

Synthesis of value added fatty alcohols and FAMES by non-catalytic supercritical methanol transesterification of jojoba (*Simmondsia chinensis*) wax



Pedro Andreo-Martínez^{a,*}, Nuria García-Martínez^a, Joaquín Quesada-Medina^{a,*},
Celían Román-Figueroa^b, Manuel Paneque^c

^a Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30071 Murcia, Spain

^b Agroenergía Ingeniería Genética S.A., Almirante Lynch 1179, San Miguel, 8920033 Santiago, Chile

^c Laboratory of Bioenergy and Environmental Biotechnology, Department of Environmental Sciences and Natural Resources, Faculty of Agricultural Sciences, University of Chile, Santa Rosa 11, 315, La Pintana, 8820808 Santiago, Chile

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ABSTRACT

Nowadays jojoba (*Simmondsia chinensis*) wax production with an industrial or energetic objective can be focused on a bio-refinery processing perspective where the fatty alcohols are the main products and fatty acid methyl esters (FAMES) the by-products. To date, jojoba wax methanolysis has been performed using catalytic processes where long reaction times and downstream separation and purification steps are required. However, jojoba wax transesterification using a non-catalytic process such as the supercritical methanolysis has not been reported yet. The yield of jojoba fatty alcohols and FAMES was determined in the temperature and reaction time ranges of 250–350 °C (12–42 MPa) and 15–90 min, respectively, at a methanol-to-wax molar ratio of 15:1. The maximum experimental yield of fatty alcohols and FAMES (95.3 and 95.4 mol%, respectively) was reached at 350 °C after 90 min of reaction. Therefore, no thermal decomposition of jojoba alcohols and FAMES was observed under the most severe experimental reaction conditions studied, which can be explained by the highly monounsaturated nature of the products obtained and the protective antioxidant effect of β -sitosterol present in jojoba wax. The rate constants obtained for this process were: 1×10^{-5} , 3×10^{-5} , 1.1×10^{-4} , 4.1×10^{-4} and $6.5 \times 10^{-4} \text{ s}^{-1}$, at 250, 275, 300, 325 and 350 °C, respectively, with an activation energy of 115.5 kJ/mol. In addition, response surface methodology was used to determine the optimal reaction conditions that maximize the yield of fatty alcohols and FAMES: 338.9 °C and 90 min to obtain yields of 96.8 mol% and 97.0 mol%, respectively. Thus, it can be concluded that jojoba wax methanolysis under non-catalytic supercritical conditions is an alternative way to obtain high-added value compounds and biodiesel.

1. Introduction

Vegetable oils and animal fats are widely used as raw materials to obtain different products and compounds with industrial uses such as lubricants, plasticizers, surfactants, polyurethanes, biodiesel and pharmaceutical products [1–4]. Thus, 80.5% of vegetable oil world production is used for food, 8.2% for biodiesel and 11.3% for other industrial uses [1]. One of the oils of greatest interest to both the scientific community and society is the jojoba wax-oil because its derivatives (mainly fatty alcohols and fatty acid alkyl esters) have a high-added value [4].

A comprehensive review about jojoba (*Simmondsia chinensis*) wax has been recently published by Sánchez et al. [4], but it is noteworthy

that the jojoba plant produces oleaginous nuts which contain about 50% of a liquid wax. This oleaginous liquid wax has a distinct molecular structure in comparison with the rest of vegetable oils and fats, which are formed mainly by triglycerides (TG). Jojoba wax is composed of a long chain of monounsaturated esters (around 97%) formed by fatty acids and fatty alcohols, and hence it does not contain glycerol [5,6]. Jojoba wax also contains minor amounts of free fatty acids (FFAs), free fatty alcohols, phytosterols, tocopherols, phospholipids and triacylglycerol traces [7].

The meal obtained after the wax extraction process from jojoba seeds contains interesting compounds, such as simmondsin (it reduces the food intake as it induces a satiation process) and simmondsin-20-ferrulate (glucoside with insecticidal, antifungal and antifedant

* Corresponding authors.

E-mail addresses: pam11@um.es (P. Andreo-Martínez), quesamed@um.es (J. Quesada-Medina).

activity). This meal can also be used as biomass for energetic purposes (heating value of 15.34 MJ/kg) and as animal feed even though it is formed by 15% toxic glycosides. The liquid wax extracted from jojoba seeds can be transformed by transesterification into valuable compounds, such as monounsaturated fatty alcohols (11-eicosenol, 13-docosenol, and 15-tetracosenol) and fatty acid methyl esters (FAMES) (methyl oleate, methyl gadoleate, methyl erucate and methyl nervonate). These alcohols have a high economic value (current price higher than \$40/g) and are used in pharmaceutical applications, while FAMES can be used as a green fuel (biodiesel) [4]. Therefore, jojoba seeds can be converted into valuable products within a biorefinery approach where the main products are the fatty alcohols and residual meal, and the byproducts are the FAMES [4,8,9], thus giving an economic and environmental role to the jojoba industry.

Jojoba wax transesterification for obtaining fatty alcohols and FAMES has been conventionally conducted by both homogeneous and heterogeneous catalytic processes. The catalysts are able to reduce reaction time and to improve transesterification yields [10,11]. For example, El-Boulifi et al. [8] achieved a maximum jojoba wax conversion of 94% at 60 °C after 300 min of reaction using CH_3OK as a homogeneous catalyst, while Sánchez et al. [9] reported a maximum conversion of 96.3% at 140 °C (1 MPa) and 300 min using CaO as heterogeneous catalyst. After the catalytic transesterification reaction it is necessary to separate the catalyst from the products, which requires expensive and time-consuming separation and purification steps [4,11–15].

Transesterification of jojoba wax can also be carried out by a one-step process that does not require the use of catalysts, such as the supercritical methanol process. Non-catalytic supercritical methanol transesterification of jojoba wax may help to shorten the reaction time [16,17] because supercritical methanol and oil exist in a single phase [18,19]. Temperature, pressure, reaction time and methanol-to-triglycerides molar ratio are the main parameters affecting the non-catalytic supercritical transesterification [20,21], their optimum values to reach maximum conversions being in the range of 290–400 °C, 20–35 MPa, 5–75 min and 40:1–45:1, respectively, depending on the type of feedstock and reactor used. Since under these supercritical reaction conditions the products can be degraded [18,22,23], it is interesting to consider their thermal stability.

The objective of this study was to evaluate the non-catalytic supercritical methanol transesterification of jojoba wax esters in a batch reactor at a methanol-to-wax esters molar ratio of 15:1. This work represents the first research on the non-catalytic transesterification of jojoba wax esters in supercritical methanol to obtain fatty alcohols and FAMES and it is not an economic analysis of this process. The influence of temperature (250–350 °C) and reaction time (15–90 min) on the experimental yield of both individual and total fatty alcohols and FAMES was studied, as well as the kinetics of the reaction at the aforementioned experimental temperatures. The supercritical process was also evaluated by response surface methodology (RSM) and analysis of variance (ANOVA).

2. Material and methods

2.1. Raw material and chemicals

The crude jojoba wax used in this study was obtained by cold pressing of *Simmondsia chinensis* seeds collected in Punitaqui (Región de Coquimbo, Chile). The fatty alcohols and fatty acids composition of the extracted jojoba wax is shown in Table 1. The profiles of fatty alcohols and fatty acids of other jojoba waxes of different origin reported in previous works are also included in this table for comparison purposes and were similar to those obtained for jojoba wax in this research. Moreover, the content of FFAs of extracted jojoba wax in this study was 0.36%.

Anhydrous methanol was provided by Panreac Química, S.A.U.

(Barcelona, Spain), while methyl heptadecanoate was supplied by Sigma–Aldrich (Madrid, Spain) and used as internal standard.

2.2. Reaction procedure

The supercritical process was performed in an 83 ml stainless steel cylindrical tank reactor, operated in shaken batch mode, to study the influence of the temperature (250, 275, 300, 325 and 350 °C) and reaction time (15, 30, 45, 60, 75 and 90 min). The general scheme of the reaction is illustrated in Fig. 1. For each experiment, the reactor was filled with 55 g of a methanol-jojoba wax mixture, with a molar ratio of 15:1. This molar ratio was chosen assuming that the optimal methanol-to-oil molar ratio for the supercritical methanol transesterification of TG, composed of a glycerol molecule linked by ester bonds to three fatty acids, ranged from 40:1 to 45:1 [19,30–36]. As jojoba wax is composed of complex esters, each one only containing an ester bond (see Fig. 1), its supercritical methanolysis will require three times less amount of methanol (*i.e.*, a molar ratio of 13–15:1) compared to the supercritical transesterification of TG.

The reactor, with the sample inside, was introduced into a molten salt bath, which permits the reaction mass to reach the desired temperature in about 10–15 min. The reaction time started when the reactor was immersed in the salt bath. The reactor was stirred at 70 rpm during the process and the pressure reached (12, 22, 31, 38 and 42 MPa at 250, 275, 300, 325 and 350 °C, respectively) was produced only by the effect of temperature. The supercritical reaction was stopped by immersing the reactor in a water bath. Finally, the content of the reactor was evaporated in a rotary evaporator to remove the excess methanol and then stored in a refrigerator before its analysis.

2.3. Analysis methods

The analysis of total and individual fatty alcohols and FAMES in the samples was carried out by gas chromatography (GC/FID) using the standard UNE-EN 14103:2003, as described elsewhere [18]. The chromatograph used was a 3900 Varian gas chromatograph equipped with a CP 8400 Varian autosampler and coupled with a FID detector. Analyses were performed in triplicate and the errors in determining the yield of fatty alcohols and FAMES were $\pm 2.9\%$.

The identification of compounds, such as fatty alcohols and FAMES, among the supercritical reaction products was performed by GC–MS and by comparing their retention times with those of reference compounds. The mass spectra of the compounds were compared with those of the NIST database, identifying those compounds having a minimum similarity of 93% between their mass spectra. The GC–MS analysis was conducted on a 6890 N Agilent gas chromatograph equipped with a 5973 N mass selective detector (MSD). The apparatus was fitted with a HP-5ms capillary column (30 m \times 250 μm , 0.25 μm film). Helium was used as carrier gas at a flow rate of 1 ml/min with a split ratio of 1:20. The temperature of the injector was maintained at 250 °C, whereas that of the detector was maintained at 280 °C. The initial temperature of the oven was 150 °C and the temperature programming was as follows: an initial heating rate of 3 °C/min up to 160 °C, a holding time of 2 min at 160 °C, and a final temperature ramp of 2 °C/min up to 220 °C.

The content of FFAs of the crude jojoba wax was measured by non-aqueous acid-base titration following the EN 14104:2003 method.

2.4. Statistical design and model optimization

The appropriate use of response surface methodology (RSM) requires an adequate selection of responses, factors and levels to carry out an adequate fit of the experimental data to a polynomial model. A statistical design of five-level-two-factor central composite design (CCD) was chosen to study the effect of temperature and reaction time on two responses (the yield of total fatty alcohols and FAMES). Based on the experimental results obtained in the conditions described in Section

Table 1
Composition of fatty alcohols and fatty acids of different jojoba waxes (mol%).

	Miwa [24]	Spencer et al. [25]	Tobares et al. [26]	Nashy et al. [27]	Abdelmoez et al. [28]	Busson-Breyse et al. [7]	Shah et al. [29]	This work
<i>Fatty alcohols</i>								
C16:1	0.60							
C18:1	1.40	1.10	0.60			0.60		0.70
C20:0	2.00					0.40		1.40
C20:1	44.00	44.00	41.90			45.4		40.20
C22:0	2.00	1.00				0.70		
C22:1	42.00	45.00	48.10			46.4		48.30
C24:1	8.00	8.90	9.40			6.50		9.30
<i>Fatty acids</i>								
C16:1	0.40	0.61			0.12	0.30		0.27
C18:0	0.11	0.22		0.50	0.15	0.20		0.22
C18:1	11.79	9.52	12.48	14.85	12.31	9.30	11.00	8.04
C18:2	0.13			0.41			0.10	
C18:3	0.23			6.86			0.40	
C20:0	0.20	0.10			0.20			
C20:1	70.40	71.52	73.77	63.75	70.68	76.70	59.50	70.46
C22:0	0.48	0.64			0.27		0.20	
C22:1	12.99	12.56	11.42	10.31	12.93	12.10	12.30	14.90
C24:0	0.10	0.42			0.02	0.10		
C24:1	1.71	2.56	0.79	1.14	1.39	1.00	1.70	4.91

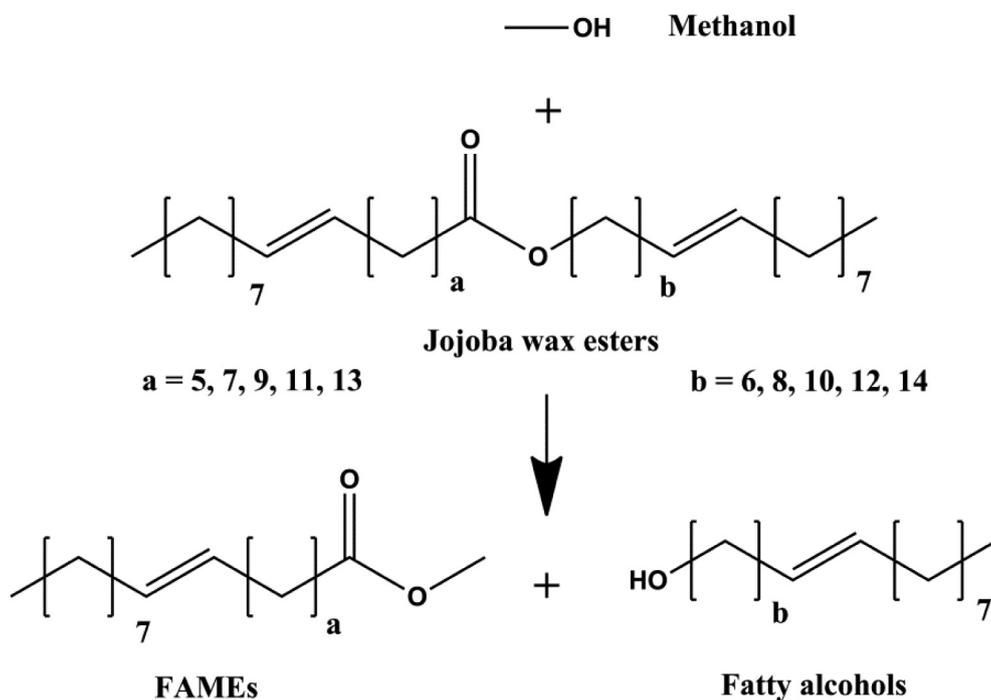


Fig. 1. Scheme of the methanolysis of jojoba wax esters.

2.2 and in order to minimize the standard error of the regression, ranges of temperature and reaction time of 300–350 °C and 60–90 min were selected, respectively, in which the yield of fatty alcohols and FAMES was close to its maximum value. The experimental design conditions and the codel levels of the independent variables are shown in Table 2. Each data point was obtained by triplicate, introducing its average value in the statistical design. In the case of the central data point (0,0), which is crucial in determining the experimental error and the reproducibility, it was replicated six times, including each single data point (experiment) in the design. Therefore, a total of 14 randomized runs were included in the CCD.

RSM was used to evaluate the effect of the operating parameters on the yields of fatty alcohols and FAMES. Once the design was completed, the experimental data were fitted to a quadratic polynomial equation (Eq. (1)):

$$Y = a_0 + \sum_{i=1}^k a_i X_i + \sum_{i=1}^k a_{ii} X_i^2 + \sum_{i=1, i < j}^{k-1} \sum_{j=2}^k a_{ij} X_i X_j \quad (1)$$

where Y is the predicted response, a_0 is the constant term, a_i , a_{ii} and a_{ij} are coefficients estimated from regression (linear, quadratic and interactions, respectively), X_i , X_j are the independent variables and k is the number of factors.

The results were analyzed using SYSTAT software (version 13.0) and the regression terms were interpreted by analysis of variance (ANOVA) at a confidence interval of 95%. In addition, three-dimensional surface response plots were obtained and a simultaneous optimization procedure based on desirability function analysis was employed to select the optimum operating parameters that maximize fatty alcohol and FAME yield.

Table 2

Central composite design matrix, and experimental and predicted results during the supercritical methanol transesterification of crude jojoba wax.

Run order	T (°C)	t (min)	X_1	X_2	FAME yield (mol%)		Fatty alcohol yield (mol%)	
					Experimental	Predicted	Experimental	Predicted
1	312.5	67.5	-0.5	-0.5	58.5	58.5	56.6	57.9
2	312.5	82.5	-0.5	0.5	69.1	71.8	68.8	71.1
3	337.5	67.5	0.5	-0.5	90.5	90.2	88.9	89.5
4	337.5	82.5	0.5	0.5	93.6	96.0	94.0	95.7
5	300	75	-1	0	38.3	37.6	38.3	37.3
6	350	75	1	0	94.0	93.5	93.9	93.5
7	325	60	0	-1	71.7	72.4	71.6	71.4
8	325	90	0	1	93.4	91.5	92.1	90.8
9	325	75	0	0	85.0	84.6	84.3	83.8
10	325	75	0	0	83.0	84.6	82.1	83.8
11	325	75	0	0	87.0	84.6	81.4	83.8
12	325	75	0	0	84.9	84.6	88.0	83.8
13	325	75	0	0	83.0	84.6	85.3	83.8
14	325	75	0	0	87.1	84.6	84.6	83.8

T = temperature; t = reaction time; X_1 = coded value of temperature; X_2 = coded value of reaction time.

3. Results and discussion

3.1. Characterization of crude jojoba wax

In order to determine the fatty alcohols and fatty acids that form part of the structure of jojoba wax esters, the fatty alcohols and FAMES present in the supercritical reaction product obtained at 350 °C and 90 min reaction time were analyzed by GC-MS. The chromatogram obtained is shown in Fig. 2. Five fatty alcohols and twelve FAMES were identified. The most abundant fatty alcohols were 11-eicosenol (C20:1), 13-docosenol (C22:1) and 15-tetracosenol (C24:1), while the most abundant FAMES were methyl oleate (C18:1), methyl gadoleate (C20:1), methyl erucate (C22:1) and methyl nervonate (C24:1); the evolution of these most abundant compounds during the supercritical process will be studied below.

β -Sitosterol was also found among the reaction products (see peak 18 in Fig. 2). This compound is present in jojoba wax [7] and is a natural antioxidant that could improve the oxidative stability of the reaction products (monounsaturated fatty alcohols and FAMES) [37]. The content of sterols in jojoba wax is around 0.37–0.40 wt% [7,38], β -

sitosterol being the most abundant sterol, accounting for around 70% of the sterolic fraction [7,29].

In order to determine the amount of jojoba wax for obtaining a methanol-to-wax molar ratio of 15:1 and the yields of fatty alcohols and FAMES in mol% it is necessary to know the molecular weight of jojoba wax. For this purpose, the data of wax ester composition published by Busson-Breysse et al. [7], Spencer et al. [25], and Hegel et al. [38] (see Table 3) have been used in this study. Based on these data, the average molecular weight of the jojoba wax esters was calculated as 605.92 g/mol (the mean of 606.34, 606.31 and 605.12 g/mol in Table 3). This value, which will be used in this study, is practically the same as that reported by Wisniak [39] (606 g/mol), Miwa [24] (606 g/mol), and Cappillino et al. [40] for plantations in the United States (606.2 g/mol), and slightly lower than those reported by Cappillino et al. [40] for plantations in Israel, Peru and Argentina (607.4 g/mol), and Chile (610.3 g/mol). It is noteworthy that El-Boulifi et al. [8] reported a molecular weight of 657 g/mol for a jojoba wax from Israel with a composition of esters similar to those shown in Table 3, which lead us to suppose that this high value is a typographical mistake.

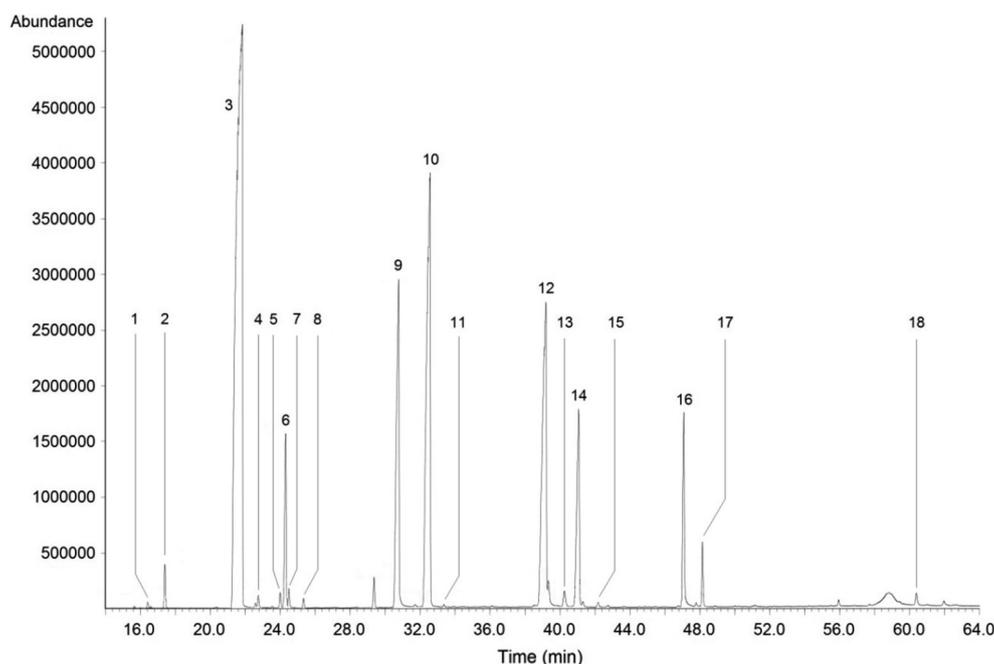


Fig. 2. GC-MS chromatogram of the supercritical reaction product obtained at 350 °C and 90 min. Identified peaks: 1 = methyl palmitoleate (FAME C16:1); 2 = methyl palmitate (FAME C16:0); 3 = methyl heptadecanoate (FAME C17:0; internal standard); 4 = oleyl alcohol (FA C18:1); 5 = methyl linoleate (FAME C18:2); 6 = methyl oleate (FAME C18:1, cis); 7 = methyl *trans*-9-octadecenoate (FAME C18:1, trans); 8 = methyl stearate (FAME C18:0); 9 = 11-eicosenol (FA C20:1); 10 = methyl gadoleate (FAME C20:1); 11 = methyl arachidate (FAME C20:0); 12 = 13-docosenol (FA C22:1); 13 = 1-eicosanol (FA C20:0); 14 = methyl erucate (FAME C22:1); 15 = methyl behenate (FAME C22:0); 16 = 15-tetracosenol (FA C24:1); 17 = methyl nervonate (FAME C24:1); 18 = β -sitosterol.

Table 3
Calculation of molecular weight of the jojoba wax esters.

Wax ester	Molecular weight (g/mol)	Composition (wt%)			Weighted molecular weight (g/mol)		
		Busson-Breyse et al. [7]	Spencer et al. [25]	Hegel et al. [38]	Busson-Breyse et al. [7]	Spencer et al. [25]	Hegel et al. [38]
C34	504.75		0.10	0.10		0.50	0.50
C36	534.94	0.50	2.00	1.66	2.67	10.70	8.86
C38	560.98	6.50	7.00	8.07	36.46	39.27	45.25
C40	589.04	31.40	30.00	32.24	184.96	176.71	189.89
C42	617.05	51.70	50.00	47.99	319.01	308.53	296.13
C44 (C20:0/C24:1)	647.16	0.20			1.29		
C44	645.13	9.60	10.00	8.93	61.93	64.51	57.61
C46	673.21		0.80	0.94		5.39	6.32
C48	701.29		0.10	0.08		0.70	0.56
TOTAL		100	100	100	606.34	606.31	605.12

3.2. Yield of fatty alcohols and FAMES

The yields of individual and total FAMES were expressed as the moles of the individual and total FAMES generated, respectively, with respect to the moles of the initial wax esters, while those of individual and total fatty alcohols were expressed as the moles of the individual and total fatty alcohols generated, respectively, with respect to the moles of the initial wax esters.

Fig. 3A shows how fatty alcohols evolved with the reaction time at different temperatures. As observed, the yield of total fatty alcohols increased gradually with the reaction time for all temperatures studied, reaching maximum values of 5.7, 16.7, 50.8, 92.1 and 95.3 mol% at 250, 275, 300, 325 and 350 °C, respectively, after 90 min of reaction. The yield followed a sigmoidal behavior at 325 and 350 °C, which was much more accentuated at 350 °C, reaching a plateau of about 93–95 mol% for reaction times longer than 45 min at 350 °C. In addition, the yield of total fatty alcohols increased with the temperature whatever the reaction time used.

The evolution of the FAMES generated during the supercritical reaction is shown in Fig. 3B. As it can be seen and as expected, FAME yield behaved similarly to that of fatty alcohols since the methanolysis of jojoba wax esters produces fatty alcohols and FAMES with a molar ratio of 1:1. Thus, the yield of FAMES increased with the reaction time and temperature, reaching a maximum value of 95.4 mol% at 350 °C and 90 min (the most severe reaction conditions tested).

In general, FAME yield that can be obtained from crude jojoba wax during supercritical methanol transesterification can be higher than that of fatty alcohols due to the presence of FFAs in the crude wax

[38,41]. Non-catalytic supercritical methanol process effectively transforms FFAs into FAMES by esterification [42]. However, most of the authors [4,43,44] reported low contents of FFAs in jojoba wax (0.28–0.71%), which would give rise to very little difference between the yields of FAMES and fatty alcohols. This is the case of the crude jojoba wax used in the present study, which has a FFA content of 0.36%.

To the author's best knowledge, no research has been conducted to date on the non-catalytic supercritical alcoholysis of jojoba wax. Until now, the methanolysis of jojoba wax esters has only been conducted by both homogeneous and heterogeneous catalytic processes. Thus, in relation to the homogeneous catalysts, Shah et al. [43,45] reported maximum conversions into FAMES of 93–96% using 1% dibutyltin diacetate as catalyst after around 2000 min of reaction at 60 °C and a methanol-to-wax molar ratio of 23:1. El-Boulifi et al. [8] studied the transesterification of jojoba wax with methanol, ethanol, 1-propanol and 1-butanol at 60, 75, 78 and 85 °C, respectively, using an alcohol-to-wax molar ratio of 6:1 and 1.5% potassium methoxide as catalyst. They observed that the reaction rate increased as the length of the alcohol's carbon chain decreased, reaching a maximum conversion of 96% after 300 min of reaction when methanol was used. Bouaid et al. [5] also carried out the methanolysis of jojoba wax using a methanol-to-wax molar ratio of 6:1 and potassium hydroxide as catalyst. They found a maximum conversion of 83.5% at low temperatures (25 °C) and a catalyst concentration of 1.35% after 60 min. In addition, other authors such as Canoira et al. [46], Fatah et al. [47] and Radwan et al. [41] conducted the methanolysis of jojoba wax at 60–65 °C using methanol-to-wax molar ratios of 6–8:1 and reached conversions into FAMES of

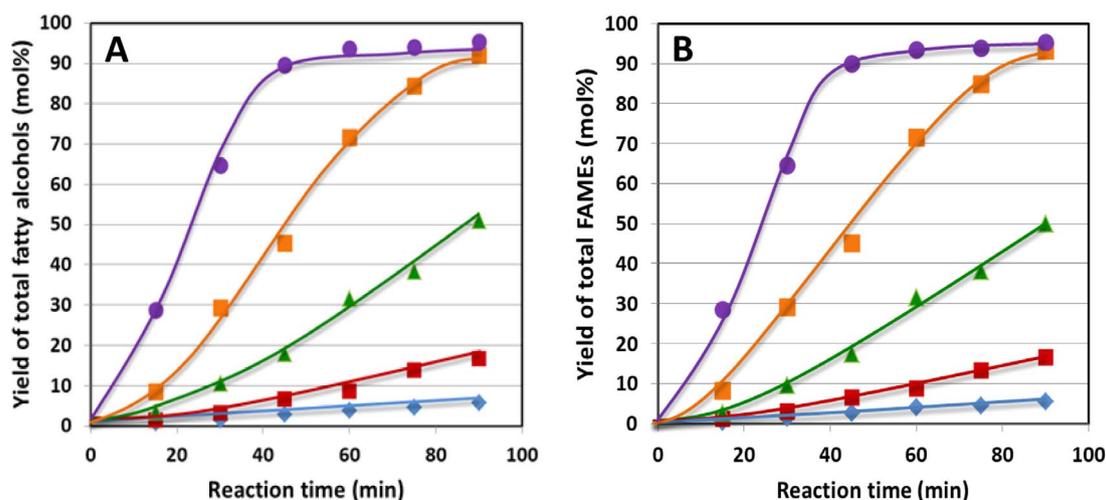


Fig. 3. Evolution of the yield of total fatty alcohols (A) and FAMES (B) during the supercritical methanol transesterification of crude jojoba wax at temperatures of: ◆ 250 °C; ■ 275 °C; ▲ 300 °C; ■ 325 °C and ● 350 °C.

90–93% after 240, 180 and 60 min of reaction when using 1% sodium methoxide, 0.5% potassium hydroxide and 1% sodium hydroxide, respectively. The homogeneous catalyzed alcoholysis with ethanol, isopropanol, pentanol and octanol of jojoba wax has also been assisted by microwave radiation using sodium ethoxide as catalyst [48], and a maximum conversion of 95% was reached with ethanol after 10 min of radiation at 800 W.

As regards heterogeneous catalyzed alcoholysis, Sánchez et al. [9,49] used calcium oxide (derived from mussel shells) as catalyst to optimize the jojoba wax methanolysis at atmospheric pressure and in a pressurized reactor. A maximum conversion of 93.3% was reached under atmospheric pressure at 65 °C after 600 min of reaction when using a methanol-to-wax molar ratio of 9:1 and 8% of catalyst content [49]. However, the use of a pressurized atmosphere (1 MPa) and a temperature of 140 °C increased the experimental conversion up to 96.3% and shortened the reaction time by half (300 min) [9].

Alkaline homogeneous catalyzed transesterification is the most widely used reaction on an industrial scale to produce biodiesel as it gives rise to the simplest and cheapest process. The reaction requires the use of a raw material with a content of FFAs and water lower than 0.5% and 0.06% [11–15], respectively, which is usually the case of crude jojoba wax [49]. However, the homogeneous catalyzed alcoholysis of jojoba wax results in a single phase composed of fatty acid alkyl esters, monounsaturated fatty alcohols, unreacted wax, the excess of short-chain alcohol and the used catalyst. As mentioned earlier jojoba wax is not formed by triglycerides and hence glycerol, which assists in the product purification due to the formation of two phases, is not generated in the reaction medium. Therefore, various purification steps, such as vacuum distillation and washing, affecting the yield of the overall process are needed. Moreover, the formation of products from jojoba wax takes much longer than from conventional vegetable oils, making the process much less efficient [49].

In the case of the heterogeneous catalyzed transesterification of jojoba wax, a cleaner reaction medium is obtained because catalysts are easy to separate from the medium. However, although heterogeneous catalysts can be reused several times, they have some associated disadvantages, such as mass transfer limitations, slower reaction rates, and higher operating pressures and temperatures [49].

The non-catalytic supercritical methanol transesterification leads to similar or even higher yields of FAMES in much shorter reaction times [17,19,31,32,50]. In this sense, the results of the present study showed that this process reached similar or even better fatty alcohol and FAME yields (95.3 and 95.4 mol%, respectively) in less time (90 min) compared to the aforementioned studies, except the one using microwave technique together with homogenous catalysis [48]. In addition, no washing of the product is needed due to the absence of catalyst, thus facilitating the development of a continuous process. Therefore, it can be concluded that the non-catalytic supercritical methanolysis of jojoba wax is an interesting alternative to both homogeneous and heterogeneous catalytic transesterification processes.

The mixture of products formed during the methanolysis of jojoba wax needs to be separated to obtain high-added value fatty alcohols and FAMES, which was not the objective of the present work. The separation of jojoba fatty alcohols from FAMES has been widely studied by the scientific community. For example, Canoira et al. [46] conducted a single crystallization step using low boiling point petroleum ether in a volumetric ratio of 2:1 at –18 °C and obtained a solid and liquid fraction with contents of 80% of fatty alcohols and FAMES, respectively. Shah et al. [29] adapted the above-mentioned method by repeating the same procedure on the liquid fraction until no precipitate was observed at about –18 °C. The best separation, protected under the patent WO2014140392 (A1), was reported by Aracil et al. [51], who conducted three crystallization steps using a mixture of hexane and diethyl ether in a volumetric ratio of 4:1 at –20 °C and yielded a fatty alcohol fraction of very high purity containing 97% of the fatty alcohols present in the jojoba wax.

The quality of the biodiesel (FAMES) produced from jojoba wax has been studied by different authors and there is no clear consensus on this matter. Some authors, such as Canoira et al. [46] and El-Boulifi et al. [8], reported that the jojoba biodiesel does not meet all the requirements of the standard UNE-EN 14214, while Radwan et al. [52] declared that it accomplished the biodiesel quality standard ASTM D6751 and can be used directly in diesel engines without any modification. Either way, the fact that a biodiesel does not comply with all the requirements of the quality standards is common [32] and this problem can be solved by blending the biodiesel produced with other biodiesels of complementary features to produce a biofuel meeting all the standard specifications [29].

The behavior of the main individual fatty alcohols (11-eicosenol, 13-docosenol and 15-tetracosenol) and FAMES (oleic, gadoleic, erucic and nervonic acid methyl esters) generated during the non-catalytic supercritical methanolysis of crude jojoba wax was also studied. The yield of the three individual fatty alcohols behaved similarly to each other as well as to that of total fatty alcohols for all temperatures and reaction times studied. The maximum yields of 11-eicosenol, 13-docosenol and 15-tetracosenol were 38.4, 46.1 and 8.9 mol%, respectively, which were reached at 350 °C and 90 min of reaction. These values were very close to the contents of the respective fatty alcohols in the crude jojoba wax (see Table 1), thus reflecting that the maximum possible yield of these fatty alcohols was practically reached. This fact also indicates that none of these fatty alcohols decomposed under the reaction conditions tested.

As occurred with the individual fatty alcohols, the four individual FAMES behaved similarly to each other as well as to the total FAMES. Methyl oleate (C18:1), methyl gadoleate (C20:1), methyl erucate (C22:1) and methyl nervonate (C24:1) reached maximum yields of 7.7, 67.2, 14.2 and 4.7 mol%, respectively, at 350 °C and 90 min, conditions at which the maximum yield of total FAMES was also reached. These values were practically the same as the contents of the respective fatty acids in the crude jojoba wax (see Table 1), thus indicating that no thermal decomposition of these monounsaturated FAMES was observed in the experimental conditions used [18].

Thermal decomposition of a fatty acid methyl ester is related to the unsaturation degree (number of double bonds) of its fatty acid chain: the greater the number of double bonds, the more easily it decomposes [31]. More than 98% of the fatty acid chains of jojoba wax are monounsaturated (one double bond). Some studies reported that no thermal decomposition of monounsaturated FAMES was evidenced at temperatures of 350 °C and below [17,18,53], while others showed that thermal decomposition of monounsaturated FAMES began to appear at 350 °C and reaction times longer than 30–60 min [31,32,50,54]. Either way, the thermal stability of monounsaturated fatty alcohols and FAMES observed under the experimental conditions used in the present study can also be influenced by the presence of β -sitosterol in crude jojoba wax (see Section 3.1). It has been found that this compound could have some protective effect against oxidative degradation of the supercritical reaction products [37].

3.3. Kinetics of jojoba wax non-catalytic supercritical methanolysis

As mentioned earlier, during the methanolysis of jojoba wax 1 mol of jojoba wax esters reacts with 1 mol of methanol to produce 1 mol of FAMES and 1 mol of fatty alcohols (see Fig. 1). Therefore, a first order kinetic model can be used to determine the kinetic parameters of the reaction. To this purpose, the rate of disappearance of jojoba wax esters can be written as:

$$-\frac{d[\text{jojoba wax esters}]}{dt} = K_1[\text{jojoba wax esters}][\text{methanol}] \quad (2)$$

where [jojoba wax esters] and [methanol] represent the concentrations of jojoba wax esters and methanol, respectively, and k_1 is the rate constant. As methanol is in large excess (methanol-to-wax molar ratio

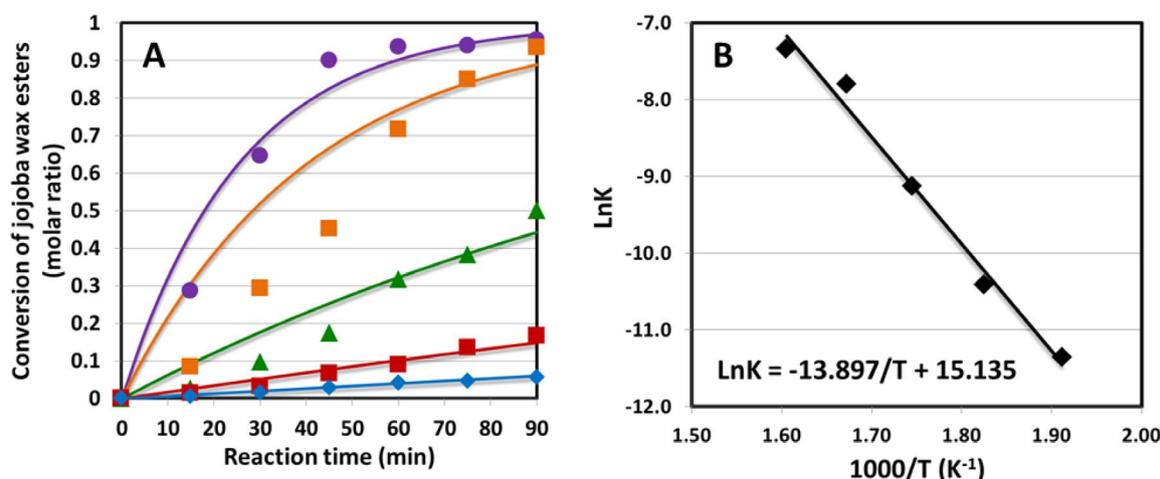


Fig. 4. Conversion of jojoba wax esters at different temperatures: \blacklozenge 250 °C; \blacksquare 275 °C; \blacktriangle 300 °C; \blacksquare 325 °C and \blacklozenge 350 °C, where the solid lines represent the first order fit (A). Variation of rate constants with inverse of temperature (Arrhenius plot) (B).

of 15:1) its concentration can be considered a constant parameter. Thus, Eq. (2) can be rewritten as:

$$-\frac{d[\text{jojoba wax esters}]}{dt} = K[\text{jojoba wax esters}] \quad (3)$$

where $K = K_1[\text{methanol}]$. Eq. (3) can be rewritten in terms of conversion as:

$$-\ln(1-X) = Kt \quad (4)$$

where $X = 1 - \frac{[\text{jojoba wax esters}]_t}{[\text{jojoba wax esters}]_0}$.

It can be assumed that $[\text{jojoba wax esters}]$ is equal to the concentration of FAMES or fatty alcohols due to the fact that no thermal decomposition has been observed. $[\text{jojoba wax esters}]_0$ is the initial concentration of jojoba wax esters.

The rate constant (k) for each reaction temperature was obtained from the slope of the plot of $-\ln(1-X)$ versus reaction time (t), while the activation energy was obtained from the Arrhenius plot. Fig. 4a represents the conversion of jojoba wax esters versus reaction time, where the first order kinetic model is shown by solid lines. Rate constants of 1.0×10^{-5} , 3.0×10^{-5} , 1.1×10^{-4} , 4.1×10^{-4} and $6.5 \times 10^{-4} \text{ s}^{-1}$ were obtained at 250, 275, 300, 325 and 350 °C, respectively. Fig. 4b shows the variation of rate constants versus inverse of temperature (Arrhenius plot), from which an activation energy of 115.5 kJ/mol was calculated.

The rate constant values of this study are similar to those reported for other vegetable oils under non-catalytic supercritical methanol conditions (1.5×10^{-4} – $1.0 \times 10^{-3} \text{ s}^{-1}$ at 250–350 °C for sura hone oil, 9.9×10^{-5} – $7.9 \times 10^{-3} \text{ s}^{-1}$ at 250–425 °C for mahua oil, 5.7×10^{-5} – $2.3 \times 10^{-3} \text{ s}^{-1}$ at 250–425 °C for neem oil, $9.7 \times 10^{-3} \text{ s}^{-1}$ at 350 °C for canola oil [55,56] and $2.5 \times 10^{-5} \text{ s}^{-1}$ at 380 °C for sea mango oil [57]). However, the activation energy calculated was higher than all of the aforementioned studies (47.4 kJ/mol for sura hone oil, 75.0 kJ/mol for mahua oil, 61.8 kJ/mol for neem oil [55,56] and 40.0 kJ/mol for sea mango oil [57]).

The kinetics of jojoba wax heterogeneous catalyzed methanolysis was studied by Sánchez et al. [49]. They reported a maximum jojoba wax conversion of 95.0% using 8% CaO as catalyst after 600 min of reaction at 65 °C and a methanol-to-wax molar ratio of 12:1. The activation energy reported for this reaction was 55.1 kJ/mol, while the rate constants (which were calculated by the authors of the present study from the data of Ref. [49]) were 1.02×10^{-7} , 1.93×10^{-7} and $3.52 \times 10^{-7} \text{ s}^{-1}$ at 45, 55 and 65 °C, respectively. Thus, the rate constants obtained during non-catalytic supercritical methanol transesterification of jojoba wax were between 2 and 3 orders of magnitude higher than those obtained during the heterogeneous catalyzed

transesterification process. However, as expected, a lower activation energy was reported for the catalyzed process due to the effect of the catalyst. Therefore, the non-catalytic supercritical methanol transesterification of jojoba wax was found to be better than the catalyzed process because similar conversions were reached at shorter reaction times.

It's noteworthy that the first 4 points of each temperature series did not properly fit the kinetic model (see Fig. 4a), which can be explained by a limitation of the experimental device used in the present study. The reactor contents reached 250, 275, 300, 325 and 350 °C (reaction temperatures) in 11, 12, 13, 14 and 15 min, respectively. That way, in the case of the sample taken after 15 min and due to the fact that the reaction time started when the reactor was immersed in the salt bath, the reactor contents only remained at 250, 275, 300, 325 and 350 °C during a lapse of time of 4, 3, 2, 1 and 0 min, respectively. In this sense, all samples suffered a delay in reaching the reaction temperature, which was less remarkable at low temperatures and long reaction times. Therefore, the fit of the data to a first order kinetic model is not very good at high temperatures and short reaction times (see Fig. 4a), and discussions with other kinetic studies using supercritical methanol [55,56] should be handled with caution.

3.4. Optimization of non-catalytic supercritical methanolysis of jojoba wax by RSM

Quadratic regression models were used to determine the influence of the experimental process variables (temperature and reaction time) on the yields of total fatty alcohols and total FAMES. The fitting of the experimental data shown in Table 2 to Eq. (1) gave rise to the following models:

$$Y_1 = 83.807 + 28.130X_1 + 9.694X_2 - 18.409X_1^2 - 2.701X_2^2 - 7.036X_1X_2 \quad (5)$$

$$Y_2 = 84.580 + 27.980X_1 + 9.554X_2 - 19.031X_1^2 - 2.658X_2^2 - 7.515X_1X_2 \quad (6)$$

where Y_1 is the predicted yield of total fatty alcohols, Y_2 the predicted yield of total FAMES, X_1 the coded reaction temperature and X_2 the coded reaction time. Positive coefficients meant that with the increase of variable X , variable Y also increased, while negative coefficients meant that with the increase of variable X , variable Y decreased.

As one might expect, the fitted equations for the yields of total fatty alcohols and FAMES were very similar to each other due to the fact that the transesterification reaction of jojoba wax results in the formation of fatty alcohols and FAMES with a molar ratio of 1:1 and no thermal decomposition of these products was observed.

ANOVA analysis shows the significance level of the regressions and

Table 4

Results of ANOVA analysis of response surface quadratic models for the supercritical synthesis of fatty alcohols and FAMES from jojoba wax.

Source	DF	Total fatty alcohols				Total FAMES			
		Sum of squares	Mean squares	F-value	p-value	Sum of squares	Mean squares	F-value	p-value
Regression	5	3185.533	637.107	121.459	0.000	3190.339	638.068	142.222	0.000
Linear	2	2655.868	1327.934	253.160	0.000	2622.565	1311.283	292.279	0.000
Quadratic	2	517.289	258.644	49.308	0.000	553.655	276.827	61.704	0.000
Interaction	1	12.376	12.376	2.359	0.163*	14.119	14.119	3.147	0.114*
Residual	8	41.963	5.245			35.891	4.486		
Lack of fit	3	14.203	4.734	0.853	0.522*	19.553	6.518	1.995	0.233*
Pure error	5	27.761	5.552			16.338	3.268		

Total fatty alcohols: $R^2 = 0.993$; Adj $R^2 = 0.987$; Pred $R^2 = 0.979$; $SD = 2.290$.Total FAMES: $R^2 = 0.994$; Adj $R^2 = 0.989$; Pred $R^2 = 0.982$; $SD = 2.118$.

* Not significant.

of the linear, quadratic and interaction terms of each model on function of p-value and F-value (see Table 4). Thus, p-values less than 0.05 were considered significant, and the higher the F-value, the more significant the term is considered. In view of the results, it can be stated that both quadratic models were significant at a 95% confidence level due to p-values less than 0.001 and high F-values (121.5 and 142.2 for the yields of total fatty alcohols and total FAMES, respectively). Besides, high coefficients of determination (R^2) (near to 1.000) as well as low standard errors of the estimate (SD) were obtained in both cases, reflecting a good fit between model predictions and experimental data. In other words, the experimental observations were close to the curves fitted by the quadratic regression models. In addition, the lack of fit of the model provides information about the suitability of the experimental ranges chosen for the independent variables. Thereby, lack of fit p-values greater than 0.05 mean that the experimental ranges selected for the independent variables are suitable to apply the RSM, which was the case here. Finally, linear and quadratic terms showed a high significance, while interaction terms were not significant for both yields of total fatty alcohols and FAMES (p-values higher than 0.05 and low F-values). Taking into account that the quadratic coefficients X_2^2 are smaller than the nonsignificant interaction coefficients in both equations it can be concluded that X_1X_2 and X_2^2 terms could be neglected in Eqs. (5) and (6). However, despite the fact that simplified equations provide a good fit, full equations have been used to fit experimental data in order to minimize errors in determination of the optimal conditions (temperature and reaction time) which maximize the yields of fatty alcohols and FAMES.

Fig. 5 shows the response surface 3D plots of the yields of total fatty

alcohols and total FAMES as a function of temperature and reaction time. These plots provide an easy and convenient visualization of the results that allows the understanding of the interaction between the independent variables and facilitates the determination of the optimum values of the independent variables that maximize the responses. It can be observed that both yields increased by increasing the temperature and lengthening the reaction time. It can also be appreciated in Eqs. (5) and (6) that the estimated linear coefficients for temperature and reaction time were positive, meaning that the increase of these variables improves the yields of total fatty alcohols and FAMES. The positive influence of these parameters on the yield of FAMES during the supercritical methanol transesterification of vegetable oils has been previously reported using RSM [58,59]. However, the negative quadratic terms in Eqs. (5) and (6), which lead to a convex curvature of the 3D surfaces (see Fig. 5), could be an indicator of thermal decomposition of monounsaturated fatty alcohols and FAMES. The quadratic coefficients for temperature were more negative than those for reaction time, indicating a more pronounced curvature of the response surfaces with respect to the temperature. The influence of these quadratic terms was responsible for the stabilization of both yields at high temperatures and long reaction times.

The quadratic polynomial models obtained are able to predict yields at temperatures and reaction times not tested. Although experimentally no thermal decomposition was observed, the RSM model demonstrated that from 338.9 °C and 90 min of reaction the yield of total FAMES and fatty alcohols started to decrease slightly. Under these optimal conditions, maximum predicted yields of total FAMES and fatty alcohols of 97.0 mol% and 96.8 mol% were reached, respectively.

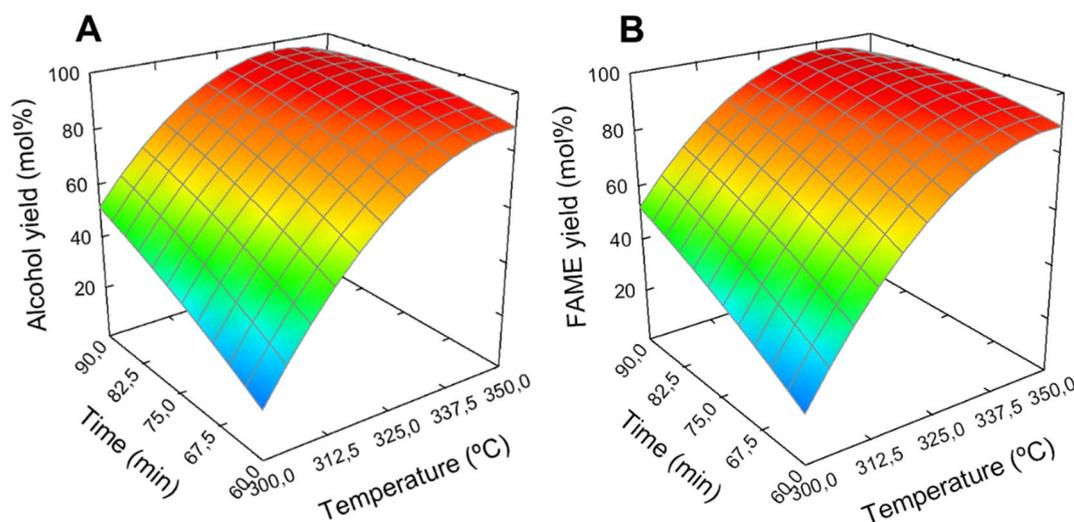


Fig. 5. Response surface 3D plot for combined effects between reaction time and temperature on the yields of total fatty alcohols (A) and total FAMES (B) during the supercritical methanol transesterification of crude jojoba wax.

In order to validate the predictions of the models, three confirmatory experiments were carried out at the optimal conditions previously indicated. Experimental average yields of total FAMES and total fatty alcohols of 96.7 ± 2.7 mol% and 96.1 ± 2.1 mol%, respectively, were obtained, which were in accordance with the predicted values (97.0 and 96.8 mol%, respectively). Therefore, RSM is an effective tool for predicting the yield of total FAMES and total fatty alcohols under the optimal conditions during the non-catalytic supercritical methanol transesterification of jojoba wax.

4. Conclusions

Jojoba (*Simmondsia chinensis*) wax transesterification using supercritical methanol in a non-catalytic one-step batch process was evaluated. A large number of temperatures and reaction times was tested to find the optimal conditions for producing fatty alcohols and FAMES. The experimental yields of fatty alcohols and FAMES increased gradually with increasing reaction temperature and time. Maximum experimental yields of fatty alcohols and FAMES of 95.3 and 95.4 mol%, respectively, were reached at 350 °C and 90 min of reaction (the most severe reaction conditions tested), which is in accordance with the jojoba wax methanolysis stoichiometry producing fatty alcohols and FAMES with a 1:1 molar ratio. Fatty alcohols and FAMES did not suffer thermal decomposition under the most severe conditions tested, which was probably due to the fatty acid chain monounsaturated nature of these compounds and the protective effect of β -sitosterol present in jojoba wax. As regards the kinetic parameters of the non-catalytic supercritical methanol reaction, the rate constants were 2–3 orders of magnitude higher than those obtained from heterogeneous catalyzed transesterification process.

The joint use of response surface methodology and desirability function analysis has allowed the authors to obtain the optimal conditions for maximizing, simultaneously, the yield of fatty alcohols and FAMES in this study (338.9 °C and 90 min obtaining yields of 96.8 mol% and 97.0 mol%, respectively), which was verified experimentally. Therefore, the supercritical methanolysis of jojoba wax is an interesting alternative method to produce high-added value fatty alcohols and FAMES.

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