Kinetics of nopyl acetate synthesis by homogeneously catalyzed esterification of acetic acid with nopol

Cinética de la síntesis de acetato de nopilo mediante esterificación de ácido acético con nopol homogéneamente catalizada

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ABSTRACT: The esterification of nopol with acetic acid to produce nopyl acetate using sulfuric acid as homogeneous catalyst was studied. The reactions were carried out in a batch reactor, at different temperatures (50, 60, 70 and 80 °C), catalyst concentrations (0.0184, 0.0275, 0.0367 and 0.0480 $molL^{-1}$ and molar ratio of acetic acid to nopol (1: 1, 1:2, 1:3 and 1: 4); the chemical equilibrium composition was measured at those reaction conditions. It was found that the equilibrium composition is a weak function of temperature, equilibrium conversion was 63, 68, 71 and 75% at 50, 60, 70 and 80°C, respectively. The reaction was described with a simple power-law model with a second-order kinetic model for both the forward and the backward reaction, using concentration and activities which were predicted by the Universal Functional group Contribution (UNIFAC) method for considering non-ideal behavior of the liquid phase. The forward reaction rate and the equilibrium constants increased with temperature; the relation of the pre-exponential factor with the catalyst amount was evaluated. The activation energy and pre-exponential factor estimated for the forward reaction using the kinetic model based on concentration, were respectively, 28.08 $kJmol^{-1}$ and 11126 $Lmol^{-1}h^{-1}$ with a concentration of catalyst of 0.0275 M. Using the kinetic model based on activities, the forward reaction rate constant was 28.56 $kJmol^{-1}$ and the $k_{fo,act}$ was 33860 $Lmol^{-1}h^{-1}$. The enthalpy (34.90 $kJmol^{-1}$) and the entropy (0.12 $kJmol^{-1}K^{-1}$) of reaction were determined using van't Hoff equation.

RESUMEN: Se estudió la esterificación de nopol con ácido acético para producir acetato de nopilo utilizando ácido sulfúrico como catalizador homogéneo. Los experimentos se llevaron a cabo en un reactor por lotes variando la temperatura (50, 60, 70 y 80 °C), la concentración del catalizador (0.0184, 0.0275, 0.0367 y 0.0480 $molL^{-1}$) y la relación molar de ácido acético a nopol (1: 1, 1:2, 1:3 y 1: 4); la composición del equilibrio químico se midió a las condiciones de reacción. La conversión de equilibrio fue 63, 68, 71 y 75% a 50, 60, 70 y 80°C, respectivamente. La reacción se describió con un modelo de potencia simple con un modelo de segundo orden en ambas direcciones, usando concentraciones y actividades, las cuales se predijeron con el método de contribución de grupos UNIFAC. Se determinaron las constantes de velocidad de la reacción directa y la constante de equilibrio, las cuales aumentaron con la temperatura; se evaluó la relación del factor pre-exponencial con la cantidad de catalizador. La energía de activación y el factor pre-exponencial estimados para la reacción hacia adelante usando el modelo basado en concentración fueron respectivamente 18.08 $kJmol^{-1}$ y 11126 $Lmol^{-1}h^{-1}$ con una concentración de catalizador de 0.0275 M. Usando el modelo basado en actividades la constante de velocidad directa fue 28.56 $kJmol^{-1}$ y el factor pre-exponencial 33860 $Lmol^{-1}h^{-1}$. La entalpía (34.90 $kJmol^{-1}$) y la entropía (0.12 $kJmol^{-1}K^{-1}$) de reacción se determinaron usando la ecuación de van't Hoff.

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1. Introduction

Esters are compounds that are widely studied due to their properties and uses in various industries such as food,

fragrances, paints, fuels, among others [1, 2]. The esters used in this kind of industries [3–6] are obtained from esterification of terpenols that are obtained from sources as turpentine. Nopyl acetate (6-6 - dimethylbicyclo-(3, 1,1)-2-heptene-2-ethyl acetate) is an ester that is not found in nature and it is used as a low cost alternative to linalyl acetate in a variety of perfumes and household products because of its pleasant sweet fruity-woody odor [7, 8]. Currently, nopyl acetate is obtained from the Prins reaction between β -pinene (1) and paraformaldehyde (2) with a subsequent acetylation of its intermediary nopol (3) with acetic anhydride (4) at temperatures from 115°C for the catalyzed reaction with $ZnCl_2$ to 230˚C without using catalyst, Scheme 1 [9, 10].

The simplest way to produce esters with high performance is by direct esterification of acids with alcohol using homogeneous or heterogeneous catalysts [11, 12]. As the esterification reactions are very slow they require typically several days to attain the equilibrium in the absence of a catalyst [13]. The esterification reactions of carboxylic acids are traditionally carried out using homogeneous catalysts, usually strong acids as HCl, HI, H_3PO_4 and H_2SO_4 [13–15]. It has been reported that although acetic acid itself may act as a catalyst, its activity for reaction is very low due to its weak acidic nature [16]. Esterification of acetic acid with ethanol in absence of catalyst yields less than 10% even at a higher temperature, which shows that the reaction is very slow and that it needs a catalyst to enhance the rate [17]. Concentrated H_2SO_4 catalyst is used in the industries for the esterification reactions because it is more efficient and economical than other catalysts [18]; its better catalytic activity has been attributed to its greater density of acid sites per gram [14]. H_2SO_4 has Brønsted-type acid sites and, is stable and liquid in (nearly) the pure form; moreover, concentrated sulfuric acid is a great dehydrating agent. As sulfuric acid is neither a strong oxidant (nitric acid) nor a strong reductant (hydroiodic acid), it reduces the possibility for undesired side reactions [19].

Liu et al. [20] reported the use of acid ionic liquids for the synthesis of terpinyl acetate with a selectivity of 87% from α-terpineol (conversion of 99%) and by esterification of α-pinene with acetic acid with a yield of 35.7% [21, 22]. Sulfonic functionalized ionic liquids (SFILs) were reported for the synthesis of terpene esters from several terpenols (geraniol, nerol, citronellol, terpinol, dihydromyrcenol) and acetic anhydride; the kinetics for SFILs in the esterification of geraniol was determined using a pseudohomogeneous model considering the main reaction and the transformation of geraniol into linalool [23]. Liquid-phase esterification of camphene was reported over silica supported $H_3PW_{12}O_{40}$ producing isobornyl carboxylates with 80–90% yield [23].

For the reaction mechanism of esterification, reactions in presence of strong acids such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and para-toluene sulfonic acid (p-TSA), it has been probed that the catalysts promote the protonation of the carbonyl oxygen on the carboxylic group that is then activated with nonprotonated alcohol (slowest step) to yield a tetrahedral intermediate that, by decomposition, produces the products of reaction, ester and water [13, 24–27].

For acetic acid esterification with nopol using homogeneous catalysts, no kinetic data are reported. In this contribution, the nopyl acetate production, Scheme 2, using sulfuric acid as a homogeneous catalyst and at different temperatures, feed molar ratios and concentrations of catalyst was analyzed. In this research, the reaction was followed by titration of the acetic acid with standard solution of NaOH at different reaction times, a methodology that has been also reported for following the kinetic of an esterification reaction [28]; also the kinetics of this type of reaction has been determined following the water concentration using Karl Fischer titrator [29]. A kinetic model was proposed based on the acetic acid conversion at different reaction conditions, constant parameters of the kinetic equation were determined and the kinetics was modeled based on concentrations and activities.

2. Experimentation

2.1 Reagents

Toluene (JT Baker, 99.5% w/w), nopol (Boc Sciences, 99.15% w/w), acetic acid (Merck, 99.5% w/w), and sulfuric acid (JT Baker, 97.99% w/w) were used. For the preparation and standardization of the titration solution to quantify the acetic acid, potassium hydrogen phthalate (Merck), sodium hydroxide (Carlo Erba) and deionized water were used; the indicator used for titrations was phenolphthalein in ethanol solution (Chemi, 0.1% w/w).

2.2 Catalytic tests

The esterification reactions were carried out in a 25 mL three neck round-bottom flask heated by an oil bath placed in a hot plate with magnetic stirring and temperature controller (Heidolph MR Hei - Standard, EKT Hei-Con). Stirring was kept constant at 500 rpm to ensure uniform mixing. The reaction was studied at several temperatures (50, 60, 71 and 80°C) with a molar ratio of acetic acid to nopol of 1:1, at several molar ratios of acetic acid to nopol (1:1, 1:2, 1:3 and 1:4) at 80°C with a constant concentration of nopol and catalyst concentrations (0.0184, 0.0275, 0.0367 and 0.0480 $molL^{-1}$) with a molar ratio of acetic acid to nopol of 1:1 and at 80°C. A 0.3 M solution of
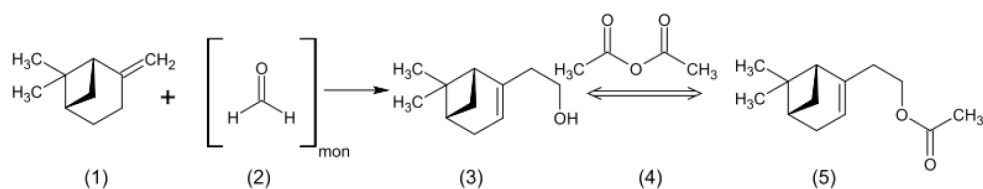
Scheme 1 Synthesis of nopyl acetate starting from β-pinene and paraformaldehyde

$$\text{Nopol} + \text{Acetic acid} \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} \text{Nopyl acetate} + \text{Water}$$
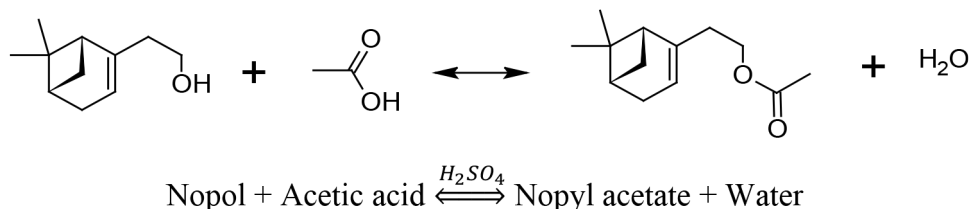
Scheme 2 Synthesis of nopyl acetate ($C_{13}H_{20}O_2$) starting from nopol ($C_{11}H_{18}O$) and acetic acid (CH_3COOH)

nopol in toluene (20 mL) was added first into the reactor and then heated to the desired temperature, when the temperature was reached, the acetic acid and the sulfuric acid was added. Samples of 0.160 mL were taken at regular time intervals and equal volume of solvent was added for keeping the reaction mixture volume constant; the sample was mixed with 20 mL of distilled water and settled into an ice bath for stopping the reaction and their acetic acid concentration was determined by titration with a standard solution of NaOH 0.1 N and phenolphthalein as an indicator using a Dosimat 775. The acetic acid concentration of each sample was determined with Equation (1) and the acetic acid conversion was obtained with Equation (2). Despite the catalytic activity of acetic acid itself [30, 31], the autocatalysis could be ignored under the present experimental conditions because of its negligible contribution to the overall reaction rate. Considering the reaction stoichiometry, the concentrations of the other reactants were calculated from the acetic acid concentration.

$$(C_f)_A = \frac{V_{NaOH} * C_{NaOH}}{0.16} \tag{1}$$

$$X_A(\%) = \frac{(C_i - C_f)_A}{(C_i)_A} * 100\% \tag{2}$$

Where $\mathbf{C_i}$ and $\mathbf{C_f}$ are the initial and final concentration $(molL^{-1})$ respectively and A is acetic acid. As NaOH used in titration procedure could also react with sulfuric acid present in the sample, blank tests were carried out with solvent, nopol and sulfuric acid solution at several temperatures and catalyst concentrations, and the volume found in those titrations was subtracted of the volume of NaOH solution required for the titration of each reaction sample. From repeated experiments, it was found that

standard deviation of calculated concentrations was 0.008, 0.013, 0.021 and 0.015 for catalytic tests at 50, 60, 70 and 80°C, respectively.

3. Results and discussion

3.1 Effect of temperature

The influence of temperature between 50 and 80°C for a fixed acetic acid to nopol ratio of 1:1 and catalyst concentration of 0.0275 M, was evaluated in the conversion of acetic acid over time, as shown in Figure 1. The conversion of acetic acid increases with temperature because of acceleration of the forward reaction, however the temperature effect is higher after 20 h of reaction. The rate of reaction and hence conversion increases as temperature increased. Equilibrium conversions of 63, 68, 71 and 75% were respectively achieved at 50, 60, 70 and 80°C.

3.2 Effect of catalyst concentration

The effect of the amount of catalyst at 80°C, Figure 2, was evaluated. It was found that at low concentrations of sulfuric acid, acetic acid conversion was lower for short reaction times, but when the reaction reaches the equilibrium the lowest concentrations are favored. It is noteworthy that the reaction performed at 0.0184 M did not reach equilibrium in the studied time. The equilibrium conversion was 76, 75 and 60% for concentrations of catalyst of 0.0275, 0.0367 and 0.0458 M respectively. The amount of catalyst influences the reaction rate, because more H^+ions become available when the amount of catalyst in the mixture increases. The addition of catalyst
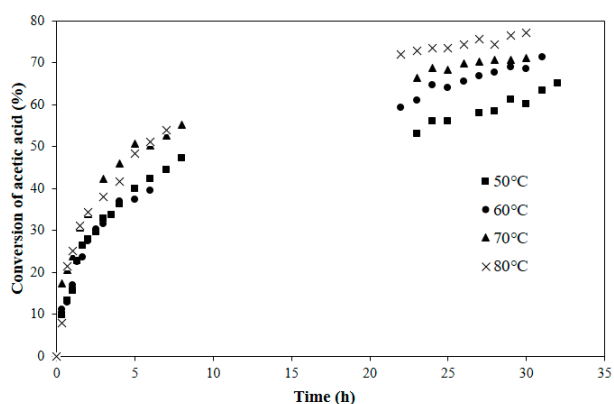
Figure 1 Effect of temperature on reaction kinetics. Reaction conditions: C_{H2SO4}= 0.0275 M, acetic acid:nopol molar ratio of 1:1, C_{Nopol} = 0.2941 M, 500 rpm
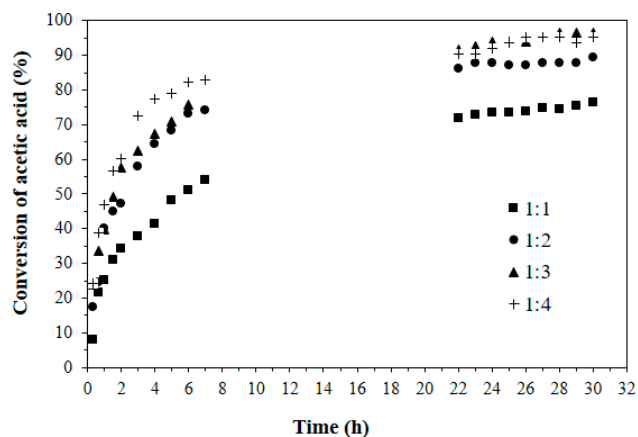

Figure 3 Effect of acetic acid to nopol initial mole ratio on the acetic acid conversion. Reaction conditions: 80°C, C_{Nopol} = 0.2941 M, C_{H2SO4} = 0.0275 M

caused a change of color of the reaction mixture and the formation of a precipitate when the highest amount of catalyst was used; perhaps this was the cause of its lower activity at high reaction time.
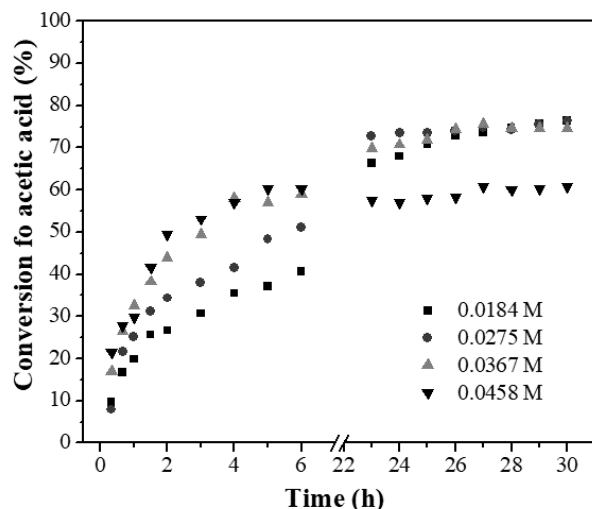

Figure 2 Effect of catalyst concentration on reaction kinetics. Reaction conditions: 80°C, acetic acid:nopol molar ratio 1:1, C_{Nopol} = 0.2941 M, 500 rpm

3.3 Effect of initial reactant mole ratio

The effect of feed mole ratio at 80°C and with a catalyst concentration of 0.0275 M was studied, as shown in Figure 3. It is remarkable that for an acid: alcohol mole ratio of 1:1 the conversion of acetic acid is much less than for other molar ratios evaluated, this was expected because the reactions with a feed molar ratio of 1: 2, 1: 3 and 1: 4 have an excess of nopol available to react with acetic acid. This trend is similar to those reported

for other reactions of esterification with acetic acid [11, 28, 29], and in the esterification of myristic acid with isopropanol and n-propanol using p-toluene sulphonic acid, where the equilibrium conversion decreased when alcohol concentration diminished [30]. It is also noted that for reactions with excess of alcohol, the equilibrium conversion is similar, reaching values greater than 90%. The highest acetic acid conversion (96%) was obtained with a molar feed ratio of acid: alcohol of 1:3 after 28 h of reaction.

3.4 Kinetic model

Concentration based model

Some kinetic models for esterification reactions in presence of homogeneous catalysts have been reported, in the esterification of acetic acid with methanol in the presence of hydrogen iodide [28], sulfuric acid [31] or acetic acid itself [32]; kinetic models were proposed based on concentrations and activity coefficients. Authors found that the fit of the model with the concentration-based description was very good [13]; a reversible second order kinetic rate equation in the case of the use of sulfuric acid as catalyst [28] and the use of activities in the kinetic model instead of mole fractions results in a much smaller residual error [31]. In the esterification of n-butanol with acetic acid catalyzed by noncorrosive Brønsted acidic ionic liquids, it was found that a pseudohomogeneous (PH) kinetic model successfully correlates the experimental data [32]. It was reported that the esterification of myristic acid with isopropanol with n-propanol using p-toluene sulphonic acid as catalyst for a temperature range of 343–403 K, the reactions follow first order kinetics in all components [30]. The majority of the researchers report that an esterification reaction follows second order kinetics, first-order with respect to each reagent

[2, 14, 19, 30]. It is assumed an elementary second-order reversible reaction, first-order with respect to each reagent for the reactions carried out with a molar ratio of 1:1 of acetic acid to nopol. The reaction rate expression is presented in Equation (3) [33].

$$-r_A = -\frac{dC_A}{dt} = (k_f C_A C_B - k_b C_C C_D) \quad (3)$$

Where C_A, C_B, C_C, C_D are the concentrations of acetic acid, nopol, nopyl acetate and water respectively, k_f and k_b are the forward and backward reaction rate constants, respectively. The reaction rate constants k_f and k_b are assumed to be linearly dependent on the catalyst concentration. Various studies support this assumption [2, 34–36]. As at the beginning of the reaction the acetic acid and nopol concentrations are the same (molar ratio 1:1), there is no presence of nopyl acetate and water and the reaction volume was maintained constant during the reaction, using the definition of conversion, X_A, Equation (4) and relating all concentrations in terms of conversion Equation (5) is obtained, where C_{A0} is the initial concentration of acetic acid.

$$X_A = 1 - \frac{C_A}{C_{A0}} \quad (4)$$

$$-r_A = C_{A0}\frac{dX_A}{dt} = (k_f C_{A0}^2(1 - X_A)^2 - k_b(C_{A0}X_A)^2) \quad (5)$$

With the definition of the equilibrium constant, Equation (6) [33], the Equation (7) is obtained.

$$K_{eq} = \frac{k_f}{k_b} \quad (6)$$

$$-r_A = \frac{dX_A}{dt} = k_f C_{A0}\left((1 - X_A)^2 - \frac{X_A^2}{K_{eq}}\right) \quad (7)$$

Since at equilibrium the reaction rate, Equation (7), is zero, the K_{eq} in terms of the equilibrium conversion of acetic acid, X_{Ae}, is given by Equation (8) for an equimolar initial concentration.

$$K_{eq} = \frac{X_{Ae}^2}{(1 - X_{Ae})^2} \quad (8)$$

Equation (9) is obtained by combining Equations (7) and (8).

$$\frac{dX_A}{dt} = k_f C_{A0}\left[(1 - X_A)^2 - \frac{X_A^2}{K_{eq}}\right] \quad (9)$$

$$\frac{dX_A}{dt} = \frac{k_f C_{A0}}{K_{eq}}\left[K_{eq}(1 - X_A)^2 - X_A^2\right] \quad (10)$$

$$\int \frac{k_f C_{A0}}{K_{eq}}dt = \int \frac{dX_A}{[(K_{eq} - 1)X_A^2 - 2K_{eq}X_A + K_{eq}]} \quad (11)$$

The solution of Equation (11) can be obtained using Equation (12).

$$\int \frac{dX}{aX + bX + c} = \frac{1}{a(p-q)}\ln\left[\frac{q}{p}\left(\frac{X-p}{X-q}\right)\right]$$
$$for\ b^2 > 4ac \quad (12)$$

$$a = K_{eq} - 1\ , b = -2K_{eq}, c = K_{eq}$$

$$\ln\left[\frac{q}{p}\left(\frac{X_A - p}{X_A - q}\right)\right] = \frac{a(p-q)k_f C_{A0}}{K_{eq}}tp =$$
$$\frac{-b + \sqrt{4K_{eq}^2 - 4K_{eq}(K_{eq} - 1)}}{2(K_{eq} - 1)}, q = \quad (13)$$
$$\frac{-b - \sqrt{4K_{eq}^2 - 4K_{eq}(K_{eq} - 1)}}{2(K_{eq} - 1)}$$

Figure 4 to Figure 7 show linear fits of Equation (13) for reactions performed at 50, 60, 70 and 80°C respectively, with a catalyst concentration of 0.0275 M. In general, a good adjustment of the data was obtained at the tested temperatures, with the lowest value of the correlation coefficient at 70°C.
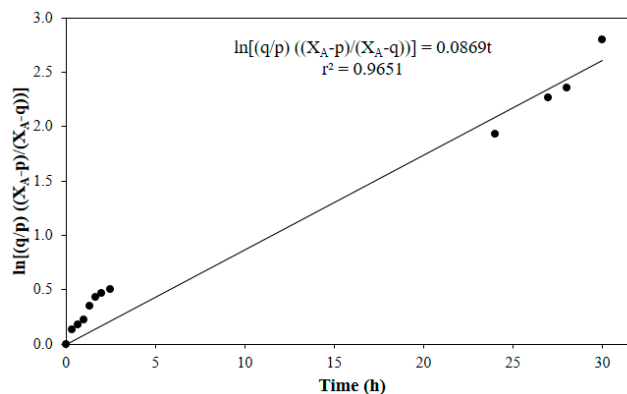

Figure 4 Linear fit of Equation (13) for reaction at 50°C, C_{H2SO4}= 0.0275 M, acetic acid to nopol molar ratio of 1:1, C_{Nopol} = 0.2941 M

Table 1 shows the values of the equilibrium constant and the forward and the backward reaction constants at each reaction temperature. Equilibrium constants were determined from Equation (8), the forward reaction rate constants were calculated with the slope of Figure 4 to Figure 7, backward reaction rate constants were determined from the K_{eq} relation, Equation (6). The equilibrium constant values found in this research are in the typical values range ($\sim 1 - 10$) [13]. For esterification of acetic acid with methanol, an equilibrium constant of 6.2 at 60°C was reported for a methanol to acetic acid molar ratio of 2 [14]. Both equilibrium constants and forward reaction rate constants increase with temperature.
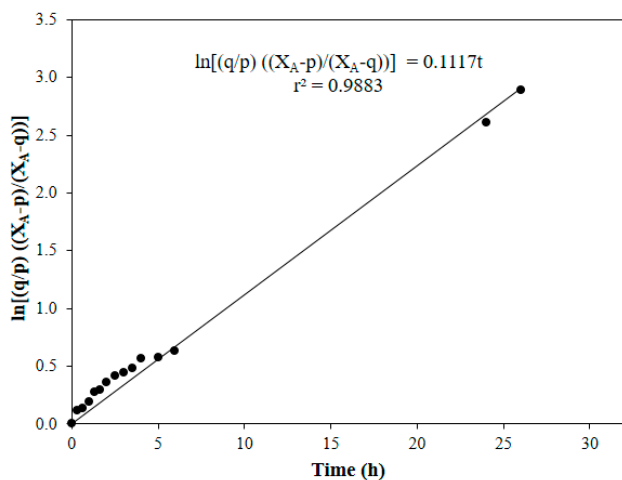
Figure 5 Linear fit of Equation (13) for reaction at 60°C, C_{H2SO4}= 0.0275 M, acetic acid to nopol molar ratio of 1:1, C_{Nopol} = 0.2941 M

Figure 6 Linear fit of Equation (13) for reaction at 70°C, C_{H2SO4}= 0.0275 M, acetic acid to nopol molar ratio of 1:1, C_{Nopol} = 0.2941 M

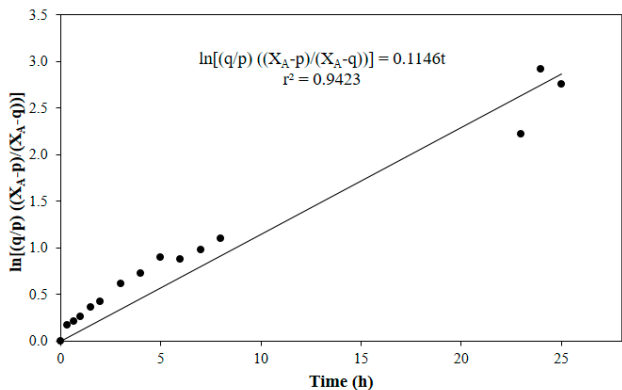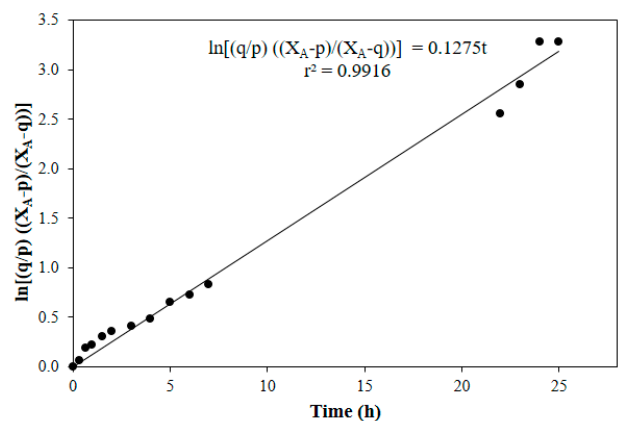**Figure 7** Linear fit of Equation (13) for reaction at 80°C, C_{H2SO4}= 0.0275 M, acetic acid to nopol molar ratio of 1:1, C_{Nopol} = 0.2941 M

Table 1 Reaction rate constants and equilibrium constants from concentration model for the esterification reaction of nopol with acetic acid

Temperature (°C)	K_{eq}	k_f(L mol^{-1} h^{-1})	k_b(L mol^{-1} h^{-1})
50	2.90	0.254	0.088
60	4.52	0.410	0.091
70	5.99	0.469	0.078
80	9.00	0.662	0.074

C_{H2SO4}= 0.0275 M, 500 rpm

The effect of catalyst concentration on the reaction rate is taken in account on the pre-exponential factor (k_{f0}); Figure 8 shows a linear ratio between k_{f0} and the catalyst concentration at 80°C.

The temperature dependence of the forward reaction rate constant was estimated with the Arrhenius (14), by plotting the logarithm of the forward reaction rate constants shown in Table 1 with respect to the inverse of temperature.
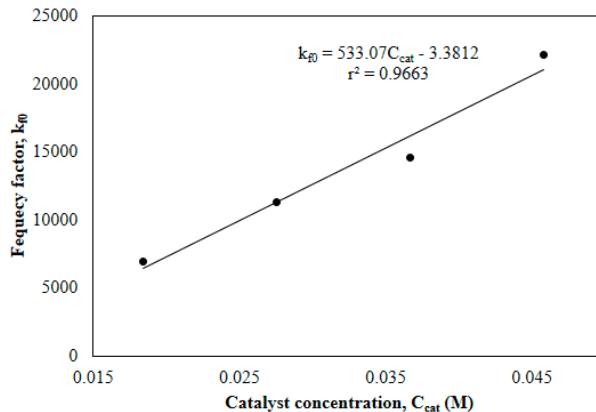

Figure 8 Relation between pre-exponential factor and catalyst concentration

$$k_f = k_{f0} \exp\left(\frac{-E_f}{RT}\right) \qquad (14)$$

Where k_{fo} is the pre-exponential factor, R is the gas constant, T is the temperature in Kelvin, and E_{af} is the activation energy of the forward reaction.

Figure 9 shows that the Arrhenius plot has a good linear fit, the slope of the straight line corresponds to $-E_f/R$, so the activation energy of the forward reaction is 28.08 $kJmol^{-1}$. The exponential of the intercept corresponds to k_{fo} and was 11213 L $mol^{-1}h^{-1}$. In the esterification of geraniol using a geraniol/acetic anhydride molar ratio of 1:1 and acid ionic liquid, the reported activation energy was 61.8 $kJmol^{-1}$ [23]; values of 52.3 $kJmol^{-1}$ for
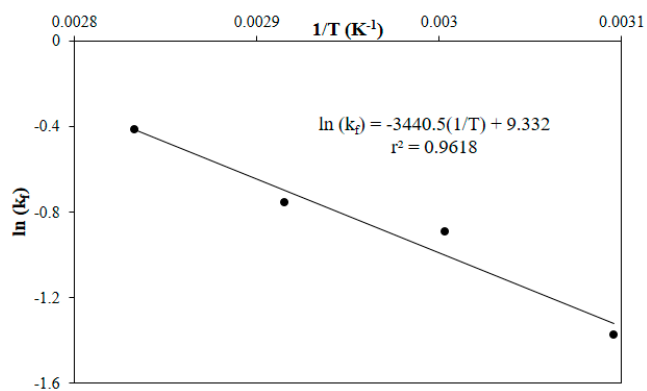
Figure 9 Arrhenius plot of k_f for nopol with acetic acid for the model based on concentration

The plot shows: $\ln(k_f) = -3440.5(1/T) + 9.332$, $r^2 = 0.9618$

Table 2 Values of published groups structural parameters used in the calculations [42]

Group No. in UNIFAC list	Group	R_k	Q_k
1	CH_3	0.9011	0.848
1	CH_2	0.6744	0.540
1	CH	0.4469	0.228
1	C	0.2195	0.000
5	OH	1.0000	1.200
7	H_2O	0.9200	1.400
20	COOH	1.3013	1.224
41	COO	1.3800	1.200

Table 3 Values of published group interaction parameters used in the calculations, a_{mk} (K) [42]

	Group 1	Group 5	Group 7	Group 20	Group 41
Group 1	0	986.5	1,318	663.5	387.1
Group 5	156.4	0	353.5	199	190.3
Group 7	300	-229.1	0	-14.09	-197.5
Group 20	315.3	-151	-66.17	0	-337
Group 41	529	88.63	284.4	1,179	0

acrylic acid with 2-ethylhexan-1-ol [37], 40.7 $kJmol^{-1}$ for palmitic acid with isopropanol [38], and 42.07 $kJmol^{-1}$ for propionic acid with benzyl alcohol [39] have been reported. The activation energy reported for the esterification of acrylic acid [18] and acetic acid [17] with ethanol in the presence of H_2SO_4 was 35.04 $kJmol^{-1}$ and 65.6 $kJmol^{-1}$, respectively.

Activity model

The non-ideality associated with the reaction mixture is evaluated with the activity coefficients, Equation (15), along with the molar concentration or mole fractions [40]. Activity coefficients are calculated using Universal Functional group Contribution (UNIFAC), Universal QUAsi Chemical (UNIQUAC), and non-random two liquid model (NRTL) models.

$$a_i = \gamma_i \; x_i = \gamma_i \frac{C_i}{C_t} \tag{15}$$

Where, γ_i, C_i x_i and C_t represent the activity coefficient, concentration, and mole fraction of each component and total concentration, respectively. The activity coefficients in the reaction mixture were calculated using the UNIFAC method [41]. The compounds used in this study were divided, in a first approach, into structural groups characteristic of the original UNIFAC (CH_3, CH_2, CH, C, H_2O, COO, COOH and OH). Values of known UNIFAC parameters (R_k, Q_k and a_{mk}), used in the simulations are taken from literature [42] and reported in Table 2 and Table 3.

The chemical activities instead of concentrations can be used in the reaction rate equation:

$$-r_A = k_f a_A a_B - k_b a_C a_D \tag{16}$$

The equilibrium constant is calculated with Equation (17). The activity coefficients of each compound at the equilibrium molar composition and the K_y at each tested temperature are included in Table 4.

$$K_{eq,act} = \frac{a_{C,eq}a_{D,eq}}{a_{A,eq}a_{B,eq}} = \frac{C_{C,eq}C_{D,eq}\gamma_C\gamma_D}{C_{A,eq}C_{B,eq}\gamma_A\gamma_B} = K_C K_\gamma \tag{17}$$

Using Equation (15) into Equation (16), the reaction rate given in terms of activity is obtained, Equation (18)

$$-r_A = k_f \frac{\gamma_A\gamma_B}{C_t^2}C_A C_B - k_b \frac{\gamma_C\gamma_D}{C_t^2}C_C C_D \tag{18}$$

As the product between the activity coefficients of both reactants and both products does not vary significantly, the rate constants of forward and backward of Equation (18) can be grouped as it is shown in Equation (19). Table 5 shows the values of the equilibrium constant and the forward and the backward reaction constants at each reaction temperature, calculated with the activity model.

$$-r_A = k_{f,act}C_A C_B - k_{b,act}C_C C_D \tag{19}$$

The forward rate parameter $k_{f,act}$ is related to the temperature through an Arrhenius relation, Equation (20)

$$k_{f,act} = k_{f0,act}\exp\left(\frac{-E_f}{RT}\right) \tag{20}$$

The temperature dependence of the forward reaction rate constant obtained from the kinetic model based on activities was estimated with the Arrhenius equation, Equation (20), and the plot is shown in Figure 10. The activation energy of the forward reaction is 28.56 $kJmol^{-1}$ and the $k_{fo,act}$ is 33860 $Lmol^{-1}h^{-1}$.

Table 4 Composition and activity coefficients of components at equilibrium of the reaction at different temperatures

Temperature °C	x_A	x_B	x_C	x_D	Υ_A	Υ_B	Υ_C	Υ_D	K_Υ
50	0.185	0.185	0.315	0.315	0.895	1.148	1.731	4.378	7.381
60	0.16	0.16	0.34	0.34	0.887	1.162	1.730	4.375	7.343
70	0.145	0.145	0.355	0.355	0.887	1.170	1.725	4.364	7.258
80	0.125	0.125	0.375	0.375	0.885	1.182	1.719	4.350	7.153

x_i is molar fraction

Table 5 Reaction rate constants and equilibrium constants from activity model for the esterification reaction of nopol with acetic acid

Temperature °C	$K_{eq,act}$	$k_{f,act}$ (L mol^{-1} h^{-1})	$k_{b,act}$ (L mol^{-1} h^{-1})
50	21.41	0.778	1.962
60	33.19	1.264	2.054
70	43.48	1.360	1.648
80	64.38	2.071	1.655

C_{H2SO4} = 0.0275 M, 500 rpm
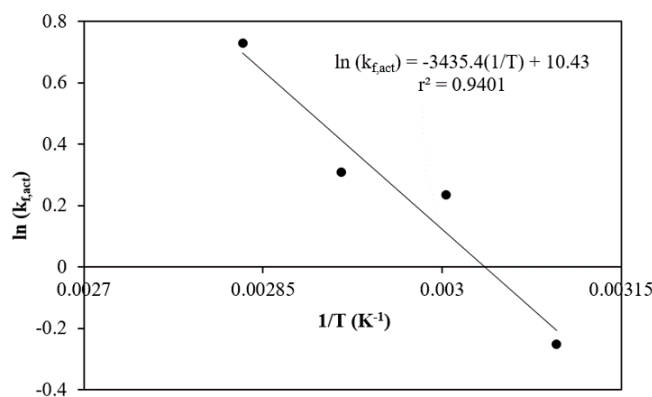
Figure 10 Arrhenius plot of k_f for nopol with acetic acid for the model based on activities

ln ($k_{f,act}$) = -3435.4(1/T) + 10.43
r² = 0.9401

Figure 11 van't Hoff plot for acetic acid esterification with nopol for nopyl acetate production
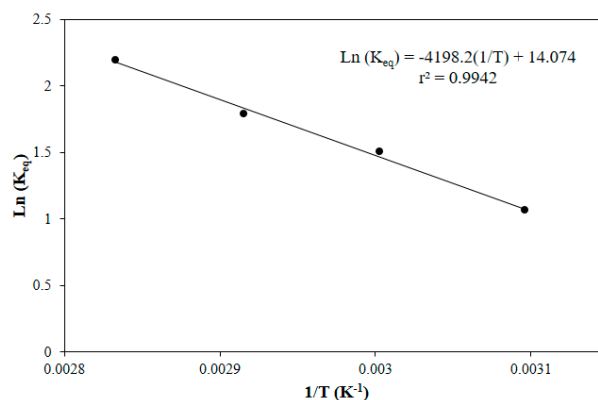
Ln (K_{eq}) = -4198.2(1/T) + 14.074
r² = 0.9942

3.5 Thermodynamic parameters

Reaction enthalpy and entropy were determined with the van't Hoff equation [43, 44], Equation (21), by plotting the logarithm of the equilibrium constant, with respect to the inverse of temperature.

$$\ln (K_{eq}) = \left(\frac{-\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right) \qquad (21)$$

Where ΔH° and ΔS° are the enthalpy and entropy of reaction respectively.

Figure 11 shows the linear fit of the van't Hoff equation in which the slope corresponds to -ΔH°/R, a negative slope means that the reaction is endothermic and a temperature increasing favors the formation of products. The heat of reaction obtained was 34.90 $kJmol^{-1}$ and the reaction entropy was 0.12 $kJmol^{-1}K^{-1}$ which means that the system tends to be more disorderly with the course of the reaction. Also for esterification kinetics of acetic acid with methanol (ΔH = 29.99 $kJmol^{-1}$) [11], esterification of acetic acid with n-amyl alcohol (6.81 $kJmol^{-1}$) [1], acrylic acid with 2-ethylhexan-1-ol (70.1–74.6 $kJmol^{-1}$) [38], acrylic acid with n-butanol (69.03 $kJmol^{-1}$) [45], and esterification of acrylic acid with ethanol (71.94 $kJmol^{-1}$) [18], endothermic reactions were reported. Because the reaction presents one favorable condition (ΔS > 0) and other unfavorable (ΔH > 0), to determine if it is spontaneous, the calculating of Gibbs free energy Δ°G is required, Equation (22) [46].

$$\Delta G^\circ = -RT \ln K \qquad (22)$$

The values of Gibbs free energy for all temperatures tested were negative, as shown in Table 6, this means that in the temperature range studied the reaction is spontaneous and the equilibrium constant increases with temperature.

Table 6 Gibbs free energy for each temperature evaluated

Temperature, °C	K_{eq}	ΔG°, kJ mol^{-1}
50	2.90	-2.86
60	4.52	-4.17
70	5.99	-5.11
80	9.00	-6.45

4. Conclusions

The esterification of nopol with acetic acid was carried out in a stirred batch reactor using sulfuric acid as catalyst, the influence of temperature, catalyst concentration and molar feed ratio was studied. The highest conversion of acetic acid was 96% that was obtained at 80°C with a sulfuric acid concentration of 0.0275 M and a molar ratio of acetic acid to nopol 1:3. The activity coefficients obtained with UNIFAC showed that the mixture is nonideal and that the activity coefficients at equilibrium was almost constant in the tested range temperature. For the reactions 1:1 second order kinetic models based on concentrations and activities were developed; the forward and backward reaction rate constants were determined using the linear fit of the model and the equilibrium constant. The forward reaction rate constants and the equilibrium constant showed a tendency to increase with temperature. For the forward reaction, the activation energy estimated was 28.08 $kJmol^{-1}$ and the pre-exponential factor was 11213 L $mol^{-1}h^{-1}$. Using the kinetic model based on activities gave a forward reaction rate constant of 28.56 $kJmol^{-1}$ and the $k_{fo,act}$ was 33860 L $mol^{-1}h^{-1}$. The enthalpy (34.90 $kJmol^{-1}$) and the entropy (0.12 $kJmol^{-1}K^{-1}$) of reaction were determined using van't Hoff equation.

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