	$C_{20}H_{42}$	1.50

respectively, confirming the high potential of the oil for polyol synthesis.

The *M. fistulifera* oil was also examined by IR and NMR analyses. Diagnostic bands for =CH (3014 cm^{-1}), C=O (1751 cm^{-1}) and C=C (1645 cm^{-1}) were identified in the IR spectrum of *M. fistulifera* oil.

Univariate assays

Influence of the molar ratios of the reagents on polyol preparation

The synthesis of the polyols from the *M. fistulifera* oil was carried out via *in situ* hydroxylation. In this study, the oil was treated with a mixture of acetic acid (or formic acid)/ H_2O_2 at 60 °C. Different experiments were conducted to evaluate the influence of different formulations (Table 1), as well as of the reaction time on the efficiency of converting the oil into polyols.

To determine the best molar ratio of the *M. fistulifera* oil, acetic acid (or formic acid) and H_2O_2, to maximize the conversion of the oil into polyols, different experiments were carried out, varying the ratio of oil/acetic acid (or formic acid)/H_2O_2. Reactions were monitored by IR spectroscopy. The presence of a stretching band of =CH (3014 cm^{-1}) in the IR spectrum of the *M. fistulifera* crude oil was noticed. This band is absent in the IR spectra in the analysis of the products obtained in the reactions in which the oil was submitted to different molar ratios of H_2O_2/acetic acid (or formic acid). In addition, the treatment of the *M. fistulifera* oil, using different H_2O_2/acetic acid (or formic acid) ratios, resulted in a decrease in the intensity of the absorptions related to the stretching of the C=C bond at 1645 cm^{-1}. Bands emerging at 791 and 820 cm^{-1}, assigned to the stretching of C–O bonds of the epoxide rings were also observed.

IR spectra stressed the process of epoxidation of the double bonds of the tryacylglycerides present in the *M. fistulifera* oil. This fact could be confirmed by ^{1}H NMR spectroscopy.

^{1}H NMR spectrum obtained by analyzing the mixture of products produced from the reaction using the ratio of oil/acetic acid/H_2O_2 (proportion 1:1.8:4.75) did not present signals corresponding to the olefinic hydrogens. Hydrogen signals of the oxirane groups were observed in the region of δ 2.8-3.2 (–C$\underline{H}$(O)C$\underline{H}$–) along with the proton signals of the methylene groups between the oxirane rings (1.75 ppm). Other changes were observed at approximately δ 2.0, with the decrease of the signals relative to allylic hydrogen atoms, when compared with the spectrum of the crude oil and at δ 1.05, corresponding to the signals to the hydrogen atoms of the methyl groups of fatty acid chains with oxirane ring on carbons 15 and 16, derived from linolenic acid epoxidation.[31]

The increase in the amount in mol of acetic acid (or formic acid) favors the epoxide ring opening with concomitant polyol formation. This fact is evidenced by the emergence of a broad band at 3440 cm^{-1}, corresponding to the stretching of the hydroxyl group. The epoxide ring opening reaction was confirmed by ^{1}H NMR spectroscopy. The analysis of the mixture of products from the reaction performed with the oil/acetic acid/H_2O_2 ratio of 1:4.5:1.5 showed the absence of olefinic hydrogen signals of the tryacylglycerols. In addition, the disappearance of the signal relative to the hydrogen atoms of the methylene groups between the oxirane rings at δ 1.75 in the epoxidized material was verified, showing that the rings formed during the epoxidation reaction were ruptured to produce polyol. The appearance of signals between δ 3.2-4.0 ppm corresponding to hydrogens attached to carbons attached to hydroxyl groups (–C$\underline{H}$(OH)–) is significant,[32] confirming the incorporation of OH groups in the oil constituents containing double bonds.
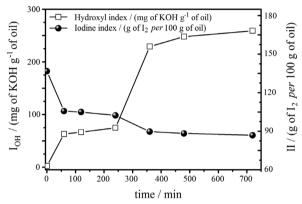
It must be emphasized that identical oil/acid/H_2O_2 ratios were used in experiments D and E (Table 1). In experiment D, glacial acetic acid was used, while formic acid was used in experiment E. Reactions using formic acid were inconvenient since an emulsion was formed upon reaction work up. Thus, glacial acetic acid was chosen as the source of organic peroxide for polyol synthesis.

Influence of time on polyol preparation

When analyzing the influence of the time on the polyol synthesis, it is verified that a broad band around 3440 cm^{-1} in the IR spectrum for reaction times lower than 360 min (6 h) is not present. In contrast, for higher reaction times, the broad band is observed, indicating the formation of hydroxyl groups, and confirming the occurrence of *in situ* hydroxylation reaction.

It was also noted that as reaction time increases (Figure 2), the iodine index values decrease, indicating a

conversion of double bonds present in the oil to the hydroxyl groups with concomitant increase of hydroxyl index. It is worth to mention that an increase in the hydroxyl index with time (20-240 min) was also observed in the hydroxylation reaction of soybean oil using the formic acid/H_2O_2 system.[19] For a reaction time of 720 min, the lowest value for iodine index and the highest value for hydroxyl index were noted when compared with the other reaction times used, showing a greater conversion of double bonds to hydroxyl groups. Thus, a reaction time of 720 min was set for the multivariate assays.

Figure 2. Effect of the reaction time of *in situ* hydroxylation reaction on the (□) hydroxyl index and (●) iodine index. Reaction conditions: reaction temperature of 60 °C after addition of H_2O_2 and mol ratio of the reagents of 1 double bond:4.5 of acetic acid:1.5 of H_2O_2 at zero time (unmodified *M. fistulifera* oil).

Optimization of the hydroxylation reaction of *M. fistulifera* oil

A 2^2 factorial CCD (Table 5) was applied, setting the following experimental conditions: reaction time of 720 min at 60 °C (after addition of 30% hydrogen peroxide), 3 drops of sulfuric acid and 20 mL of toluene.

Table 5. Responses as a function of the hydroxyl index (mg KOH g[-1] of oil) of the 2^2 factorial central composite design (CCD)

Assay	Codified variables		Response	Functionality[a]
	X_1	X_2	I_{OH} / (mg of KOH g[-1] of oil)	
1	−1	−1	260.3	4.04
2	1	−1	140.7	2.18
3	−1	1	361.1	5.60
4	1	1	123.5	1.91
5	−1.414	0	295.9	4.59
6	1.414	0	164.0	2.54
7	0	−1.414	139.1	2.16
8	0	1.414	283.4	4.40
9	0	0	244.3	3.79
10	0	0	245.6	3.81
11	0	0	236.8	3.68
12	0	0	246.8	3.83

Reaction conditions: reaction time of 720 min at 60 °C; [a]mean functionality = mean molecular weight of oil × OH content (mequivalent g[-1]).

The independent variables studied were the glacial acetic acid and hydrogen peroxide mol ratios, maintaining the ratio of *Mabea* oil fixed in 1 mol. Based on the value found for the dependent variable (hydroxyl index) for each assay, it was possible to calculate the functionality of the plant polyol obtained. Functionality is an important parameter for the stoichiometric calculation of a future reaction, where plant polyol is considered as a source of raw material for the production of polyurethanes. To achieve this, the plant polyol must react with isocyanate (NCO), which has at least two functional groups (NCO) capable of reacting with active hydrogen of polyols.[32] Thus, it was sought to analyze the applicability of the plant polyol obtained in the production of polyurethane type polymers.

The quadratic model was fitted to the data related to the I_{OH} response by verifying that all linear and quadratic coefficients for the codified variables glacial acetic acid and hydrogen peroxide were significant at 95% confidence level. The model allowed obtaining the response surface shown in Figure 3. The regression equation describes the behavior of the response depending on the mol ratios of the reagents at 5% probability. The coefficient of determination (r^2) obtained was of 0.9049, confirming the good fit of the model (equation 2)

$$I_{OH} = 243.38 - 67.97\ A - 6.51\ A^2 + 35.96\ P - 15.86\ P^2 - 29.50\ AP \quad (2)$$
Error: ±2.25   ±1.59   ±1.78   ±1.59   ±1.78

where A is the codified variable related to the acetic acid ratio and P is the codified variable related to the hydrogen peroxide ratio.

Analyzing the points in the projection of the response surface (Figure 3), it was possible to determine the different possibilities for plant polyol production. The responses obtained and expressed in hydroxyl contents present values higher than the hydroxyl index that was observed for the crude oil (Table 3), showing that in all assays the desired product was obtained. Assay 3 presented the highest value in the response. However, the choice of the reaction conditions for polyol synthesis must be analyzed according to the purpose of this product.

The product obtained in assay 7, in which the codified variables correspond to the zero level for variable X_1, and −1.414 for variable X_2 (Table 5), presents a functionality of approximately 2.0, also observed for assays 2 and 4. However, in other assays, the functionality of the polyol obtained is greater than 2.0. Besides, depending on the functionality of the polyol, the polymer being synthesized will have different characteristics. This fact has been observed for different polyurethanes derived from soybean, sunflower, canola, corn and linseed polyols. It was found
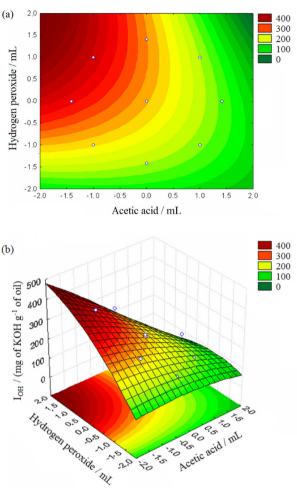

Figure 3. (a) Projection on response surface level for the optimization of the hydroxylation reaction of the oil of *M. fistulifera* Mart. and (b) response surface.

that polyols derived from canola (functionality 3.3), soybean and corn (functionalities around 3.5) afforded polyurethanes with similar mechanical properties. In the case of linseed polyol (functionality 5.2), the polyurethane derived from it had higher crosslinking density and mechanical properties.[33]

Typically, polyols that produce flexible foams and elastomers have a molecular weight between 1,000 and 6,000 and functionality between 1.8 and 3.0. Such values are observed in assays 2, 4, 6 and 7. Short-chain polyols (250 < molecular weight < 1000) and high functionality polyols (3-12) produce rigid chains with a high content of cross-links, used in rigid foams and high performance paints.[12] Functionalities higher than 3.0 are observed in the other assays.

Thus, since the aim of this work is to produce a rigid polymeric material to be used as adsorbent for the treatment of water contaminated by organic compounds, the ratios found with functionality above 3.0 are ideal for such purpose.

Conclusion

It was possible to synthesize polyols from the *M. fistulifera* Mart. oil, a raw material rich in unsaturated fatty acids, essential for polyol production. By means of univariate assays, it was possible to establish the optimum value for the time parameter.

Using a 2^2 factorial central composite design (CCD) for the optimization of the experimental condition regarding the molar ratio of reagents, it was possible to obtain polyols with different functionalities. These products obtained with diversified characteristics can be utilized for the production of polyurethane resins morphologically differentiated.

Supplementary Information

Supplementary data (^{1}H NMR spectrum of the *M. fistulifera* oil and table presenting the assignments of the principal signals observed, IR spectra for the reactions between *M. fistulifera* oil, acetic acid (or formic acid) and H_2O_2 at different molar ratios, ^{1}H NMR spectra of the epoxidized and hydroxylated *M. fistulifera* oil and IR spectra of the products of the *in situ* hydroxylation reaction at different reaction times) are available free of charge at http://jbcs.sbq.org.br as PDF file.

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Supplementary Information

Synthesis of Polyols from *Mabea fistulifera* Mart. (Euphorbiaceae) Oil

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Table S1. Chemical shifts (δ) and assignments of the principal signals observed in the ^{1}H NMR spectrum of *M. fistulifera* oil

Signal number	Chemical shift δ / ppm	Assignment
1	7.25	CHCl$_3$
2	5.35	CH=CH
3	5.25	−CHOCOR
4	4.30-4.10	−CH_2OCOR
5	2.76	CH=CHCH_2CH=CH
6	2.30	−COCH_2
7	2.03	−CH_2CH=CH
8	1.59	−COCH$_2$CH_2
9	1.30	(CH_2)$_n$
10	0.97	CH=CHCH$_2$CH_3
11	0.89	CH_3

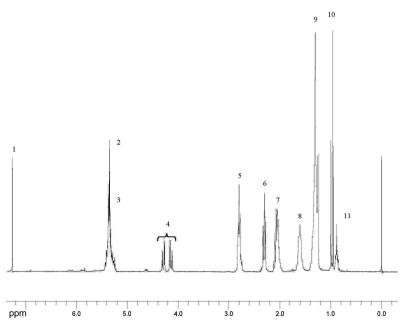R: alkyl portion of the tryacylglycerides.

Figure S1. ^{1}H NMR spectrum (CDCl$_3$, 300 MHz) of *M. fistulifera* oil.

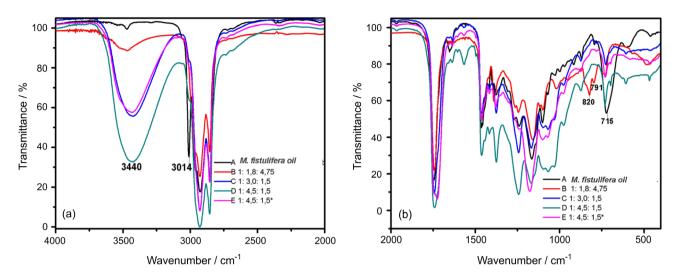*e-mail: julieta_neta@yahoo.com.br, julieta@cpatu.embrapa.br

Figure S2. Spectra in the IR region: (a) 4000-2000 cm^{-1}, (b) 2000-500 cm^{-1}, for the reactions between *M. fistulifera* oil, acetic acid (or formic acid) and H$_2$O$_2$ at different molar ratios.

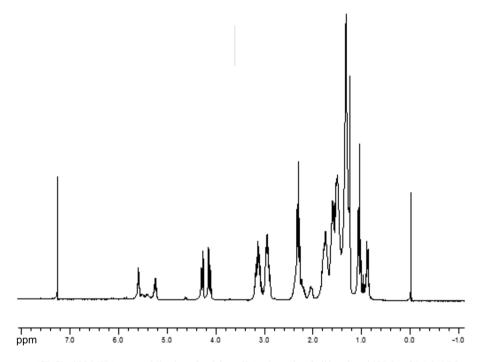
Figure S3. ^{1}H NMR spectra (CDCl$_3$, 300 MHz) to epoxidized *M. fistulifera* oil (molar ratio of oil/acetic acid/H$_2$O$_2$ of 1:1.8:4.75)
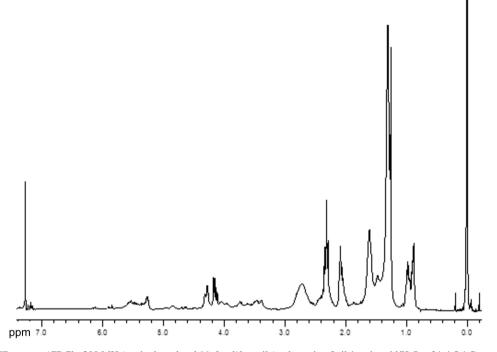
Figure S4. ^{1}H NMR spectra (CDCl$_3$, 300 MHz) to hydroxylated *M. fistulifera* oil (molar ratio of oil /acetic acid/H$_2$O$_2$ of 1:4.5:1.5).
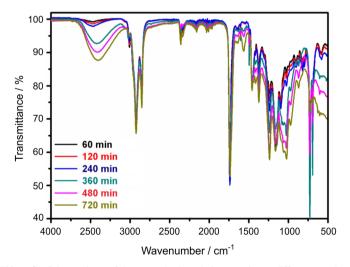

Figure S5. Infrared spectra (4000-500 cm^{-1}) of the products of the *in situ* hydroxylation reaction at different reaction times.