Advances on kinetics and thermodynamics of non-catalytic supercritical methanol transesterification of some vegetable oils to biodiesel

Authors

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Abstract

Kinetic and thermodynamic parameters of the non-catalytic supercritical methanol transesterification reaction of castor, jatropha, pongamia, tobacco, soybean and jojoba oils to biodiesel production were evaluated in the present study. The experiments were conducted in an 83 ml closed batch reactor at different temperatures (250–350 ºC) and reaction times (15–90 min), and at optimal methanol-to-oil molar ratios (15:1 in the case of jojoba wax-oil and 43:1 for the rest of the oils). The pressure reached in the reactor ranged from 10 to 43 MPa. Integral method was used to determine appropriated reaction orders by an adjustment of experimental data to pseudo-zero, pseudo-first and pseudo-second order kinetic equations using Levenberg-Marquardt algorithm. Pseudo-first-order kinetic equation was found to be the most appropriated to describe the supercritical transesterification reaction of the vegetable oils studied. Rate constants and Arrhenius parameters were calculated, the activation energy following the sequence: castor oil < jatropha oil < tobacco oil < pongamia oil < soybean oil < jojoba wax-oil. It is difficult to explain the behavior of jojoba and castor oils in relation to that of the rest of vegetable oils because they have a very different structure and fatty acid composition, respectively. However, the aforementioned sequence observed for the rest of vegetable oils (jatropha, tobacco, pongamia and soybean oils), which have a similar structure and fatty acid composition, can be attributed to the content of linolenic acid in the oil: the higher the content of linolenic acid, the higher the activation energy and the lower the reaction rate. Finally, thermodynamic study showed that the non-catalytic supercritical methanol transesterification reaction is non-spontaneous (endergonic) and endothermic in nature.

Keywords

Kinetics; Thermodynamics; Vegetable oils; Supercritical methanol; Transesterification

1. Introduction

It is widely known that the reserves of fossil fuels are running out and the concern over environmental degradation and over-exploitation of natural resources has driven the search for alternatives renewable energies to fossil fuels for the future [1, 2]. In addition, mitigating anthropogenic changes due to Global Warming will require “abatement” technologies or renewable energies in order to reduce greenhouse gasses emissions [3]. Biodiesel can be one of these renewable energies due to it has been reported that around 50–80% of CO2 emissions can be saved by using biodiesel compared to petroleum diesel [4]. Biodiesel is defined as a mixture of long chain fatty acid methyl esters (FAMEs) derived from renewable lipid feedstocks, such as vegetable oils or animal fats, which are formed mainly by triglycerides (TGs). Biodiesel is composed by FAMEs with fatty acid chain lengths of C14:0-C24:3 [1] for its use in compression ignition engines, among others. Biodiesel offers several advantages compared to diesel fuel, such as no sulfur emissions, less CO production and significant reduction in smoke [5].

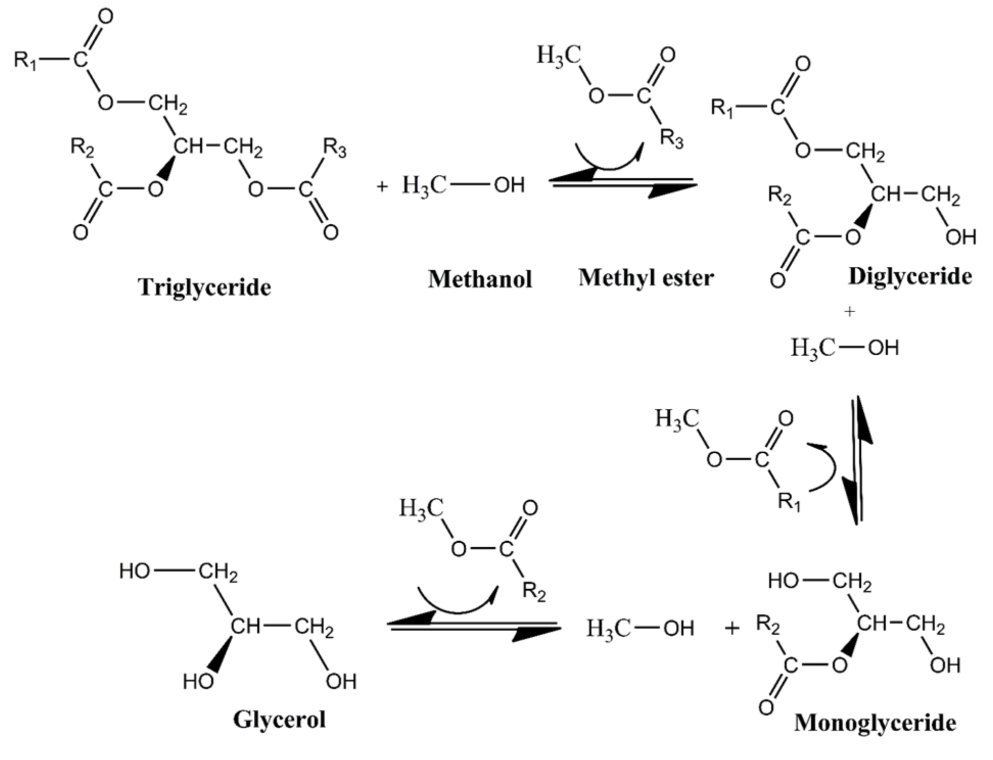
Several methods for the transesterification of vegetable oils and animal fats to biodiesel production have been reported to date, such as homogeneous and heterogeneous acid- and alkali-catalyzed, enzyme-catalyzed, microwave- and ultrasound-assisted, and non-catalytic supercritical processes [6]. Among all the aforementioned methods, the supercritical process has undergone vigorous development as the technology offers several advantages over other methods, including the fact that it does not require either the use of catalysts, or the pretreatment of feedstocks, and can be applied to a wide variety of feedstocks with a high reaction rate and short residence times [2, 7]. Moreover, the purification of the products is much simpler and more environmentally-friendly compared to conventional catalytic processes in which saponification products and catalyst have to be removed from the biodiesel fuel [2, 7, 8].

There are two fundamental aspects to consider while studying chemical reactions, one dynamic (kinetics) and one static (thermodynamics). Chemical kinetics deals with the speed with which a reaction occurs, the variables that affect it (generally, reactant nature, concentration, temperature, pressure, phase or phases in which the reaction occurs and catalyst presence) and the mechanism through which takes place the reaction. Therefore, kinetics informs of the time necessary for equilibrium to be reached. In the case of thermodynamics, only the initial and final states of the system are of interest. Thus, thermodynamics deals with the systems in equilibrium, studies the direction and extent of the reaction, and report whether a reaction is possible or not. Hence, from the kinetic and the thermodynamic study it can be known the path through which the reaction takes place (*i.e.*, the mechanism of the reaction) [9].

The typical transesterification reaction of TGs in the presence of methanol for producing both FAMEs and glycerol occurs in three consecutive and reversible steps (see Fig. 1). In the first one, 1 mol of methyl ester and 1 mol of diglyceride (DG) are obtained from the one initial mol of TG. In the second stage, 1 mol of monoglyceride (MG) and a new mol of methyl ester are produced from the mol of DG formed in the first stage. In the last step, the mol of MG from the second stage produces a new mol of methyl ester and 1 mol of glycerol [2].

The alcohol-to-oil molar ratio for the supercritical alcohol transesterification of vegetable oils has been widely studied in the literature and there is a clear consensus that the optimal alcohol-to-oil molar ratio ranged from 40:1 to 45:1, regardless the type of oil used [2, 5, 7, 10-19]. In the case of jojoba wax-oil, which is composed of complex esters (each one containing only an ester bond) of monounsaturated fatty alcohols and acids instead of TGs, the optimal alcohol-to-oil molar ratio for its supercritical transesterification (occurring in only one reversible step) ranged from 13:1 to 15:1 [7]. Therefore, optimal methanol-to-oil molar ratios of 15:1 and 43:1 were used in the present study for the supercritical transesterification of jojoba and the rest of vegetable oils, respectively.

The kinetic study of the transesterification reaction is usually carried out by both integral and differential methods. The complexity of this type of reactions makes it necessary to use approximations in order to simplify the calculations, such as to consider alcohol in excess, which obliges to ignore the inverse reactions, and the transesterification global reaction without intermediate steps [20-24]. Conversely, some authors take into account the reaction intermediates to calculate the kinetic parameters [25, 26]. In the case of non-catalytic supercritical transesterification and esterification, some different kinetic models for single-step global reactions have been reported in the literature, such as first-order and irreversible transesterification solved by the integral method [20, 21, 27]; first-order and irreversible transesterification solved by the differential method [28]; first-order and reversible esterification solved by the differential method using non-linear optimization [29]; first-order and irreversible esterification solved by the integral method [30]; pseudo-first-order and irreversible transesterification solved by the integral method using non-linear regression fitting [31]; and second-order and irreversible microwave-assisted esterification solved by the differential method using non-lineal regression fitting [32].



R_1, R_2 or R_3 = C_{14} to C_{24} saturated, monounsaturated or polyunsaturated

Fig. 1. General scheme of transesterification reaction of triglycerides using methanol.

As can be appreciated, a wide variety of ways to calculate the kinetic parameters of non-catalytic supercritical transesterification of vegetable oils has been used. However, to the best authors' knowledge, in order to establish the best reaction order, no study has yet been carried out on the fitting of the experimental data to integrated kinetic equations for different reaction orders. Therefore, the aim of the present study is to provide the best fit functions and kinetic parameters for the kinetic modeling of non-catalytic supercritical methanol transesterification of castor, jatropha, pongamia, tobacco, soybean and jojoba oils by testing different reaction orders. In addition, the values of some thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy of activation (ΔH) and entropy of activation (ΔS) were calculated using the activation complex theory.

2. Material and methods

2.1 Raw materials

Crude vegetable oils extracted from seeds of castor, jatropha, pongamia, tobacco, soybean and jojoba were used in this study. Castor and jojoba oils were furnished by Dr. Manuel Paneque from University of Chile (Santiago, Chile), while jatropha and pongamia oils were supplied by Dr. Naveen Kumar from Delhi Technological University (New Delhi, India). Tobacco and soybean oils were supplied by the companies Innotecno Development, S.L. (Valencia, Spain) and Lesieur Cristal (Casablanca, Maroc), respectively. The fatty acid composition of these oils, which was previously published by our research group [2,5,7,10,12,33], is shown in Table 1.

Anhydrous methanol (99.8% by GC) was supplied by Panreac Química, S.A.U.

(Castellar del Vallés, Barcelona, Spain), while methyl heptadecanoate (≥99% by GC) was furnished by Sigma-Aldrich (Tres Cantos, Madrid, Spain) and used as internal standard.

The content of free fatty acids, the saponification index and the density of the vegetable oils was measured by the EN 14104:2003, ISO 3657:2002 and IUPAC 2.101 methods, respectively.

Table 1. Fatty acid composition of various vegetable oils (mol%).

Fatty acid	Castor oil [33]	Jatropha oil [12]	Pongamia oil [5]	Tobacco oil [2]	Soybean oil [10]	Jojoba wax-oil [7]
Myristic (C14:0)				0.20 ± 0.00		
Palmitic (C16:0)	1.06 ± 0.04^{a}	16.77 ± 0.32^{b}	11.79 ± 0.35^{c}	8.90 ± 0.31^{d}	10.20 ± 0.31^{e}	
Palmitoleic (16:1)						0.27 ± 0.01
Stearic (C18:0)	1.15 ± 0.40^{a}	4.63 ± 0.18^{b}	6.53 ± 0.26^{c}	3.50 ± 0.14^{d}	3.80 ± 0.16^{d}	0.22 ± 0.01^{e}
Oleic (C18:1)	3.71 ± 0.14^{a}	41.49 ± 1.66^{b}	52.57 ± 2.36^{c}	14.10 ± 0.50^{d}	24.7 ± 1.00^{e}	8.04 ± 0.33^{f}
Ricinoleic (C18:1-OH)	88.09 ± 3.53					
Linoleic (C18:2)	5.41 ± 0.20^{a}	37.04 ± 1.30^{b}	19.53 ± 0.74^{c}	70.10 ± 2.80^{d}	53.5 ± 2.00^{e}	
Linolenic (C18:3)	0.58 ± 0.02^{a}		3.88 ± 0.16^{b}	1.00 ± 0.12^{c}	7.20 ± 0.30^{d}	
Arachidic (C20:0)			1.35 ± 0.04^{a}	0.30 ± 0.12^{b}		
Gadoleic (C20:1)			1.12 ± 0.04^{a}	0.15 ± 0.05^{a}		70.46 ± 2.12^{b}
Behenic (C22:0)			3.23 ± 0.13^{a}	0.25 ± 0.07^{b}		
Erucic (C22:1)						14.90 ± 0.60
Nervonic (C24:1)						4.91 ± 0.12
Others		0.07 ± 0.03^{a}		1.50 ± 0.20^{b}	0.60 ± 0.10^{c}	1.20 ± 0.10^{b}
SFAs	2.21 ± 0.40^{a}	21.40 ± 0.37^{b}	22.90 ± 0.46^{c}	13.15 ± 0.37^{d}	14.00 ± 0.35^{d}	0.22 ± 0.01^{e}
MUFAs	$91.80^{*} \pm 3.53^{a}$	41.49 ± 1.66^{b}	53.69 ± 2.36^{c}	14.25 ± 0.50^{d}	24.70 ± 1.00^{e}	98.58 ± 2.23^{f}
PUFA	5.99 ± 0.30^{a}	37.04 ± 1.30^{b}	23.41 ± 0.76^{c}	71.10 ± 2.80^{d}	60.70 ± 2.02^{e}	
UFA	$97.79^{*} \pm 3.55^{a}$	$78.53 \pm 2.11^{b,c,d}$	77.10 ± 2.48^{b}	$85.35 \pm 2.85^{d,e}$	$85.40 \pm 2.26^{c,e}$	98.58 ± 2.23^{a}
Other oil properties						
Acid value (mg KOH g^{-1})	0.7	6.5	7.1	20	0.7	0.7
Saponificaction value (mg KOH g^{-1})	192	205	190	198	195	95
Density at 25ºC (kg m^{-3})	958	920	926	956	919	870

Different letters within each row indicate statistically significant differences between means (p-value ≤ 0.05).
SFAs = saturated fatty acids, MUFAs = monounsaturated fatty acids (including ricinoleic fatty acid), PUFAs = polyunsaturated fatty acids, UFAs = unsaturated fatty acids.

2.2 Reaction procedure

The non-catalytic supercritical methanol transesterification reactions were performed in an 83 ml SS316 batch reactor. The experimental temperatures and reaction times ranged from 250 to 350 ºC and from 15 to 90 min, respectively. The pressure reached in the reactor was endogenous (isochoric conditions) and ranged from 10 to 43 MPa (see Table 2). For each experiment, the reactor was filled with around 50 g of a mixture consisting of methanol and vegetable oil with a methanol-to-oil molar ratio of 43:1 (15:1 in the case of jojoba wax-oil). The reactor was immersed in a preheated salt bath by means of a pneumatically controlled mechanical arm to reach the desired temperature in approximately 10–15 min. The reaction time was measured from the moment the reactor was introduced in the salt bath. Temperature and pressure were monitored during the reaction by a thermocouple and a pressure gauge, respectively, placed in the reactor lid. Once the reactor was immersed in the bath, it was stirred at 70 rpm by means of the pneumatic arm. The transesterification reaction was stopped by immersing the reactor in a water bath. Once the process was finished, the reaction products were evaporated in a rotary evaporator to remove the excess methanol and stored in a refrigerator before the analysis of the samples by GC.

Additional information about the reaction procedure can be consulted in previous publications of our research group [2,5,7,10,12,33].

2.3 Analysis methods

The analysis of TGs and FAMEs in the samples was performed according to the standards UNE-EN 14105:2003 and UNE-EN 14103:2003, respectively, as described elsewhere [2,5,7,10,12,33]. In the case of jojoba wax-oil, for the calculation of the conversion of jojoba wax esters it was assumed that the conversion was equal to the yield of FAMEs due to the fact that no thermal decomposition of FAMEs was observed and 1 mol of jojoba wax esters reacts with 1 mol of methanol to produce 1 mol of FAMEs according to its reaction path. The yield of FAMEs is expressed as the moles of total FAMEs generated with respect to the moles of the initial jojoba wax esters.

The device used was a 3900 Varian gas chromatograph equipped with a CP 8400 Varian autosampler and coupled with a FID detector. Analyses of samples were performed in triplicate and the error in the determination of the content of TGs and FAMEs was ±3.1%.

2.4. Kinetic modeling

The transesterification of TGs using methanol is a complex reaction that proceeds in three reversible and consecutive steps (see Fig.1). However, the overall transesterification reaction (TG + 3 $CH_3OH \leftrightarrow$ 3 FAME + Glycerol) resulting in the formation of three moles of FAMEs can also be considered. Therefore, in order to simplify the kinetic modeling of the supercritical transesterification reaction the following assumptions has been taken into account [8, 31, 34]:

i) The rate constants were determined considering overall transesterification reactions without intermediate steps.

ii) The high excess methanol used drives the transesterification equilibrium toward the right side according to Le Châtelier's principle and, therefore, reverse reactions were ignored.

iii) The concentration of methanol was regarded as a constant due to the high excess methanol used and, hence, the kinetic modeling was simplified to a pseudo-order equation.

iv) The extent of glycerol–methanol reactions was ignored in relation to the formation of fatty acid methyl esters.

v) The effect of mass transfer was negligible due to the stirring of the medium (70 rpm) and to the existence of a homogeneous reaction medium as a consequence of the supercritical conditions used.

Molecularity and order of reaction are identical in elementary reactions. However, both parameters may become different in complex reactions, which is the case in this work. Unlike most of publications on kinetic studies of overall supercritical transesterification assuming an order equal to its molecularity (pseudo-first-order reaction with respect to TGs concentration) [8,27,35], the reaction order was determined in this research by fitting the experimental data to integrated kinetic models of pseudo-zero, pseudo-first and pseudo-second orders and then calculating the best goodness of fit.

Under the aforementioned assumptions, the integrated kinetic equations in this study were deduced for the irreversible overall transesterification reaction (TG + 3 CH_3OH → 3 FAME + Glycerol). Thus, the rate of disappearance of TGs can be expressed by the following reaction rate equation:

$$-r = -\frac{dC_A}{dt} = -\frac{1}{3}\frac{dC_B}{dt} = k'C_A^{\alpha}C_B^{\beta} \qquad \text{(Eq. 1)}$$

where C_A represents the concentration of TGs (or wax esters in the case of the jojoba wax-oil), C_B the concentration of methanol, k' the reaction rate constant, and α and β are the partial reaction orders with respect to A and B, respectively.

Since methanol concentration is assumed to be constant, then $k = k'C_B^{\beta}$ and Equation 1 can be written as:

$$-r_A = -\frac{dC_A}{dt} = kC_A^{\alpha} \qquad \text{(Eq. 2)}$$

Rearranging Equation 2 gives:

$$\frac{dC_A}{C_A^{\alpha}} = -k\,dt \qquad \text{(Eq. 3)}$$

The integration of Equation 3 between t = 0 and reaction time t leads to the following expression:

$$\int_{C_0}^{C_A} \frac{dC_A}{C_A^{\alpha}} = \int_0^t -k\, dt \qquad \text{(Eq. 4)}$$

where C_0 is the initial concentration of TGs (at reaction time $t = 0$). This integration gives different equations, linking concentration of TGs to reaction time, on function of reaction order:

$$\text{Pseudo} - \text{zero order reaction:} \quad C_A = C_0 - k\, t \qquad \text{(Eq. 5)}$$

$$\text{Pseudo} - \text{first order reaction:} \quad C_A = C_0\, e^{-k\, t} \qquad \text{(Eq. 6)}$$

$$\text{Pseudo} - \text{second order reaction:} \quad C_A = \left(\frac{1}{C_0} + k\, t\right)^{-1} \qquad \text{(Eq. 7)}$$

The last three equations can be rewritten in terms of conversion of TGs (X) as:

$$\text{Pseudo} - \text{zero order reaction:} \quad 1 - X = 1 - k''\, t \qquad \text{(Eq. 8)}$$

$$\text{Pseudo} - \text{first order reaction:} \quad 1 - X = e^{-k\, t} \qquad \text{(Eq. 9)}$$

$$\text{Pseudo} - \text{second order reaction:} \quad 1 - X = (1 + k''\, t)^{-1} \qquad \text{(Eq. 10)}$$

where $X = 1 - \frac{C_A}{C_0}$ and $k'' = k\, C_0^{(\alpha\text{-}1)}$.

Statistic SYSTAT software (version 13.0) was used to fit the experimental data to Equations 8, 9 and 10. The estimation of the rate constant (k) and goodness of fit was done using the Levenberg-Marquardt algorithm adopted by the software, which adjust the parameters of a model function to minimize the sum of the squares of the errors between the function and the measured data point. Goodness of fit parameters such as R^2 (coefficient of determination), MSE (Mean Square Error) and SSE (Summed Square Error) were used to select the most appropriate reaction order in each case.

The values of the reaction rate constant (k) calculated for the pseudo-first order reactions were chosen for comparative purposes between the different vegetable oils used. These values were used to calculate activation energy (Ea) and pre-exponential factor (A) by Arrhenius equation (see Eq. 11). The kinetic parameters A and Ea were obtained from the intercept and slope, respectively, of the linear correlation resultant of plotting ln k versus T^{-1} (see Eq. 12). In addition, goodness of fit parameters such as R^2, SD (standard deviation) and p-value were evaluated for the linear regressions.

$$k = A\, e^{-\frac{Ea}{RT}} \qquad \text{(Eq. 11)}$$

$$lnk = lnA - \frac{Ea}{RT} \qquad \text{(Eq. 12)}$$

where k, A, Ea, R and T are the rate constant (min^{-1}), the pre-exponential factor (min^{-1}), the activation energy (kJ mol^{-1}), the gas constant (8314 kJ mol^{-1} K^{-1}) and the reaction temperature (K), respectively.

2.5 Thermodynamic model

There are two equations (the Arrhenius and Eyring equations [36]) that describe the dependence of the reaction rate with the temperature, both being derived from the statistical thermodynamics in the kinetic theory of gases. Eyring equation (see Eq. 13), a theoretical construction based on transition state model, establishes a relationship between some parameters letting to determine the Gibbs free energy change (ΔG), which evaluates the spontaneity of a chemical reaction.

$$k = k^{\ddagger}\, \frac{k_B\, T}{h}\, e^{\left(-\frac{\Delta G}{R\, T}\right)} \qquad \text{(Eq. 13)}$$

where k is the rate constant (min^{-1}), $k^{\ddagger}$ is the transmission coefficient (usually takes a value of 1 [37]), k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}), and h is the Planck constant (6.63×10^{-34} J s).

The calculation of some thermodynamic parameters [enthalpy change (ΔH) and entropy change (ΔS)] of the non-catalytic supercritical methanol transesterification reaction of the vegetable oils studied can be carried out by replacing the Gibbs free energy equation at constant temperature and pressure ($\Delta G = \Delta H - T\Delta S$) in Equation 13 and taking natural logarithms, resulting in the following equation:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \left[lnk^{\ddagger} + ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R}\right] \quad \text{(Eq. 14)}$$

The values of ΔH and ΔS can be obtained from the slope and intercept, respectively, of the linear plot of ln (k/T) versus T^{-1}.

2.6 Statistical analysis

Besides the kinetic fitting described above, an analysis of one-way ANOVA variance with Tukey post-hoc tests was performed to assess differences in the fatty acid composition of feedstocks. Samples were considered significantly different at p-values ≤ 0.05.

3. Results and discussion

3.1 Kinetic study of the transesterification reaction

The critical properties of the starting reaction mixtures (methanol + triglyceride-based vegetable oil), estimated according to the Ambrose method (one of the best critical properties estimating methods) for a methanol-to-oil molar ratio of 43:1, were: pseudocritical temperature and pressure of 250 °C and 6.1 MPa [38], respectively. In addition, the variation of this critical point with the fatty acid composition of the oil is small. Hence, it can be said that practically all experiments in this study were carried out above the critical point of the reaction mixtures.

3.1.1. Reaction orders

The evolution of the ratio between the current and initial experimental concentrations of TGs ($1 - X$) as a function of reaction time is depicted in Fig. 2 for all the vegetable oils (castor, jatropha, jojoba, pongamia, soybean and tobacco oils) and temperatures (250, 275, 300, 325 and 350 ºC) studied. As it can be observed, the concentration of TGs and jojoba wax esters decreased gradually with reaction time for all temperatures tested. In addition, as previously reported [2, 5, 7, 10, 12, 33], the higher the temperature, the more pronounced this decrease.

An examination of these graphs reveals in most of the cases the appearance of a high reaction rate region at the beginning of the process, followed by a lower reaction rate region as the reaction approaches completion. This behavior is typical for supercritical transesterification reactions of TGs, in which an initial fast kinetically controlled region exists, followed by a final slow region as equilibrium is approached [25]. In the case of non-supercritical transesterification reactions, an initial slow mass transfer-controlled region is also observed. However, there are no diffusional limitations during supercritical transesterification reactions as the reaction medium is considered to be in a single phase [39] and hence the transfer-controlled region is not observed. The only exception to this behavior was evidenced for the jojoba wax-oil supercritical transesterification at temperatures below 325 °C (see Fig. 2C). Jojoba wax-oil has a low chemical reactivity compared to TG-based oils [40] due to its chemical structure consisting of complex wax esters [40] and, therefore, it requires higher reaction temperatures than the rest of the vegetable oils studied to achieve high conversion values at short reaction times.

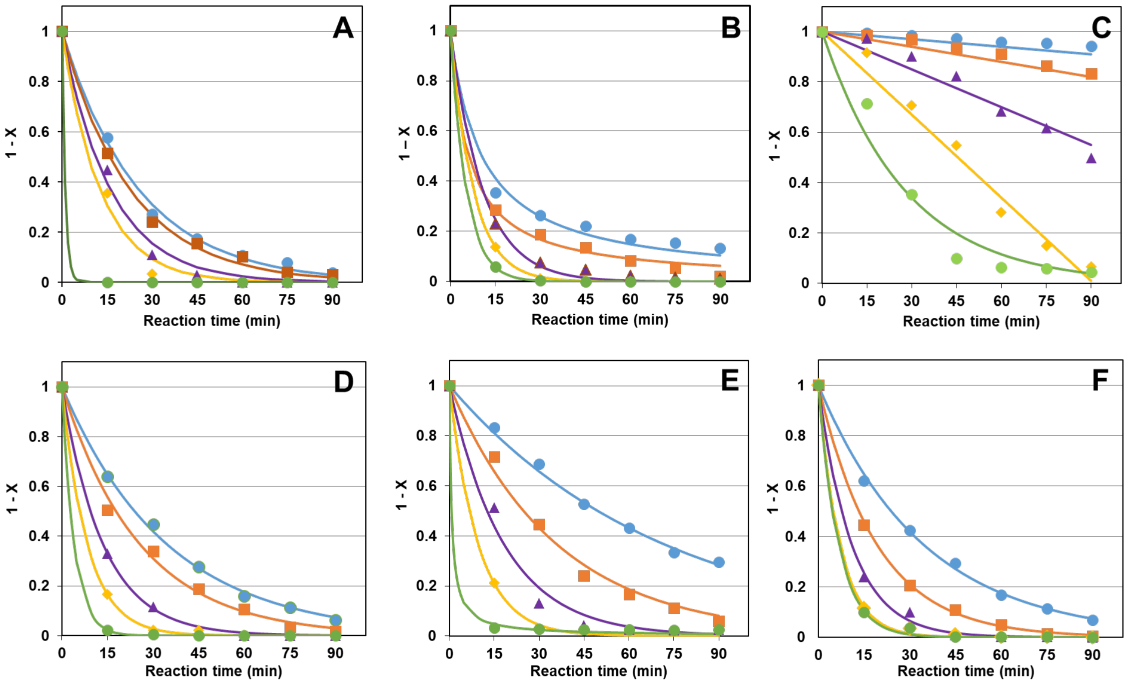


Fig. 2. Plots of C_A/C_0 ($1 - X$) versus reaction time for supercritical transesterification of vegetable oils of castor (A), jatropha (B), jojoba (C), pongamia (D), soybean (E) and tobacco (F) at temperatures of: –●– 250 ºC, –■– 275 ºC, –▲– 300 ºC, –◆– 325 ºC and –●– 350 ºC. The solid lines represent the best-fitting curves.

It can also be seen in Fig. 2 that a good adjustment was obtained between the experimental data (represented as symbols) and the theoretical curves of the best fitting kinetic models (represented as solid lines).

Although differential methods allow the direct calculation of the kinetic parameters, they provide fractional values for the reaction order as the reaction rate is determined from the slope of the curve of concentration of TGs versus reaction time [41]. For this reason, three different reaction order kinetic models were obtained in this study for each feedstock and temperature studied using an integral method consisting of fitting the experimental data to Eqs. (8)–(10). The reaction order chosen in each case was the one that led to the best-fitting kinetic model.

The goodness-of-fit parameters (R^2, MSE and SSE) for the pseudo-zero, pseudo-first and pseudo-second order kinetic models are summarized in Table 2 for all feedstocks and temperatures studied. A good fit of the experimental data to the kinetic model functions is obtained for high R^2 values (close to 1.000). In addition, the lower the values of MSE and SSE (close to 0.000), the more suitable the model function fitted.

Table 2. Statistical parameters for the pseudo-zero, pseudo-first and pseudo-second order kinetic models adjusted to the experimental data during supercritical transesterification of various vegetable oils at different temperatures.

Feedstock	T (ºC)	Pseudo-zero order reaction			Pseudo-first order reaction			Pseudo-second order reaction		
		R^2	MSE	SSE	R^2	MSE	SSE	R^2	MSE	SSE
Castor oil	250	0.794	0.047	0.281	0.997	0.000	0.003	0.967	0.005	0.032
	275	0.770	0.055	0.332	0.998	0.000	0.002	0.974	0.004	0.026
	300	0.672	0.089	0.534	0.994	0.001	0.007	0.950	0.009	0.055
	325	0.588	0.116	0.696	0.993	0.001	0.007	0.959	0.007	0.043
	350	0.375	0.192	1.154	1.000	0.000	0.000	1.000	0.000	0.000
Jatropha oil	250	0.611	0.078	0.467	0.927	0.012	0.069	0.991	0.001	0.007
	275	0.627	0.093	0.558	0.978	0.004	0.024	0.996	0.000	0.003
	300	0.544	0.126	0.753	0.999	0.000	0.002	0.995	0.001	0.006
	325	0.466	0.157	0.945	1.000	0.000	0.000	0.995	0.001	0.006
	350	0.413	0.177	1.063	1.000	0.000	0.000	0.999	0.000	0.001
Pongamia oil	250	0.896	0.022	0.133	0.998	0.000	0.001	0.961	0.006	0.036
	275	0.829	0.042	0.255	0.994	0.001	0.004	0.968	0.005	0.031
	300	0.622	0.105	0.631	0.999	0.000	0.001	0.976	0.004	0.026
	325	0.489	0.148	0.889	1.000	0.000	0.000	0.994	0.001	0.006
	350	0.392	0.185	1.113	1.000	0.000	0.000	1.000	0.000	0.000
Tobacco oil	250	0.889	0.024	0.144	0.998	0.000	0.001	0.968	0.005	0.028
	275	0.737	0.068	0.411	1.000	0.000	0.000	0.973	0.005	0.029
	300	0.564	0.123	0.740	0.998	0.000	0.001	0.989	0.002	0.012
	325	0.462	0.158	0.946	0.999	0.000	0.001	0.998	0.000	0.002
	350	0.453	0.161	0.967	0.999	0.000	0.001	0.998	0.000	0.002
Soybean oil	250	0.969	0.003	0.019	0.996	0.000	0.002	0.973	0.003	0.017
	275	0.896	0.021	0.123	0.994	0.001	0.006	0.943	0.010	0.058
	300	0.682	0.081	0.486	0.987	0.002	0.012	0.940	0.010	0.062
	325	0.497	0.140	0.843	0.999	0.000	0.002	0.991	0.001	0.008
	350	0.382	0.180	1.081	0.999	0.001	0.003	0.999	0.000	0.001
Jojoba wax-oil	250	0.988	0.000	0.000	0.988	0.000	0.000	0.988	0.000	0.000
	275	0.975	0.000	0.001	0.967	0.000	0.001	0.959	0.000	0.002
	300	0.974	0.002	0.010	0.947	0.003	0.019	0.914	0.005	0.029
	325	0.984	0.003	0.016	0.937	0.014	0.082	0.854	0.028	0.168
	350	0.813	0.040	0.240	0.971	0.005	0.030	0.905	0.018	0.107

The kinetic model that best described the experimental data for the oils of castor, pongamia, tobacco and soybean at all temperatures was that of pseudo-first order, for which the highest values of R^2 (higher than 0.985) and the lowest values of MSE (lower than 0.002) and SSE (lower than 0.012) were obtained (see Table 2). These results agree with those reported by Asri et al. [35] during the supercritical transesterification of soybean oil. Similar results were also reported by Varma et al. [42] and Rathore et al. [43] in supercritical conditions from castor and pongamia oils, respectively, using a differential method. In the case of tobacco oil, no kinetic studies on the non-catalytic supercritical synthesis of biodiesel have been reported yet.

The selection of the best kinetic equation that allows us to choose the reaction order for the jatropha and jojoba oils was not evident due to the fact that the best-fitting model depends on the reaction temperature. Thus, kinetic equations of pseudo-second order were the most adequate to describe the evolution of the experimental concentration of TGs from jatropha oil at low temperatures (250 ºC and 275 ºC), while at higher temperatures pseudo-first order equations fitted better to the data. In the case of jojoba wax-oil, the pseudo-zero order equation showed the best fit to the experimental data at temperatures of 325 ºC and below, while above this temperature the experimental results were fitted better by the pseudo-first order equation.

In these cases where the reaction order depends on the temperature it is possible to select an average reaction order to describe the behavior of the reaction. Thus, Zeng et al. [41], who carried out the synthesis of biodiesel from soybean by supercritical methanol transesterification, obtained relative reaction orders at different temperatures and then calculated an average value for determining the kinetic equation. However, kinetic models of pseudo-first order have been selected (and no fractional orders have been used) in this study for comparative purposes to calculate the kinetic parameters of the supercritical transesterification for all vegetable oils studied, including jatropha and jojoba oils. The values of the goodness-of-fit parameters of the pseudo-first order kinetic models for these two last feedstocks were similar to those obtained for the best-fitting models (see Table 2). Kafuku et al. [44], Rathore et al. [43] and Andreo-Martínez et al. [7] also assumed this same reaction order (pseudo-first order) for the supercritical synthesis of biodiesel from these two feedstocks.

3.1.2. Kinetic parameters

Reactant nature, reactant concentration, temperature, pressure, phase in which the reaction occurs and catalyst presence/absence are among the most important variables influencing the rate of a chemical reaction. All these variables are constant in the present study, with the only exception of the vegetable oil nature and the reaction temperature. In the case of pressure, it was a direct consequence of the temperature applied (batch operation) [7] and was practically the same regardless of the feedstock used (see Table 3). Therefore, only the effect of the reaction temperature and vegetable oil nature on the kinetic parameters of the supercritical transesterification will be discussed.

Rate constants calculated using the pseudo-first order kinetic model (see Equation 9), and pre-exponential factors and activation energies obtained from the Arrhenius plot, which is shown in Fig. 3A, are presented in Table 3 for all vegetable oils and reaction conditions tested. In addition, this table shows some goodness-of-fit parameters (R^2, SD and p-value) of the Arrhenius fit. Low SD values and high R^2 values indicate a good fit between the natural logarithm of k and the inverse of the reaction temperature, while p-values less than 0.05 indicate a high significance of the linear regression function at a 95% confidence level.

In view of the statistical parameters presented in Table 3 for the Arrhenius fit, it can be said that all linear regression functions obtained for the different vegetable oils showed an adequate significance level and provided a good fit to the data. However, in the case of castor oil, the linear model calculated for all data pairs ($\ln k$ - $1/T$) was not significant (a p-value of 0.091) and provided a high SD value (0.863) and a low R^2 value (0.668). This bad fit was caused by the data point corresponding to the higher reaction temperature (350 ºC) (see Fig. 2A), which was then removed from the Arrhenius plot (see Fig. 3A). Therefore, the values of *Ea*, *A*, R^2, SD and p-value showed in Table 3 for the supercritical transesterification of castor oil were calculated considering only four data points.

Table 3. Kinetic and adjustment parameters for the pseudo-first order supercritical transesterification reaction from various vegetable oils at different temperatures.

Feedstock	Pressure (MPa)	T (ºC)	*k* (min^{-1}) ± SE	*A* (min^{-1})	*Ea* ($kJ\ mol^{-1}$)	R^2	SD	p-value
Castor oil	10	250	0.039 ± 0.001	13.97	25.79	0.958	0.082	0.021
	14	275	0.044 ± 0.001					
	21	300	0.062 ± 0.004					
	31	325	0.079 ± 0.006					
	43	350	0.921 ± 0.061					
Jatropha oil	12	250	0.043 ± 0.007	399.02	39.74	0.999	0.019	0.000
	18	275	0.065 ± 0.008					
	26	300	0.093 ± 0.005					
	35	325	0.132 ± 0.002					
	43	350	0.189 ± 0.000					
Pongamia oil	12	250	0.029 ± 0.001	$1.69 \cdot 10^4$	58.40	0.969	0.175	0.002
	18	275	0.039 ± 0.002					
	26	300	0.074 ± 0.002					
	35	325	0.120 ± 0.003					
	43	350	0.250 ± 0.006					
Tobacco oil	12	250	0.029 ± 0.001	$1.53 \cdot 10^3$	46.87	0.963	0.154	0.003
	18	275	0.052 ± 0.001					
	26	300	0.091 ± 0.004					
	35	325	0.141 ± 0.005					
	43	350	0.150 ± 0.007					
Soybean oil	12	250	0.014 ± 0.000	$3.22 \cdot 10^5$	73.92	0.996	0.083	0.000
	18	275	0.028 ± 0.001					
	26	300	0.055 ± 0.004					
	35	325	0.104 ± 0.005					
	43	350	0.222 ± 0.042					
Jojoba wax-oil	12	250	0.001 ± 0.000	$1.12 \cdot 10^7$	101.26	0.990	0.176	0.000
	22	275	0.002 ± 0.000					
	31	300	0.006 ± 0.001					
	38	325	0.018 ± 0.003					
	42	350	0.036 ± 0.004					

The results in Table 3 show that, as expected, the rate constants increased with increasing temperature for all vegetable oils, thus indicating the positive effect of temperature on the supercritical transesterification reaction. This fact can be easily explained by the collision theory, as described by Ong et al. [31]. These authors indicated that an increase in temperature during supercritical transesterification favors the homogeneity of the reaction mixture and increases the kinetic energy of the system, thus leading to a higher collision frequency between reactive molecules.

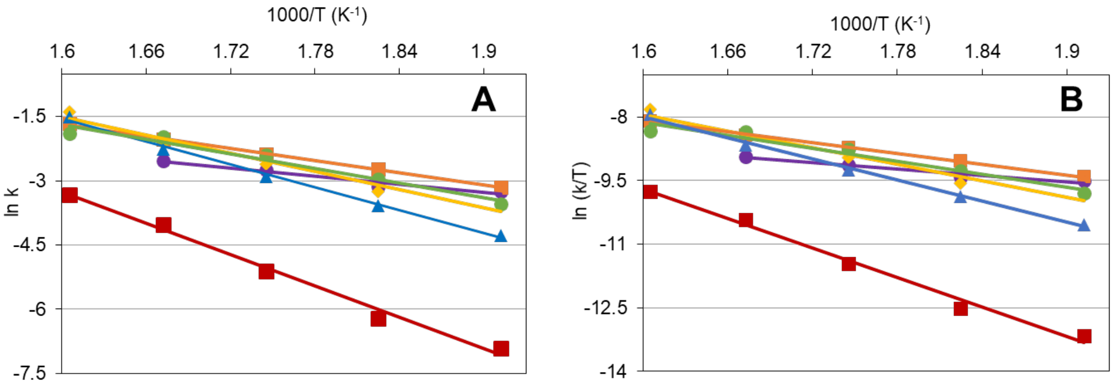


Fig. 3. Arrhenius plot (A) and Eyring plot (B) for the supercritical transesterification reaction from the oils of: ● castor, ■ jatropha, ■ jojoba, ◆ pongamia, ▲ soybean, and ● tobacco.

The activation energy, which is the minimum energy that is needed for a chemical reaction to occur, depends on the rate of change of the *k* values with temperature: the higher the rate of change, the greater *Ea* values. The *Ea* values for the supercritical transesterification of the different vegetable oils studied decreased in the following order: jojoba wax-oil > soybean oil > pongamia oil > tobacco oil > jatropha oil > castor oil.

The pre-exponential factor, which is a specific parameter of each chemical reaction, depends on how often molecules collide with each other and on the probability of an effective collision (a collision where reactant molecules have enough energy and are oriented properly) to be produced [31, 45]. Thus, high A values mean a great probability of successful collisions leading to the formation of reaction products. The A values increased in the following order for the vegetable oils used during the supercritical reaction: castor oil < jatropha oil < pongamia oil < tobacco oil < soybean oil < jojoba wax-oil. According to this sequence, the probability of effective collisions between methanol and jojoba wax esters during the supercritical transesterification was much higher than that between methanol and TGs.

Some values of the kinetic parameters found in the literature for the non-catalytic supercritical methanol transesterification of various feedstocks are shown in Table 4. The *k* values shown for castor, jatropha and pongamia oils were calculated by the authors of the present study from the data of references [42], [43] and [44].

Table 4. Kinetic and thermodynamic parameters obtained by other authors for the supercritical transesterification of the same vegetable oils used in this study at different reaction conditions.

Feedstock	Vessel volume (ml)	Pressure (MPa)	T (°C)	Methanol-to-oil molar ratio	k (min^{-1})	Ea (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})	Ref.
Castor	11 [batch]	20	250	40:1	0.03337	35.00	145.24	30.54	-0.22	[42]
			300		0.07065		156.21			
			350		0.12246		167.17			
Jatropha	11 [batch]	19-20	250	40:1-50:1	0.12369	11.40	139.55	6.45	-0.25	[43]
			300		0.16203		152.27			
			350		0.18637		165.00			
	12 [batch]		300	50:1	0.14086	33.40	152.67	25.14	-0.22	[44]
			330		0.20805		159.35			
			360		0.26185		166.03			
			390		0.31664		172.71			
			420		0.45384		179.38			
Pongamia	11 [batch]	19-20	250	40:1-50:1	0.11884	10.50	177.56	42.15	-0.26	[43]
			300		0.15259		190.50			
			350		0.16696		203.45			
			400		0.19398		216.39			
Soybean	200 [continuous]	28	240	42:1	0.02196	56.00	144.47	51.49	-0.18	[8]
			250		0.02530		146.28			
			260		0.03150		148.09			
			270		0.04692		149.90			
			280		0.05286		151.72			
	8.8 [batch]	8	250	24:1	0.00740	89.32	142.43	40.99	-0.19	[35]
			270		0.02650		146.31			
			290		0.03050		150.19			
Jojoba	83 [batch]	12	250	15:1	0.00070	115.50	162.46	110.8	-0.10	[7]
		22	275		0.00180		164.93			
		31	300		0.00650		167.40			
		38	325		0.02450		169.87			
		42	350		0.03880		172.33			

In general, the rate constants obtained in the present study tend to be similar to or lower than those reported in the literature for the same feedstocks at similar reaction conditions (see Table 4), except at the highest temperature used (350 °C), at which the rate constants were higher. The fact of lower rate constants being obtained can be explained by the heating time needed for the reactor to reach the reaction temperature [6,7], which in turn depends on the volume of the batch reactor used: the greater the reactor volume, the greater the thickness of the reactor wall and, therefore, the longer the heating time. In addition, the longer the heating time, the shorter the time the reactor is at the reaction temperature (the heating time is included in the reaction time in this study) and, hence, the slower the reaction. The volume of the reactor used in the present study (83 ml) was greater than those used in other studies on the supercritical transesterification of the same vegetable oils (see Table 4) and the reactor took between 10 and 15 min to reach the desired reaction temperature. In the case of soybean oil, He et al. [8] used a 200 ml continuous reactor, where no heating problems occur, and reported higher rate constants than in this study at similar reaction conditions.

Another factor influencing the reaction rate during supercritical transesterification is the operating pressure: the higher the pressure, the higher the reaction rate [8]. This fact was evident at the highest temperature used (350 °C) at which a very considerable working pressure was reached (43 MPa), which led in general to higher rate constants. This is the case of castor and pongamia oils with which higher values of rate constants were obtained compared to those reported in previous studies working at 20 MPa at this temperature [42,43].

Finally, it is necessary to emphasize that the kinetic parameters statistically optimized in the present work for the supercritical transesterification of jojoba wax-oil were similar to those previously published by our research group [7].

It has been previously reported that the composition of vegetable oils influences the rate of the non-catalytic supercritical transesterification reaction [20,21,31,42,43,46]. The oils of jatropha, pongamia, tobacco and soybean are formed by TGs containing practically the same set of fatty acids (palmitic, stearic, oleic, linoleic and linolenic acids) and, therefore, they can be compared to each other. However, it is difficult to compare the oils of castor and jojoba with the rest of vegetable oils since they are basically composed of TGs of a single and very different fatty acid (ricinoleic acid, a hydroxy fatty acid) [42] and linear long esters of monounsaturated fatty alcohols and acids [7], respectively. Ricinoleic acid is the most reactive of all fatty acids and, therefore, triglycerides of ricinoleic acid (castor oil) should react with supercritical methanol at a faster rate than the rest of triglycerides (vegetable oils), which was confirmed experimentally; the supercritical transesterification of castor oil provided the lowest value of Ea (see Table 3). Some authors have also calculated the kinetic parameters of the supercritical esterification reaction of the main fatty acid present in castor oil (ricinoleic acid) [47]. In the case of jojoba wax-oil, the supercritical methanolysis provided the slowest reaction rate.

It has been reported that the supercritical methanol transesterification of TG-based vegetable oils containing large amounts of saturated fatty acids (SFAs) evolves at a higher reaction rate [42], which was not observed in the present study. According to the content of SFAs, the supercritical reaction rate should have followed the following order: pongamia oil > jatropha oil > soybean oil > tobacco oil (see Table 1). However, based on the values of *Ea* obtained in this work (see Table 3), the reaction rates for the TG-based oils with the same set of fatty acids followed the sequence (a decrease of *Ea* values basically corresponds to a faster reaction): jatropha oil > tobacco oil > pongamia oil > soybean oil. This sequence can be explained by the content of triunsaturated fatty acids (mainly linolenic acid, C18:3) in the oil: the higher the content of linolenic acid (see Table 1), the slower the supercritical reaction. Of note, these vegetable oils showed significant differences in the content of C18:3 in the same order as the sequence described above. This relationship was already observed by Rathore et al. [43], who observed that the supercritical transesterification reaction rate decreases with increasing the content of triunsaturated fatty acid triglycerides in the oil. Triunsaturated fatty acid triglycerides react at a lower reaction rate than those of diunsaturated fatty acids, which in turn also react at a lower reaction rate than those of monounsaturated ones [43].

3.2 Thermodynamic study of the transesterification reaction

Table 5 shows the values of Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes for the non-catalytic supercritical methanol transesterification reaction of various feedstocks. These values were calculated from the Eyring plot shown in Fig. 3B, where ln (k/T) is plotted versus $T-1$. As it can be seen, the supercritical methanol transesterification of all vegetable oils studied provided positive values of ΔG, indicating that the transition state has a higher energy level than the reacting species and revealing that the reaction is endergonic (thermodynamically unfavorable or non-spontaneous reaction) in nature. Furthermore, positive values of ΔH were also obtained for all feedstocks, showing that the supercritical methanol transesterification is endothermic in nature and requires external energy supply in the form of heat to transform reactants into products. However, negative values of ΔS were calculated in all cases, which is indicative that the reactants joined to each other to form over transition states along the reaction (the degree of ordered alignment/geometry of transition state) are more ordered than the reactants in the ground state [23,24,31,41,48–50].

In view of the goodness-of-fit parameters (R^2, SD and p-value) of the Eyring fit (see Table 5), an adequate significance level of the linear regression functions was found for all vegetable oils studied and the linear functions adjusted well to the data. However, it should be noted that for castor oil the point corresponding to 350 ºC was disregarded as a consequence of the poor statistical parameters to which it gave rise (R^2 = 0.635, SD = 0.867 and p-value = 0.106).

Table 5. Thermodynamic and adjustment parameters for the pseudo-first order supercritical transesterification reaction from various vegetable oils at different temperatures.

Feedstock	Pressure (MPa)	T (ºC)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1})	R^2	SD	p-value
Castor oil	10	250	146.32	20.80	-0.24	0.944	0.077	0.028
	14	275	152.32					
	21	300	158.32					
	31	325	164.32					
	43	350	170.32					
Jatropha oil	12	250	144.24	35.02	-0.21	0.999	0.018	0.000
	18	275	149.46					
	26	300	154.68					
	35	325	159.90					
	43	350	165.13					
Pongamia oil	12	250	146.63	53.69	-0.18	0.965	0.173	0.003
	18	275	151.07					
	26	300	155.51					
	35	325	159.96					
	43	350	164.40					
Tobacco oil	12	250	145.50	42.15	-0.20	0.954	0.156	0.004
	18	275	150.44					
	26	300	155.38					
	35	325	160.32					
	43	350	165.26					
Soybean oil	12	250	149.34	69.21	-0.15	0.995	0.081	0.000
	18	275	153.17					
	26	300	157.00					
	35	325	160.83					
	43	350	164.66					
Jojoba wax-oil	12	250	161.25	96.55	-0.12	0.995	0.081	0.000
	22	275	164.34					
	31	300	167.43					
	38	325	170.52					
	42	350	173.62					

The values of the thermodynamic parameters (ΔG, ΔH and ΔS) shown in Table 4 for the non-catalytic supercritical methanol transesterification of most of the same vegetable oils used in this work were calculated by the authors of the present study from the data of references [7,8,35,42–44]. As can be seen in this table, the values of ΔG, ΔH and ΔS were in general similar to those obtained in this study, which allows us to conclude that the non-catalytic supercritical methanol transesterification of vegetable oils is an endergonic and endothermic reaction.

4. Conclusions

Kinetic and thermodynamic parameters of the non-catalytic supercritical methanol transesterification to biodiesel of the vegetable oils of castor, jatropha, pongamia, tobacco, soybean and jojoba were calculated and discussed. The reaction was carried out in a one-step process and the influence of the main variables [temperatures in the range of 250-350 ºC (10-43 MPa) and reaction times in the range of 15-90 min] on the reaction was evaluated at an optimal methanol-to-oil molar ratio (43:1 or 15:1 in the case of jojoba wax-oil).

Three different integral kinetic models (pseudo-zero, pseudo-first and pseudo-second order kinetic models) were fitted to the experimental data in order to determine the best reaction order. The pseudo-first order model provided in most of the cases the best goodness-of-fit statistical parameters and was hence selected to calculate the kinetic and thermodynamic parameters of the reaction. Both the reaction temperature and the oil composition influenced the reaction rate. As expected, the temperature had a positive influence on the reaction rate for all vegetable oils studied. Based on the rate constants and activation energies obtained, the reaction rates followed the sequence: castor oil > jatropha oil > tobacco oil > pongamia oil > soybean oil > jojoba wax-oil. This reaction rate sequence for the TG-based oils with the same set of fatty acids (*i.e.*, for the oils of jatropha, tobacco, pongamia and soybean) can be explained by the content of linolenic acid in the oil: the higher the content of linolenic acid, the higher the activation energy and the lower the reaction rate.

Finally, positive values of Gibbs free energy change and enthalpy change were obtained, showing that the non-catalytic supercritical methanol transesterification reaction of vegetable oils is endergonic and endothermic in nature.

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References

[1] Demirbas A. Progress and recent trends in biodiesel fuels. Energy Convers Manage 2009;50(1):14-34.

[2] García-Martínez N, Andreo-Martínez P, Quesada-Medina J, de los Ríos AP, Chica A, Beneito-Ruiz R, et al. Optimization of non-catalytic transesterification of tobacco (*Nicotiana tabacum*) seed oil using supercritical methanol to biodiesel production. Energy Convers Manage 2017;131:99-108.

[3] de_Richter RK, Ming T, Caillol S, Liu W. Fighting global warming by GHG removal: Destroying CFCs and HCFCs in solar-wind power plant hybrids producing renewable energy with no-intermittency. Int J Greenh Gas Con 2016;49(Supplement C):449-72.

[4] Liu H, Ma X, Li B, Chen L, Wang Z, Wang J. Combustion and emission characteristics of a direct injection diesel engine fueled with biodiesel and

PODE/biodiesel fuel blends. Fuel 2017;209(Supplement C):62-8.

[5] Ortiz-Martínez VM, Salar-García MJ, Palacios-Nereo FJ, Olivares-Carrillo P, Quesada-Medina J, de los Ríos AP, et al. In-depth study of the transesterification reaction of *Pongamia pinnata* oil for biodiesel production using catalyst-free supercritical methanol process. J Supercrit Fluids 2016;113:23-30.

[6] Farobie O, Matsumura Y. State of the art of biodiesel production under supercritical conditions. Prog Energy Combust Sci 2017;63(Supplement C):173-203.

[7] Andreo-Martínez P, García-Martínez N, Quesada-Medina J, Román-Figueroa C, Paneque M. Synthesis of value added fatty alcohols and FAMEs by non-catalytic supercritical methanol transesterification of jojoba (*Simmondsia chinensis*) wax. Energy Convers Manage 2017;154:430-9.

[8] He H, Sun S, Wang T, Zhu S. Transesterification Kinetics of Soybean Oil for Production of Biodiesel in Supercritical Methanol. J Am Oil Chem Soc 2007;84(4):399-404.

[9] Laidler KJ. Chemical Kinetics, 3rd edition. Prentice Hall, New York, 1987.

[10] Olivares-Carrillo P, Quesada-Medina J. Synthesis of biodiesel from soybean oil using supercritical methanol in a one-step catalyst-free process in batch reactor. J Supercrit Fluids 2011;58(3):378-84.

[11] Demirbas A. Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics. Energy Convers Manage 2006;47(15–16):2271-82.

[12] Salar-García MJ, Ortiz-Martínez VM, Olivares-Carrillo P, Quesada-Medina J, de los Ríos AP, Hernández-Fernández FJ. Analysis of optimal conditions for biodiesel production from *Jatropha* oil in supercritical methanol: Quantification of thermal decomposition degree and analysis of FAMEs. J Supercrit Fluids 2016;112:1-6.

[13] Yusuf NNAN, Kamarudin SK. Techno-economic analysis of biodiesel production

from *Jatropha curcas* via a supercritical methanol process. Energy Convers Manage 2013;75:710-7.

[14] Tomic M, Micic R, Kiss F, Dedovic N, Simikic M. Economic and environmental performance of oil transesterification in supercritical methanol at different reaction conditions: Experimental study with a batch reactor. Energy Convers Manage 2015;99(Supplement C):8-19.

[15] Micic RD, Tomić MD, Kiss FE, Martinovic FL, Simikić MĐ, Molnar TT. Comparative analysis of single-step and two-step biodiesel production using supercritical methanol on laboratory-scale. Energy Convers Manage 2016;124(Supplement C):377-88.

[16] Micic RD, Tomić MD, Kiss FE, Nikolić-Djorić EB, Simikić MĐ. Influence of reaction conditions and type of alcohol on biodiesel yields and process economics of supercritical transesterification. Energy Convers Manage 2014;86:717-26.

[17] Madras G, Kolluru C, Kumar R. Synthesis of biodiesel in supercritical fluids. Fuel 2004;83(14–15):2029-33.

[18] Sawangkeaw R, Bunyakiat K, Ngamprasertsith S. A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001–2009). J Supercrit Fluids 2010;55(1):1-13.

[19] Quesada-Medina J, Olivares-Carrillo P. Evidence of thermal decomposition of fatty acid methyl esters during the synthesis of biodiesel with supercritical methanol. J Supercrit Fluids 2011;56(1):56-63.

[20] Lamba N, Gupta K, Modak JM, Madras G. Biodiesel synthesis from Calophyllum inophyllum oil with different supercritical fluids. Bioresour Technol 2017;241:767-74.

[21] Lamba N, Modak JM, Madras G. Fatty acid methyl esters synthesis from non-

edible vegetable oils using supercritical methanol and methyl tert-butyl ether. Energy Convers Manage 2017;138:77-83.

[22] Campanelli P, Banchero M, Manna L. Synthesis of biodiesel from edible, non-edible and waste cooking oils via supercritical methyl acetate transesterification. Fuel 2010;89(12):3675-82.

[23] Wu L, Wei T, Lin Z, Zou Y, Tong Z, Sun J. Bentonite-enhanced biodiesel production by NaOH-catalyzed transesterification: Process optimization and kinetics and thermodynamic analysis. Fuel 2016;182(Supplement C):920-7.

[24] Feyzi M, Shahbazi Z. Preparation, kinetic and thermodynamic studies of Al–Sr nanocatalysts for biodiesel production. J Chin Inst Chem Eng 2017;71(Supplement C):145-55.

[25] Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Oil Chem Soc 1997;74(11):1457-63.

[26] Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. J Am Oil Chem Soc 2000;77(12):1263-7.

[27] Kusdiana D, Saka S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. Fuel 2001;80(5):693-8.

[28] Song E-S, Lim J-w, Lee H-S, Lee Y-W. Transesterification of RBD palm oil using supercritical methanol. J Supercrit Fluids 2008;44(3):356-63.

[29] Alenezi R, Leeke GA, Winterbottom JM, Santos RCD, Khan AR. Esterification kinetics of free fatty acids with supercritical methanol for biodiesel production. Energy Convers Manage 2010;51(5):1055-9.

[30] Cho HJ, Kim SH, Hong SW, Yeo Y-K. A single step non-catalytic esterification of palm fatty acid distillate (PFAD) for biodiesel production. Fuel 2012;93(Supplement C):373-80.

[31] Ong LK, Kurniawan A, Suwandi AC, Lin CX, Zhao XS, Ismadji S. Transesterification of leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics studies. J Supercrit Fluids 2013;75(Supplement C):11-20.

[32] Lieu T, Yusup S, Moniruzzaman M. Kinetic study on microwave-assisted esterification of free fatty acids derived from Ceiba pentandra Seed Oil. Bioresour Technol 2016;211:248-56.

[33] Román-Figueroa C, Olivares-Carrillo P, Paneque M, Palacios-Nereo FJ, Quesada-Medina J. High-yield production of biodiesel by non-catalytic supercritical methanol transesterification of crude castor oil (*Ricinus communis*). Energy 2016;107:165-71.

[34] Diasakou M, Louloudi A, Papayannakos N. Kinetics of the non-catalytic transesterification of soybean oil. Fuel 1998;77(12):1297-302.

[35] Asri NP, Machmudah S, Wahyudiono W, Suprapto S, Budikarjono K, Roesyadi A, et al. Non catalytic transesterification of vegetables oil to biodiesel in sub-and supercritical methanol: a kinetic's study. Bull Chem React Eng Catal 2013;3:215–23.

[36] Eyring H. The activated complex in chemical reactions. J Chem Phys 1935;3(2):107-15.

[37] Razavy M. Quantum Theory of Tunneling. World Scientific; 2003.

[38] Olivares-Carrillo P, Quesada-Medina J, Pérez de los Ríos A, Hernández-Fernández FJ. Estimation of critical properties of reaction mixtures obtained in different reaction conditions during the synthesis of biodiesel with supercritical methanol from soybean oil. Chem Eng J 2014;241:418–32.

[39] Valle P, Velez A, Hegel P, Mabe G, Brignole EA. Biodiesel production using

supercritical alcohols with a non-edible vegetable oil in a batch reactor. J Supercrit Fluids 2010;54:61–70.

[40] Hussein LI, Elsabee MZ, Ismail EA, Naguib HF, Aziz HA, Elsawy MA. Transesterification of jojoba oil-wax using microwave technique. Int J Environ Chem Ecol Geol Geophys Eng 2014;8:286–91.

[41] Zeng D, Yang L, Fang T. Process optimization, kinetic and thermodynamic studies on biodiesel production by supercritical methanol transesterification with CH3ONa catalyst. Fuel 2017;203:739–48.

[42] Varma MN, Madras G. Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids. Ind Eng Chem Res 2007;46:1–6.

[43] Rathore V, Madras G. Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide. Fuel 2007;86:2650–9.

[44] Kafuku G, Lee KT, Mbarawa M. Non-catalytic and catalytic transesterification: a reaction kinetics comparison study. Int J Green Energy 2015;12:551–8.

[45] Ang GT, Ooi SN, Tan KT, Lee KT, Mohamed AR. Optimization and kinetic studies of sea mango (Cerbera odollam) oil for biodiesel production via supercritical reaction. Energy Convers Manage 2015;99:242–51.

[46] Varma MN, Deshpande PA, Madras G. Synthesis of biodiesel in supercritical alcohols and supercritical carbon dioxide. Fuel 2010;89:1641–6.

[47] Narayan RC, Lamba N, Javed A, Madras G. Kinetics of esterification of 10-undecenoic and ricinoleic acids with near-critical and supercritical methanol. Sustain Energy Fuels 2017;1:1425–36.

[48] Sarve AN, Varma MN, Sonawane SS. Ultrasound assisted two-stage biodiesel synthesis from non-edible Schleichera triguga oil using heterogeneous catalyst:

kinetics and thermodynamic analysis. Ultrason Sonochem 2016;29:288–98.

[49] Galvan D, Orives JR, Coppo RL, Silva EnT, Angilelli KG, Borsato D. Determination of the kinetics and thermodynamics parameters of biodiesel oxidation reaction obtained from an optimized mixture of vegetable oil and animal fat. Energy Fuels 2013;27:6866–71.

[50] Nautiyal P, Subramanian KA, Dastidar MG. Kinetic and thermodynamic studies on biodiesel production from Spirulina platensis algae biomass using single stage extraction–transesterification process. Fuel 2014;135:228–34.