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Kinetics of the Transesterification of Castor Oil with Maleic Anhydride Using Conventional and Microwave Heating

Paula Mazo · Diana Estenoz · Marisa Sponton · Luis Rios

Abstract The transesterification of castor oil with maleic anhydride was studied using conventional and microwave heating. Reactions were followed by measuring the acid value and the reaction products were characterized by FTIR and ^{1}H NMR. A kinetic model that fit the experimental data was derived. The transesterification was non-catalytic and first-order with respect to each reactant. Nonthermal effects of microwaves were not observed. Activation energy, enthalpy of activation, entropy of activation and free energy of activation were similar regardless of the heating method. Rate constants and the pre-exponential factor were lower with the use of microwave heating, which could be a consequence of the decrease in the dielectric constant of the reaction liquid as the reaction progresses.

Keywords Castor oil · Maleic anhydride · Transesterification · Esterification · Microwave heating · Maleinization

Introduction

Maleinization reactions were used to chemically modify vegetable oils through Diels–Alder reactions (conjugated dienes), esterifications (alcohols), and "ene-reactions" (compounds with allylic hydrogens) [1, 2]. These reactions were employed to increase the hydrophilicity of olefinic compounds and unsaturated fatty acids. These products and their derivatives are used as drying oils, water-soluble paints, surfactants, and modifiers for biodegradable polymers [3, 4]. For this last application, maleated castor oil (MACO) has been widely investigated [5–7]. MACO is produced by the transesterification of castor oil with maleic anhydride, as shown in Fig. 1.

Transesterification can take place without adding catalysts due to the weak acidity of the carboxylic acids themselves, but the reaction is extremely slow. Homogenous mineral acids, such as H_2SO_4, HCl or HI have been traditionally used as catalysts. These catalysts promote the protonation of the carbonyl oxygen on the carboxylic group, thereby activating nucleophilic attack by an alcohol to form a tetrahedral intermediate. Disproportionation of this intermediate complex ultimately yields the ester [8, 9]. Environmental concerns related to the disposal of salts formed during the final neutralization of acids and technical problems associated with their use, such as corrosion and separation operations, constitute a strong driving force to search for alternatives.

The use of microwaves as heating source is an interesting and alternative technology to promote esterification reactions; for instance, reductions in reaction times have been observed using microwave heating for the esterifications of lauric acid with 1,2-propanediol using commercial lipases [10], propionic acid with ethanol using Amberlyst-15 [11], and free fatty acids from palm oil with methanol using H_2SO_4 and cationic resins [12, 13].

Microwave heating is an efficient and a relatively new tool in chemistry, which widens the scope of conventional thermal heating and gives chemists novel and exciting

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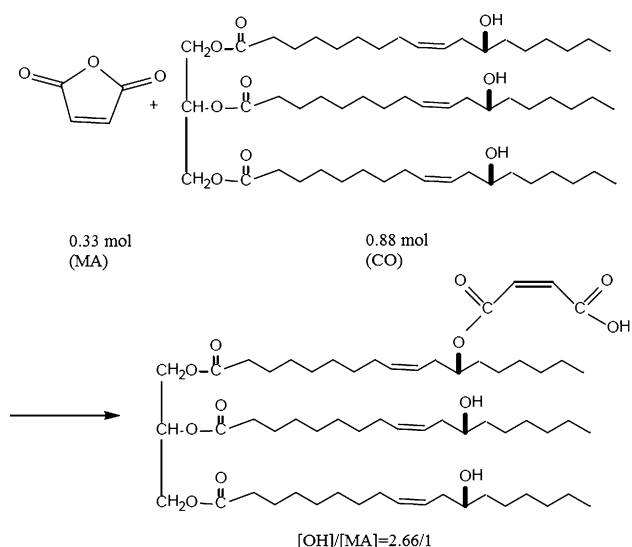Güemes 3450, 3000 Santa Fe, Argentina

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Fig. 1 Reaction scheme for transesterification of castor oil with maleic anhydride

possibilities. Microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules of solvents, reagents or catalysts. The radiation passes through the walls of the vessel directly into the bulk reaction mixture volume and an inverted temperature gradient, as compared to conventional thermal heating, results. Three main effects of microwave irradiation on reactions are distinguished: (1) thermal effects, (2) specific thermal effects, and (3) non-thermal effects. Thermal effects are those resulting from dielectric heating which may cause a different temperature regime. In the majority of cases, the reason for the observed rate enhancement of chemical processes is purely a thermal effect, i.e., the high reaction temperature achieved rapidly under microwave irradiation of polar materials increases the chemical reaction rate according to the Arrhenius law. Specific thermal effects are thermal effects caused by accelerations of chemical transformations in a microwave field that cannot be achieved or duplicated by conventional heating. Hot spots and liquid overheating are the most common specific thermal effects. Most non-thermal effects are electrostatic polar effects, which lead to dipole–dipole-type interactions between the dipolar molecules and charges in the electric field. Therefore, more polar states appear to be more stable in the electric field. These effects lead to (1) increased pre-exponential factor A of the Arrhenius equation because collision efficiency is improved by mutual orientation of polar molecules involved in the reaction), and (2) decreased activation energy ($\Delta G^{\neq}$), which is the main non-thermal effect. When considering the contribution of enthalpy and entropy to $\Delta G^{\neq}$ ($\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$), it may be predicted that the magnitude of the $-T\Delta S^{\neq}$ term would decrease in a

microwave-induced reaction, this being more organized when compared with classical heating as a consequence of dipolar polarization. To justify the reduction in the energy of activation one must assume stabilization of the transition state by the microwaves. This is presumably true when the transition state is more polar than the ground state [14–16].

This paper only presents the results on the kinetics of the transesterification of castor oil with maleic anhydride (without water condensation) with the formation of an ester bond between the 12-OH moiety of ricinoleic acyl groups and maleic acid using conventional and microwave heating. Kinetic parameters were determined, i.e., rate constants, activation energies, pre-exponential factors, as well as thermodynamic properties of activation. Comparison of these kinetic and thermodynamic properties was done to investigate the effects of microwave irradiation.

Experimental Procedures

Materials

Castor oil (CO) USB-grade (hydroxyl value 159.5 mg of KOH/g, 930 g/mol) and commercial-grade maleic anhydride (MA) were obtained from Merck (Whitehouse Station, NJ, USA). To measure and control the temperature, when using conventional and microwave heating, a thermocouple J (Omega, Stamford, CT) was used. The microwave oven was a Panasonic N665 multimode (Osaka, Japan), with a nominal power of 1,000 W.

Synthesis of Maleated Castor Oil

Maleic anhydride (32.70 g, 0.33 mol) and castor oil (311 g, 0.33 mol) were added to a 250-mL four-necked and round-bottom flask equipped with a mechanical stirrer (turbine, 500 rpm, 2.5 cm radius), a thermometer, and an inlet of dry nitrogen. The reaction proceeded with continuous stirring at various temperatures (80, 87 and 100 °C). Samples were washed with water to remove the excess anhydride and/or maleic acid. Other reaction conditions were: reaction volume of 0.351 L, initial molar concentration of acid groups from MA (C_A) of 1.90 mol/L and initial molar concentration of hydroxyl groups (C_B) of 2.52 mol/L. Experiments were performed in triplicate and the data averaged.

Characterization Methods

Reactions were monitored by determining the acid value according to the ASTM D4662-03 method [17], which involves titrating with KOH ethanol solution (0.1 mol/L). Data plotted in the figures correspond to the averages of

triplicate experiments with a relative standard deviation lower than 5% in all cases. Hydroxyl value (OH) was measured by titration according to the ASTM D4274-05 method [18]. The molecular structures of castor oil and MACO were analyzed by using proton nuclear magnetic resonance (^{1}H-NMR) and Fourier Transform Infrared (FTIR) techniques. For ^{1}H-NMR analysis, samples were prepared by dissolving approximately 20 mg of product in 0.5 mL of CDCl$_3$. This solution was then analyzed by using a Varian Mercury plus 300 NMR spectrometer (Palo Alto, CA, USA, 300 MHz, spectrum width of 3,689.22 Hz, pulse width of 4.75 µs, 32 scans at 293 K, 90° pulse width of 9.5 µs). FTIR spectra were collected in a Perkin Elmer FTIR spectrometer (Waltham, MA, USA) using a KBr transmission cell within the 400–4,000 cm^{-1} wavenumber range at 4 cm^{-1} resolution. Twenty scans were collected per sample, with an open-beam background spectrum subtracted from each scan. Karl–Fischer titration (Titrino KF Metrohm AG, Herisau, Switzerland) was used to measure water concentration. GPC analyses were performed using a Waters 208LC apparatus (Waters, Milford, MA) equipped with a refractive index detector and with four columns of Styragel (exclusion limits of 105, 3 × 104, 103, and 250 Å) connected in series. The analyses were performed at 30 °C with THF as the eluant at a flow rate of 1 mL/min. Molecular weights were calculated by calibration with polystyrene standards.

Results and Discussion

Reaction progress was assessed by measuring the acid value and the results are shown in Fig. 2a, b for conventional and microwave heating, respectively. Acid values decreased remarkably at the beginning of the reaction and tended to stabilize after 4 h. Regardless of the heating method used, the reaction was complete within 7 h at 80 °C and within 3 h at 100 °C. Water concentration, determined by Karl–Fischer titration, was less than the detection limit of the method (0.01%); this indicates that condensation or hydrolysis reactions were not likely to occur.

Since a stoichiometric feed of the reactants was employed, the reaction rate should depend on the concentration of both reactants (acid and hydroxyl groups). Therefore, assuming that the reaction is first-order with respect to free carboxylic acid groups (C_A), occurring in unreacted maleic anhydride, and first-order with respect to hydroxyl groups (C_B), contained in castor's oil ricinoleic acyl groups, the reaction rate r can be written as:

$$r = kC_A C_B \tag{1}$$

where T is absolute temperature, A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. The differential mass balance equation was calculated as shown in Eq. 2.

$$r = \frac{-C_{A_0}d\eta}{dt} \tag{2}$$

where η represents the anhydride conversion, C_{A_0} the initial molar concentration of acid groups and t reaction time. Conversion was determined by using the following equation:

$$\eta = \left(\frac{Av_0 - Av_f}{Av_0}\right) \times 2 \tag{3}$$

where Av_0 is initial acid value, and Av_f is the final acid value. Note that the coefficient 2 is necessary because the final acid value should be one-half the initial acid value for 100% conversion. Moreover, as shown in Fig. 1, only one of the two acyl groups present in maleic anhydride will react, as confirmed by GPC analysis (discussed below). After substituting Eq. 1 into Eq. 2 and then integrating, the following equations is obtained:

$$\ln\frac{M - \eta}{M(1 - \eta)} = C_{A_0}(M - 1)kt \qquad M \neq 1 \tag{4}$$

where M is the ratio C_{B_0}/C_{A_0}. After solving for η in Eq. 4 and then substituting into Eq. 3, the following equation is obtained upon rearrangement:

Fig. 2 Evolution of the acid value for the maleinization reaction using conventional heating (**a**) and microwave heating (**b**). *Dotted curves* represent the kinetic model. Reaction conditions: 0.33 mol of maleic anhydride and 0.33 mol of castor, turbine stirrer at 500 rpm (2.5 cm radius), under dry nitrogen
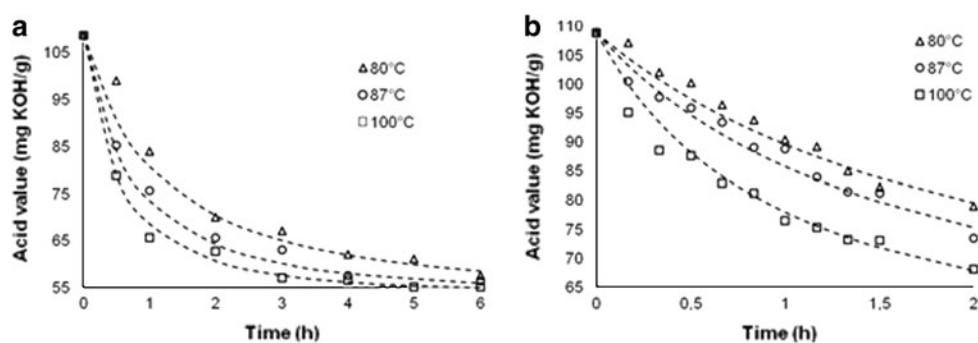
$$A_{v_f} = \frac{A_{v_0}\left(2 - \frac{Me^{kC_{A_0}(M-1)t} - M}{Me^{kC_{A_0}(M-1)t} - 1}\right)}{2} \tag{5}$$

Figure 3a, b show the plotting of Eq. 4 for conventional and microwave heating, respectively. The good fitting of data demonstrates that the kinetic assumption was correct, i.e., the reaction follows first-order kinetics with respect to each reactant at the temperatures evaluated. Dotted curves in Fig. 2a, b were obtained with the kinetic model through Eq. 5. Rate constants (k) were calculated from the slopes of these plots and are given in Table 1.

To determine the effects of microwave heating on this type of reactions, the activation energy and the pre-exponential factor were calculated by using the Arrhenius equation (Eq. 6), which correlates these two parameters with the rate constant.

$$k = A \times e^{\frac{-E_a}{RT}} \tag{6}$$

Figure 4a shows the plotting of Eq. 6 for conventional and microwave heating. There is a good fitting of the data; therefore, the activation energies were calculated from the slopes of the lines and the pre-exponential factors were calculated from the intercepts. Values are given in Table 1.

Thermodynamic reaction parameters were calculated using the Eyring equation derived from transition state theory (Eq. 7) [19, 20].

$$k = \alpha\left(\frac{k_B T}{h}\right)e^{-\frac{\Delta G^{\neq}}{RT}} = \alpha\left(\frac{k_B T}{h}\right)e^{\frac{\Delta S^{\neq}}{R}}e^{-\frac{\Delta H^{\neq}}{RT}} \tag{7}$$

Fig. 3 Kinetic fitting of the maleinization reaction data of Fig. 2, using conventional heating (**a**) and microwave heating (**b**)
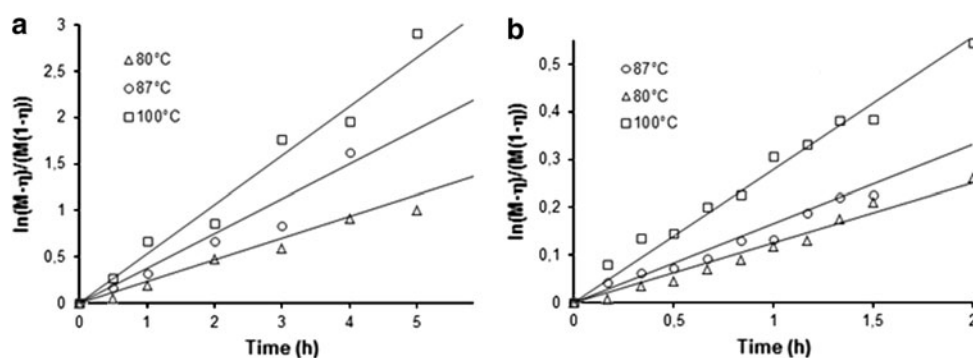

Table 1 Kinetic and thermodynamic parameters for the maleinization reaction, using conventional and microwave heating, for the data plotted in Fig. 2

Parameter	Temperature (°C)	Heating method	
		Conventional	Microwave
k (L/mol h)	80	0.38 ± 0.02	0.20 ± 0.01
	87	0.61 ± 0.03	0.27 ± 0.01
	100	0.85 ± 0.04	0.45 ± 0.02
E_a (kJ/mol)		43 ± 2	43 ± 2
A (L/mol h)		$9.53\ 10^5 \pm 0.05\ 10^5$	$6.15\ 10^5 \pm 0.03\ 10^5$
$\Delta H^{\neq}$ (kJ/mol)		40 ± 2	40 ± 2
$\Delta S^{\neq}$ (kJ/mol K)		-0.21 ± 0.01	$-0.21 + 0.01$
$\Delta G^{\neq}$ (kJ/mol)		114 ± 6	116 ± 6

E_a and A were calculated with Eq. 6. $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were calculated with Eqs. 7–9

Fig. 4 Plotting of the Arrhenius equation (**a**) and Eyring equation (**b**), using conventional and microwave heating, for the kinetic rate constant data given in Table 1
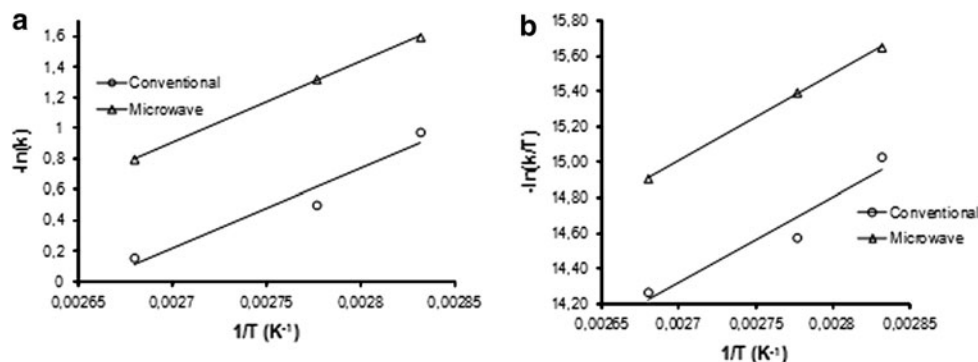
where

$$E_a = \Delta H^{\neq} + RT \tag{8}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{9}$$

and where k_B, h, and α are the Boltzmann's constant, Planck's constant, and the transmission coefficient, respectively, and $\Delta G^{\neq}$, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the standard-state free energy of activation, standard-state entropy of activation, and standard-state enthalpy of activation of transition state at the absolute temperature T, respectively. Assuming that Δ is equal to 1, i.e., there is no equilibrium between the transition state and the reactants, it is possible to calculate the thermodynamic properties in the transition state. Figure 4b shows the plotting of Eq. 7 for conventional and microwave heating. $\Delta S^{\neq}$ was calculated from the slope of the line and $\Delta H^{\neq}$ was calculated from the intercept. $\Delta G^{\neq}$ was calculated by using Eq. 9.

Table 1 shows the kinetic and thermodynamic properties for the reaction. Non-thermal effects of microwaves were not observed because activation energy, enthalpy of activation, entropy of activation and free energy of activation were similar regardless of heating method. However, rate constants and the pre-exponential factor were lower with microwave heating, which could be a consequence of the decrease in dielectric constant of the reaction liquid as the reaction progresses. Maleic anhydride, one of the reactants, has a very high dielectric constant (relative dielectric constant of 52.57, at 20 °C) compared to the dielectric constant of the other compounds present in the liquid (alcohols, esters and carboxylic acids have a relative dielectric constant of 2–5, at 20 °C) [21].

Figure 5a, b show FTIR spectra and the GPC chromatograms of final products taken at 87 °C after 3 h of reaction for conventional and microwave heating. It is observed that the heating method does not affect the product distribution. These analyses indicate that no by-products or condensation products where obtained because the molecular weight and the FTIR spectra are consistent with the MACO structure. Similar results were observed at 80–100 °C. GPC analyses show the presence of one peak corresponding to the addition of one molecule of maleic acid to one molecule of TAG. GPC results suggest the absence of ricinoleic acid oligomers (either in free form, or conjugated to the TAG), which are typically formed via condensation. In addition, Karl–Fischer titration did not show the formation of water, which indicates that condensation reactions, which would lead to products such as a maleic acid group covalently attached to two different triacylglycerols or the formation of ricinoleic acid oligomers, did not occur.

Figure 6 shows the FTIR spectra of final products taken after different reaction times when the reaction was carried out at 100 °C by using microwave heating. The band at 3450 cm^{-1}, related to –OH groups, decreased while the band at 1644 cm^{-1}, related to carbon double bonds, was increased, compared to the castor oil spectra. After 3 h, signals at 1,779 and 1,849 cm^{-1}, corresponding to cyclic anhydride, were not observed, indicating total consumption of maleic anhydride. The transesterification level of a MACO sample obtained at 100 °C using microwave heating MW and after 3 h of reaction was calculated from ^{1}H-NMR analysis (Fig. 7). The signal at 0.8 ppm, corresponding to methyl groups, was used to quantify fatty acyl groups present in castor oil. Using this value and the area of the signal at 3.54 ppm, reflecting the proton attached to the hydroxyl-bonded C12 of ricinoleic acyl groups, the conversion of hydroxyl groups was ca. 30%. Using the protons contained on the double bond of C9–C10 (5.4–5.6 ppm) to quantify the number of ricinoleic acyl groups, a similar conversion of hydroxyl groups of ca. 32% was obtained. The reaction was considered efficient because, under the experimental conditions employed, the theoretical transesterification percentage should be 37.9% to obtain the mono-ester. Signals at 7.1 ppm, related to the protons of the anhydride, were not found in the spectra; but new signals at 6.27 and 6.39 ppm appeared, confirming the formation of the ester.

Fig. 5 FTIR (**a**) and GPC analyses (**b**) of MACO final product. *Conv* conventional heating, *MW* microwave heating. 1,747 and 1,743 are the number average molecular weights (M_n) obtained via GPC
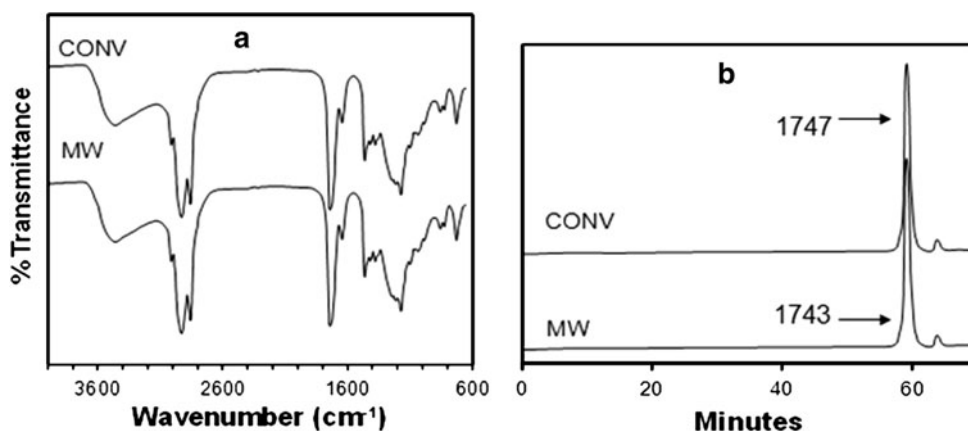
Fig. 6 FTIR spectra of MACO reaction mixtures obtained at 100 °C for (*1*) 0 h, (*2*) 1 h, (*3*) 3 h, (*4*) 6 h, for the reactions described in Fig. 2, using microwave heating
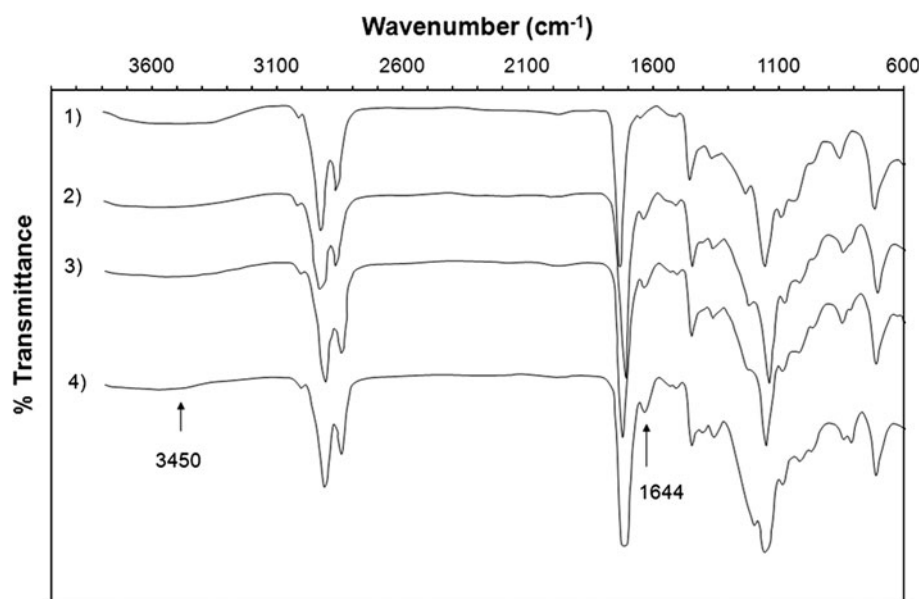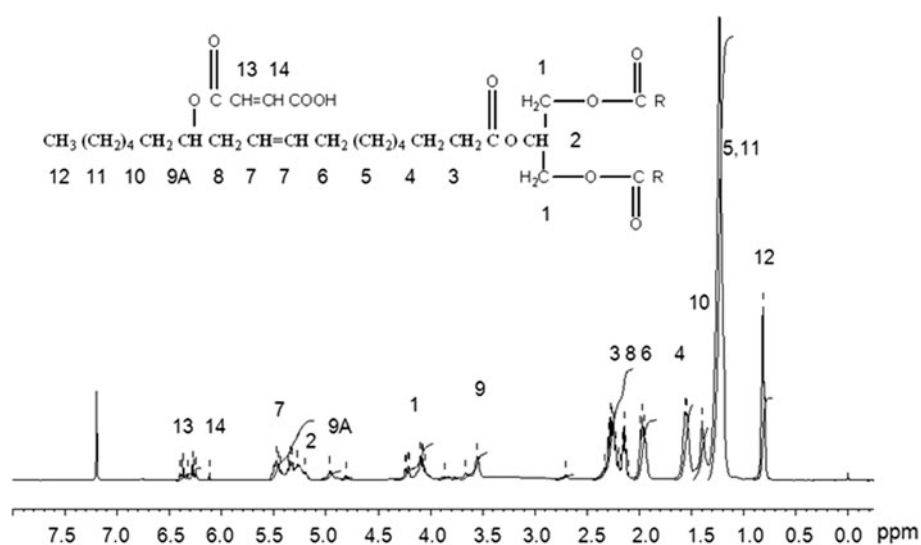

Fig. 7 ^{1}H-NMR analysis of MACO final product, for the reactions described in Fig. 2, using microwave heating. R represents the acyl groups of the triglyceride. The signal identified as 9 (3.54 ppm) reflects the proton attached to the hydroxyl-bonded C12 of ricinoleic acyl groups

The hydroxyl values, obtained by titration, for castor oil and MACO (obtained using microwaves) were 159.5 and 100 mg KOH/g sample, respectively, which indicates the consumption of hydroxyl groups present in the triglyceride. The conversion of the hydroxyl groups, calculated from the hydroxyl values, was 31.8%, a value very close to that obtained by ^{1}H NMR.

Conclusion

The transesterification of castor oil with maleic anhydride was non-catalytic and first-order with respect to each reactant. Non-thermal effects of microwaves were not observed. Activation energy, enthalpy of activation, entropy of activation and free energy of activation were similar regardless of the heating method. Rate constants and the pre-exponential factor were lower with microwave heating, which could be a consequence of the decrease in the dielectric constant of the reaction liquid as the reaction progresses.

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