Chemical Engineering Journal 185–186 (2012) 347–351

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Self-esterification of partially maleated castor oil using conventional and microwave heating

Paula Mazo[a], Luis Rios[a,*], Diana Estenoz[b], Marisa Sponton[b]

[a] Grupo Procesos Fisicoquímicos Aplicados, Sede de Investigación Universitaria, Universidad de Antioquia, cra. 53 #61-30, Medellín, Colombia
[b] Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Universidad Nacional del Litoral-CONICET, Güemes 3450, Santa Fe (3000), Argentina

ARTICLE INFO

Article history:
Received 11 August 2011
Received in revised form 20 January 2012
Accepted 21 January 2012

Keywords:
Castor oil
Maleic anhydride
Esterification
Microwave heating
Maleinization
Kinetics

ABSTRACT

The self-esterification of partially maleated castor oil was studied using conventional and microwave heating. Reactions were followed by measuring the acid number and reaction products were characterized by FTIR and ^{1}H-NMR. A kinetic model, that fit the experimental data, was found. The reaction was non-catalytic, first-order with respect to hydroxyl-groups concentration and first-order with respect to acid-groups concentration. This reaction proceeded more quickly when microwaves were used and showed the presence of non-thermal effects of microwave heating, which were evidenced by the 10% decrease in the activation energy and the 182% increase in the pre-exponential factor.

1. Introduction

Maleinization reactions have been 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 have been 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 biomodifiers for biodegradable polymers [3,4]. For this last application, maleated castor oil (MACO) has been widely investigated [5–7]. MACO is produced by the esterification of castor oil with maleic anhydride and this reaction proceeds in two stages, as shown in Fig. 1. The first stage (without condensation) is fast, non-catalytic, and first-order with respect to each reactant [8], while the second stage (self-esterification, with condensation) is a slow equilibrium reaction that can be catalyzed with acids, such as sulfuric acid, and is enhanced by removing water [9]. Therefore, 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 alternative technology to promote esterification reactions; for instance, reductions in reaction times have been observed using microwave heating in the esterifications of lauric acid with 1,2-propanediol using commercial lipases [10], propionic acid with ethanol using Amberlyst-15 [11], 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 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: (i) thermal effects, (ii) specific thermal effects, and (iii) 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 caused by the unique nature of microwave heating. These effects should be defined as accelerations of chemical transformations in a microwave field that cannot be achieved or duplicated by conventional heating, but essentially are still thermal effects. Hot spots and liquid overheating are the most common specific thermal effects. Most non-thermal

---

* Corresponding author. Tel.: +57 4 2196589; fax: +57 4 2196565.
E-mail addresses: larios@udea.edu.co, lariospfa@gmail.com (L. Rios).

1385-8947/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2012.01.099

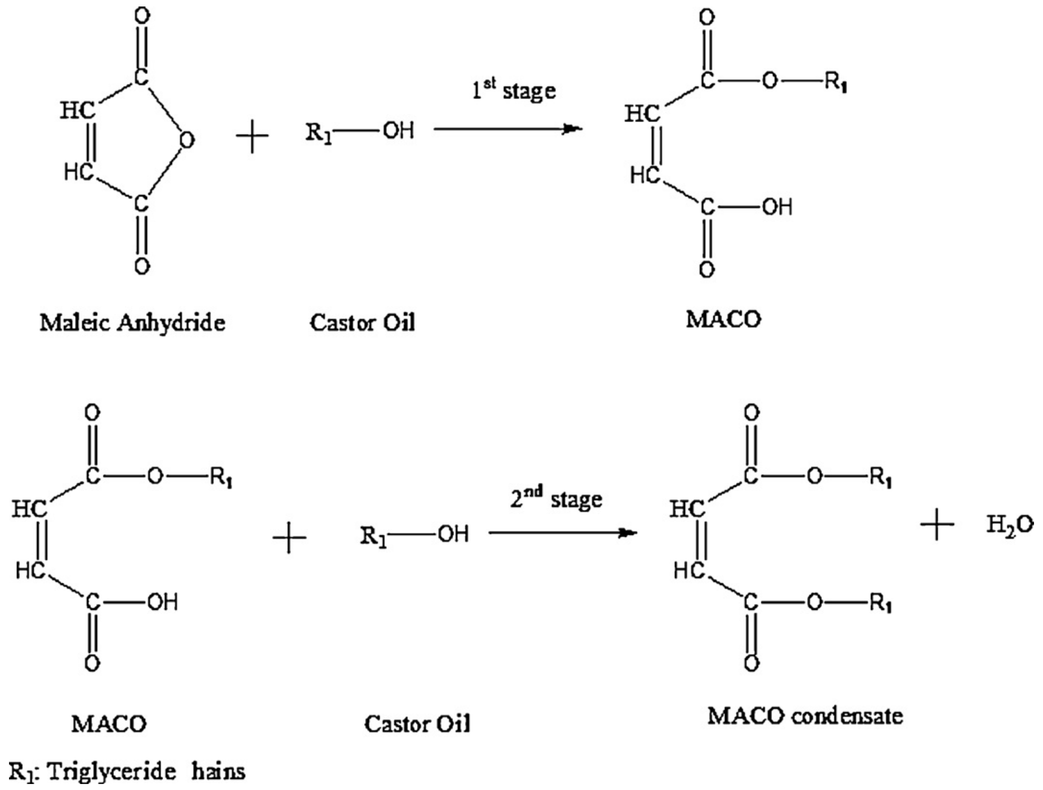

Fig. 1. Reaction scheme.

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 (i) increased pre-exponential factor *A* of the Arrhenius equation (collision efficiency can be improved by mutual orientation of polar molecules involved in the reaction); (ii) 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 manuscript presents results on the kinetics of the self-esterification of partially maleated castor oil, 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. The product of this reaction (SEMACO) is an interesting polyol for the synthesis of polymers such as polyurethanes and polyesters, because the hydroxyl value is decreased and the molecular weight is increased, compared to MACO. Besides, it can be prepared keeping some acid groups that introduce more functionality to the molecule [7].

2. Materials and methods

2.1. Materials

Castor oil (CO) USB-grade (hydroxyl value 159.5 mg of KOH/g, 930 g/mol) and commercial-grade (Merck, Whitehouse Station, NJ, USA) maleic anhydride (MA), were used. A thermocouple J was used to measure and control the temperature. The microwave oven was an ETHOS (MLS GmbH, Leutkirch, Germany) with a nominal power of 1000 W.

2.2. Synthesis of partially maleated castor oil (PMACO)

Maleic anhydride (32.7 g) and castor oil (311 g) were added to a 250 mL four-necked and round-bottom flask equipped with a mechanical stirrer (turbine, 500 rpm), a thermometer, and an inlet of dry nitrogen. The reaction proceeded with continuous stirring at 100 °C. Final product was washed with water to remove the excess anhydride and/or maleic acid. FTIR spectra of the product showed that 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. Signals at 1779 and 1849 cm^{-1}, corresponding to cyclic anhydride were not observed indicating total consumption of maleic anhydride. The esterification level of a MACO sample obtained at 100 °C was calculated from ^{1}H-NMR analyses. The signal at 0.8 ppm, corresponding to methyl groups, was taken as standard. Using this value and the area of the signal at 3.54 ppm, related to the proton of the carbon atom attached to the OH, the conversion of hydroxyl groups was ca. 30%. The reaction was considered efficient because, under the experimental conditions, the theoretical esterification percentage should be 37.9% to obtain the mono-ester. Signals at 6.27 and 6.39 ppm, related to the anhydride (double-bonded carbons vicinal to the anhydride group), were not found in the spectra, confirming the formation of the ester. Product (PMACO) had a hydroxyl value of 89.9 mg KOH/g and an acid number of 58.9 mg KOH/g.

2.3. Synthesis of self-esterified maleated castor oil (SEMACO)

Partially maleated castor oil (PMACO, 343.7 g), obtained in the first stage, was self-esterified without catalyst. The reaction

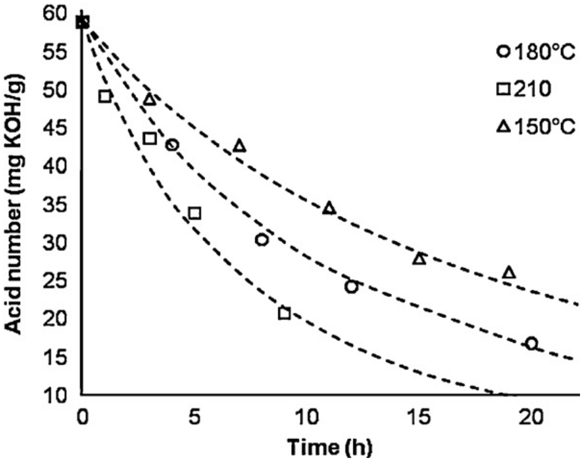

Fig. 2. Evolution of the acid number for the self-esterification reaction using conventional heating. Dotted curves are the kinetic model.

proceeded with continuous stirring (turbine, 500 rpm) at various temperatures (150, 180 and 210 °C). Water was removed to eliminate reverse hydrolysis reactions and to avoid effects of the interaction of water with microwaves. Water removal was achieved by introducing nitrogen as described by Skrzypek et al. [9]. A nitrogen flow of 6 mL/s was used. Under these conditions, Karl–Fisher titration did not show the presence of water in the reacting liquid. Other reaction conditions were: reaction volume of 0.351 L, initial molar concentration of acid groups (C_A) of 0.95 mol/L, initial molar concentration of hydroxyl groups (C_B) of 1.57 mol/L. Experiments were performed in triplicate and the data averaged.

2.4. Characterization methods

Reactions were monitored by determining the acid number according to the ASTM D4662-03 method and titrating with KOH ethanol-solution (0.1 mol/L). Hydroxyl value (OH) was measured by titration according to the ASTM D4274-05 method. 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 inspection, 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 3689.22 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 PerkinElmer FTIR spectrometer (Waltham, MA, USA) within the 400–4000 cm^{-1} wave number range at 4 cm^{-1} resolution. Samples were prepared by coating the reaction product on the surface of KBr tablets.

3. Results and discussion

Reaction progress was assessed by measuring the acid number and results are shown in Figs. 2 and 3 for conventional and microwave heating, respectively. It is evident that the reaction proceeds more quickly when microwaves are used.

Because none of the reactants is in excess, 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 acid groups (C_A) and first-order with respect to hydroxyl groups (C_B), the reaction rate r can be written as:

$$r = kC_AC_B \tag{1}$$

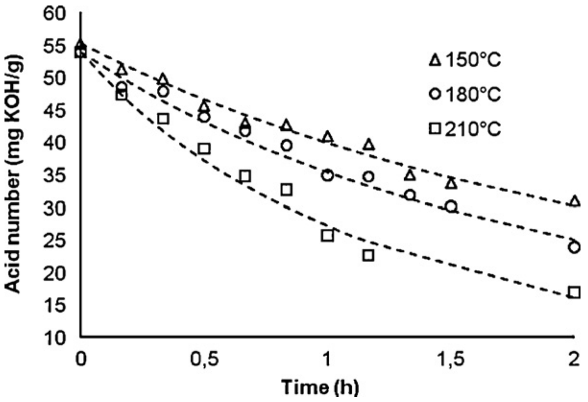

Fig. 3. Evolution of the acid number for the self-esterification reaction using microwave heating. Dotted curves are the kinetic model.

The differential mass balance equation is shown in Eq. (2) (if water were not removed from the system).

$$r = \frac{C_{A0}d\eta}{dt} \tag{2}$$

where η represents the anhydride conversion, C_{A0} is the initial molar concentration of acid groups and t is reaction time. Because the acid number was measured at variable reaction volume (after water removal), it must be converted to an acid number at constant reaction volume (without water removal). Therefore, the conversion was calculated as follows:

$$\eta = \frac{A\nu_0 - A\nu_f((56,100 - 18A\nu_0/56,100 - 18A\nu_f))}{A\nu_0} \tag{3}$$

where $A\nu_0$ is initial acid number, and $A\nu_f$ is the final acid number. 56,100 is the molecular mass of KOH expressed in mg/mol and 18 is the molar mass of water. This equation takes in account the decreasing mass due to water removed from system during the reaction course [9]. After integrating Eq. (2), the following equations were obtained (M is the ratio C_{B0}/C_{A0}):

$$\ln\frac{M-\eta}{M(1-\eta)} = C_{A0}(M-1)kt \qquad M \neq 1 \tag{4}$$

$$A\nu_f = \frac{A\nu_o(1-\eta)}{1-(18/56,100)\eta} \tag{5}$$

$$\eta = \frac{M(e^{kC_{A0}(M-1)t}-1)}{Me^{kC_{A0}(M-1)t}-1} \tag{6}$$

Figs. 4 and 5 show the plotting of Eq. (4) for conventional and microwave heating, respectively. The good fitting indicates that the

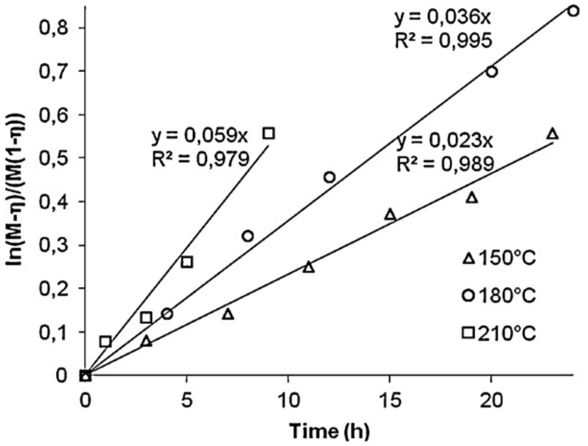

Fig. 4. Kinetic fitting of the self-esterification reaction, using conventional heating.

Table 1
Kinetic and thermodynamic parameters for the self-esterification reaction, using conventional and microwave heating.

Parameter	Temperature (°C)	Heating method Conventional	Microwaves
k (L/mol h)	150	0.04	0.23
	180	0.06	0.30
	210	0.09	0.53
E_a (kJ/mol)		26.06	23.45
A (L/mol h)		60.64	170.91
$\Delta H^{\neq}$ (kJ/mol)		22.31	19.70
$\Delta S^{\neq}$ (kJ/mol K)		–0.29	–0.28
$\Delta G^{\neq}$ (kJ/mol)		145.29	139.04

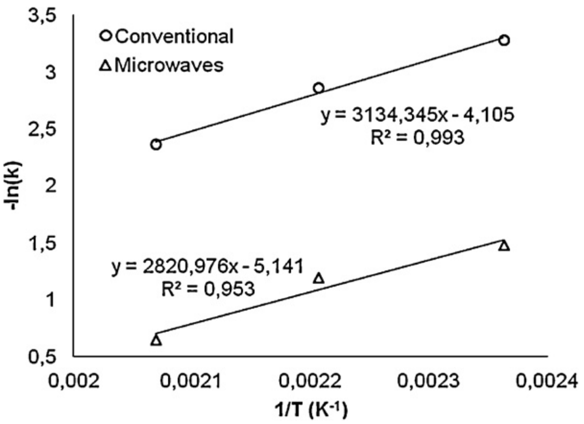

Fig. 6. Plotting of the Arrhenius equation, using conventional and microwave heating.

kinetic assumption is reasonable, i.e., the reaction follows first-order kinetics with respect to each reactant at the temperatures evaluated. Dotted curves in Figs. 2 and 3 were obtained with the kinetic model through Eqs. (5) and (6). Rate constants (k), calculated from the slopes of these plots, are shown in Table 1. The rate constants for microwave heating were considerably higher than those for conventional heating.

To determine the effects of microwave heating on this reaction, the activation energy and the pre-exponential factor were calculated by using the Arrhenius equation (Eq. (7)), which correlates these two parameters with the rate constant.

$$k = A \times e^{-E_a/RT} \tag{7}$$

where T is absolute temperature, A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). Fig. 6 shows the plotting of Eq. (7) for conventional and microwave heating. Because of the few points, just an estimation of the activation energies and pre-exponential factors was done, to obtain more precise data the reaction should be carried out at other temperatures. 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. Results are shown in Table 1.

Thermodynamic reaction parameters were calculated using the Eyring equation derived from the transition state theory (Eq. (8)) [17,18].

$$k = \alpha\left(\frac{k_B T}{h}\right) \times e^{-\Delta G/RT} = \alpha\left(\frac{k_B T}{h}\right) \times e^{\Delta S/R} \times e^{-\Delta H/RT} \tag{8}$$

$$E_a = \Delta H^{\neq} + RT \tag{9}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{10}$$

where k_B (1.38066E−23 J/K)), h (6.626068E−34 J s), 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 α 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. Fig. 7 shows the plotting of Eq. (8) 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. (10).

Table 1 shows the kinetic and thermodynamic properties for the reaction. The decrease (ca. 10%) in the activation energy and the increase (ca. 182%) in the pre-exponential factor confirm the presence of non-thermal effects when using microwave heating. It follows from Fig. 6 that to obtain any specific value of the rate constant a lower temperature is required with microwaves than with conventional heating. This indicates that thermal effects of microwaves are also present. The latter can be either rapid dielectric heating or specific thermal effects.

Fig. 8 shows FTIR spectra of SEMACO (20 mg KOH/g acid value) obtained with conventional (210 °C for 10 h) and microwave heating (210 °C for 2 h). These spectra show the presence of the same functional groups in both samples. The bands at 3450 cm^{-1} are decreased, compared to PMACO, which indicates consumption of hydroxyl groups. From the area of the signal at 3.54 ppm in the ^{1}H-NMR spectra (not shown), related to the proton of the carbon atom attached to the OH, the conversion of hydroxyl groups was ca. 36.6% for a sample obtained after 2 h with microwave heating at 210 °C.

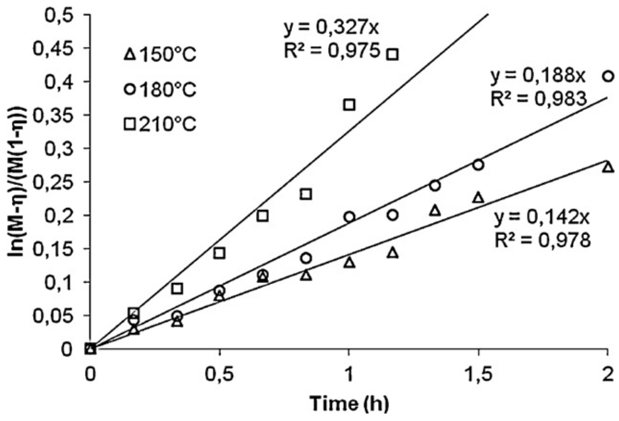

Fig. 5. Kinetic fitting of the self-esterification reaction, using microwave heating.

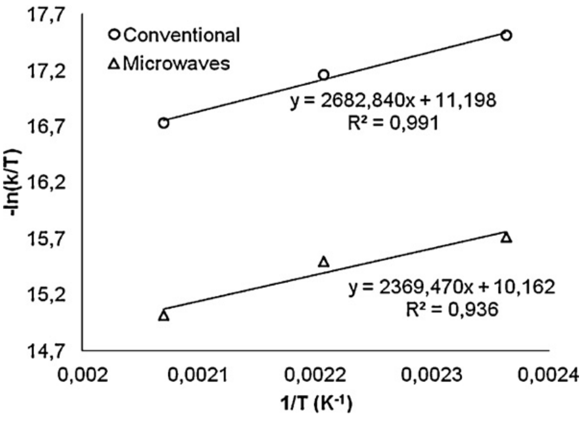

Fig. 7. Plotting of the Eyring equation, using conventional and microwave heating.

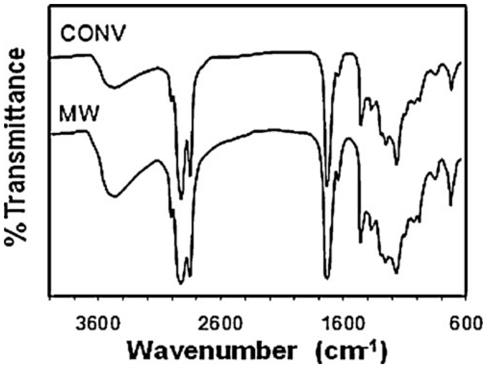

Fig. 8. FTIR spectra of SEMACO obtained with conventional (210 °C, 10 h) and microwave (210 °C, 2 h) heating.

4. Conclusions

The self-esterification of partially maleated castor was non-catalytic, first-order with respect to hydroxyl-groups concentration and first-order with respect to acid-groups concentration. This reaction proceeded more quickly when microwaves were used and showed the presence of non-thermal effects of microwave heating, which were evidenced by the 10% decrease in the activation energy and the 182% increase in the pre-exponential factor.

Acknowledgments

Authors thank to “Universidad de Antioquia”, “Departamento administrativo de ciencia, tecnología e innovación-COLCIENCIAS (Colombia)” and “Agencia Nacional de Promoción Científica y Tecnológica, ANPCyT” (Argentina) for the financial support.

References

[1] H. Warth, R. Mulhaupt, B. Hoffmann, S. Lawson, Polyester networks based upon epoxidized and maleinated natural oils, Angew. Makromol. Chem. 249 (1997) 79–92.

[2] L. Candy, C. Vaca-Garcia, E. Borredon, Synthesis and characterization of oleic succinic anhydrides: structure-property relations, J. Am. Oil Chem. Soc. 82 (2005) 271–277.

[3] H. Tomoda, Y. Sugimoto, Y. Tania, S. Watanabe, Characteristic properties of cutting fluid additives derived from the reaction products of hydroxyl fatty acids with some acid anhydrides, J. Surfactant Deterg. 1 (1998) 533–537.

[4] H.J. Wang, M.Z. Rong, M.Q. Zhang, J. Hu, H.W. Chen, T. Czigány, Biodegradable foam plastics based on castor oil, Biomacromolecules 9 (2008) 615–623.

[5] S. Ghorui, N.R. Bandyopadhyay, D. Ray, S. Sengupta, T. Kar, Use of maleated castor oil as biomodifier in unsaturated polyester resin/fly ash composites, Ind. Crops Prod. 34 (2011) 893–899.

[6] E. Mistri, S. Routh, D. Ray, S. Sahoo, M. Misra, Green composites from maleated castor oil and jute fibres, Ind. Crops Prod. 34 (2011) 900–906.

[7] P. Mazo, L. López, D. Restrepo, L. Rios, Synthesis and characterization of pressure-sensitive adhesives of waterborne polyurethane from maleinizated castor oil, Polim. Cienc. Tecnol. 20 (2010) 134–140.

[8] P. Mazo, D. Estenoz, L. Rios, Kinetics of the esterification of maleic anhydride with castor oil, Lat. Am. Appl. Res. 41 (2011) 11–15.

[9] J. Skrzypek, J.Z. Sadlowski, M. Lachowska, M. Turzański, Kinetics of the esterification of phthalic anhydride with 2-ethylhexanol. I. Sulfuric acid as a catalyst, Chem. Eng. Process. 33 (1994) 413–418.

[10] G.D. Yadav, S.L. Piyush, Intensification of enzymatic synthesis of propylene glycol mono-laurate from 1,2-propanediol and lauric acid under microwave irradiation: kinetics of forward and reverse reactions, Enzyme Microb. Technol. 38 (2006) 814–820.

[11] B. Toukoniitty, J.-P. Mikkola, K. Eränen, T. Salmi, D. Yu Murzin, Esterification of propionic acid under microwave irradiation over an ion-exchange resin, Catal. Today 100 (2005) 431–435.

[12] P. Mazo, L. Rios, Esterification and transesterification assisted by microwaves of crude palm oil. Homogeneous catalysis, Lat. Am. Appl. Res. 40 (2010) 337–342.

[13] P. Mazo, L. Rios, Esterification and transesterification assisted by microwaves of crude palm oil. Heterogeneous catalysis, Lat. Am. Appl. Res. 40 (2010) 343–349.

[14] A. Hoz, Á. Díaz-Ortiz, A. Moreno, Microwaves in organic synthesis, thermal and non-thermal microwave effects, Chem. Soc. Rev. 34 (2005) 164–178.

[15] O. Kappe, A. Stadler, Microwaves in Organic and Medicinal Chemistry, Wiley-VCH, Weinheim, 2005.

[16] A. Loupy, Microwaves in Organic Synthesis, Wiley-VCH, Weinheim, 2006.

[17] S.W. Benson, The Foundations of Chemical Kinetics, McGraw-Hill, New York, 1960.

[18] S. Glasstone, K.J. Laidler, H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.