Kinetics of Ethyl Ester Production from Soybean and Sunflower Oils Catalyzed by Sodium Ethoxide

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Abstract—*The present paper reports the kinetics of soybean and sunflower oils' ethanolysis. The transesterification reaction was carried out using a molar ratio of ethanol to oil of 9:1 and 1.0 wt% of sodium ethoxide as catalyst under stirring of 400 rpm. The reactions were performed in a stirred batch reactor at three different temperatures (308.15, 323.15 and 338.15 K) over a period of 120 min. The concentration of compounds was analyzed by High-Performance Size Exclusion Chromatography (HPSEC). The kinetic model assumed that ethanolysis occurs in a sequence of three reversible steps with the production of di- and monoacylglycerols as intermediate components. Based on the modeling approach it was possible to determine the rate constants of reaction and activation energies for the transesterification process of soybean and sunflower oils. Despite the phase splitting, no mass transfer control was observed and the proposed mathematical model fitted well the experimental data.*

Keywords: Ethanol, ethylic biodiesel, kinetics, soybean oil, sunflower oil.

I. INTRODUCTION

Biodiesel, a clean renewable fuel, is considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification [1]. Ethyl esters (ethyl biodiesel) are produced from triacylglycerols, which can react with ethanol in the presence of a catalyst, usually an alkali or acid catalyst, in a process known as transesterification. The transesterification reaction results in the production of three moles of ethyl esters (*EE*) and one mole of glycerol (*GL*) for each mole of triacylglycerol (*TG*), requiring three moles of alcohol. The reaction occurs as a sequence of three steps with intermediate formation of diacylglycerols (*DG*) and monoacylglycerols (*MG*) [2].

Most of the biodiesel produced in the world today is derived from soybean oil, however, all vegetable oils or triacylglycerols can be converted into biodiesel. Factors such as geography, climate and economics determine the vegetable oil of greater interest for potential use in biofuels. Thus, in the United States, for example, soybean oil is regarded as the main raw material and in some tropical countries, it is palm oil. The most common vegetable oils, whose raw materials are abundant in Brazil, are soybean, corn, peanuts, cotton, babassu and palm [3.4].

Methanol is most often used as alcohol in the biodiesel synthesis because of its suitable physical and chemical properties and low cost, but it is usually derived from fossil sources. The production of ethyl esters, rather than methyl esters, is of considerable interest because the ethyl ester based biodiesel is an entirely agricultural fuel [5,6].

Fatty acid esters are broadly available in nature and have been widely used as high–value fine chemicals in the food, cosmetic, pharmaceutical and rubber industries. Currently, fatty acid esters (biodiesel) are being considered as a promising substitute for conventional diesel fuels, due to environmental and economic problems related to the use of conventional fuels [7,10].

There are several variables, such as molar ratio of alcohol to vegetable oil, catalyst type, temperature, and presence of impurities, among others, that affect the transesterification process and should be investigated [11,12].

The transesterification kinetics for vegetable oils has been reported in a few studies. However, most of these studies do not take into account the formation of intermediate products, only the overall reaction, and consider the use of methanol instead of ethanol [13,16].

In this study, the kinetics of transesterification of soybean and sunflower oils with ethanol was investigated. The molar ratio of alcohol to oil, the catalyst concentration (sodium ethoxide) and the mixing intensity were kept constant while the temperature was varied. Kinetic data were collected at three temperature levels. The reaction rate constants and the activation energies were determined for all the forward and reverse reactions in the three temperature levels.

II. EXPERIMENTAL SECTION

Anhydrous ethanol and glacial acetic acid were purchased from Merck (Germany), with purity of 99.5 and 99.0 %, respectively. Tetrahydrofuran (THF) from Tedia, with purity of 99.8 %, and sodium ethoxide from Sigma Aldrich, with purity of 99 % were also used.

Refined soybean and sunflower oils were purchased in the local retail market (Bunge, Campinas/SP, Brazil).The fatty acid compositions of the vegetable oils studied in this work are presented in Table 1. These compositions were determined by gas chromatography of the fatty acid methyl esters using the official AOCS method (1–62) [17]. Prior to the chromatographic analysis the fatty compounds of the samples were converted into their respective fatty acid methyl esters using the method of Hartman and Lago[18]. The chromatographic analyses were carried out using a capillary gas chromatography system and the experimental conditions were obtained from Basso et al.[19].

TABLE 1
FATTY ACID COMPOSITIONS OF THE VEGETABLE OILS

Fatty acid	Symbol	Cx:y[a]	M^c g.mol^{-1}	Soybean oil	Sunflower Oil
				100w[d]	
Dodecanoic	L	C12:0	200.32	0.00	0.06
Tetradecanoic	M	C14:0	228.38	0.05	0.02
Hexadecanoic	P	C16:0	256.43	10.72	6.30
cis-hexadec-9-enoic	Po	C16:1	254.42	0.07	0.09
Trans - hexadec-9-enoic		C16:1t[b]	254.42	0.00	0.03
Heptadecanoic	Ma	C17:0	270.45	0.06	0.03
cis-heptadec-9-enoic	Mg	C17:1	268.45	0.00	0.03
Octadecanoic	S	C18:0	284.49	2.80	3.31
cis-octadec-9-enoic	O	C18:1	282.47	25.94	35.98
cis,cis-octadeca-9,12-dienoic	Li	C18.2	280.45	53.00	52.75
trans,trans-octadeca-9,12-dienoic		C18:2t[b]	280.45	0.13	0.11
all-*cis*-octadeca-9,12,15-trienoic	Le	C18:3	278.44	6.34	0.78
Icosanoic	A	C20:0	312.54	0.31	0.30
cis–icos–9–enoic	Ga	C20:1	310.52	0.19	0.21
Docosanoic	Be	C22:0	340.59	0.39	0.00

[a]InCx:y, x = number of carbons and y = number of double bonds. [b] trans isomer. [c]M = molar mass. [d]w = mass fraction

Based on the fatty acid compositions, the possible compositions of triacylglycerol (Table 2) of the vegetable oils were calculated using the algorithm suggested by AntoniosiFilho et al.[20]. In order to calculate the probable triacylglycerol compositions, the quantities of *transisomers* (see Table 1) were computed with their respective *cis* isomers. In Table 2 the main triacylglycerol represents the component with the greatest composition in the isomer set with x carbons and y double bonds. Additionally, iodine values of vegetable oils were calculated from their fatty acid compositions according to the official method Cd 1c-85, recommended by AOCS [17]. These values are presented in Table 3 together with tabulated values extracted from Firestone[21] for soybean and sunflower oils. The iodine value reflects the degree of unsaturation of fatty compounds, so that the higher the iodine value the higher the degree of unsaturation.

TABLE 2
POSSIBLE TRIACYLGLYCEROL COMPOSITIONS OF SOYBEAN AND SUNFLOWEROILS.

Main *TG*[a]	**Group x:y[b]**	**Molar mass ($g.mol^{-1}$)**	**Soybean oil**	**Sunflower oil**	**Main *TG*[a]**	**Group x:y[b]**	**Molar mass ($g.mol^{-1}$)**	**Soybean oil**	**Sunflower oil**
			100w[c]					**100w[c]**	
POP	50:1	833.37	0.94	0.43	LiLiP	52:4	855.38	10.63	6.05
POS	52:1	861.42	0.44	0.48	SLnO	54:4	883.43	0.28	-
SOS	54:1	889.48	-	0.14	LiLiS	54:4	883.43	2.50	3.41
PLiP	50:2	831.35	1.93	0.63	OOLi	54:4	883.43	10.30	19.90
PLiS	52:2	859.41	0.91	0.71	LiLiA	56:4	911.48	0.25	0.24
OOP	52:2	859.41	2.50	2.77	LiLiBe	58:4	939.54	0.30	-
SLiS	54:2	887.46	0.11	0.20	PLiLn	52:5	853.36	2.56	-
OOS	54:2	887.46	0.59	1.56	SLiLn	54:5	881.41	0.61	-
OOA	56:2	915.51	-	0.10	OOLn	54:5	881.41	1.24	0.20
PLiBe	56:2	915.51	0.11	-	LiLiO	54:5	881.41	21.25	29.44
PLnP	50:3	829.34	0.23	-	LnLnP	52:6	851.34	0.15	-
PLnS	52:3	857.39	0.11	-	LiLiGa	56:5	909,47	-	0,11
PLiO	52:3	857.39	10.29	8.18	OLiLn	54:6	879.40	5.10	0.88
SLiO	54:3	885.44	2.42	4.61	LiLiLi	54:6	879.40	14.61	14.52
OOO	54:3	885.44	1.66	4.48	LnLnO	54:7	877.38	0.31	-
OLiA	56:3	913.50	0.24	0.32	LiLiLn	54:7	877.38	5.27	0.64
OLiBe	58:3	941.55	0.28	-	LnLnLi	54:8	875.37	0.64	-
PLnO	52:4	855.38	1.24	-					

[a]main TG in the group with x carbons and y double bounds. [b]In x:y, x = number of carbons (except for carbons of glycerol); y = number of double bonds. [c]w = mass fraction.

TABLE 3
IODINE VALUES AND AVERAGE MOLAR MASSES OF SOYBEAN AND SUNFLOWEROILS.

VegetableOil	**IodineValue**		**Composition (100w[a])**			**Molar mass (g,mol^{-1})**			
	Calculated	**Literature [21]**	***TG***	***DG***	***MG***	***TG***	***DG***	***MG***	**Oil**
Soybean	137.03	118-139	0.9574	0.0345	0.0081	886.46	622.09	357.77	873.06
Sunflower	130.49	118-145	0.9618	0.0263	0.0119	890.66	624.90	359.17	877.35

[a] w = mass fraction.

The ethanolysis of soybean and sun flower oils was carried out at 9:1 molar ratio of ethanol to oil and the sodium ethoxide amount of 1.00 % (based on the oil weight). The reaction was conducted at atmospheric pressure and temperatures of 308.15, 323.15 and 338.15 K. An agitation speed of 400 rpm was applied in all experiments.

Glass equilibrium cells, such as those described by Silva et al.[22], were used for the experiments. The Vegetable oil (100.00 g) was stirred at the desired temperature for about 30 min. Ethanol and sodium ethoxide were kept at the desired temperature and then added to the system. Each component was weighted on an analytical balance (Precisa, model XT220A, Sweden), accurate to (0.0001 g). The agitation was maintained with a magnetic stirrer (IkaWerke, model RH-KT/C, Staufen, Germany), and the temperature was controlled with a thermostatic bath (Cole Parmer model 12101-55, Chicago, U.S.A.) accurate to (0.01 K). During the reaction samples (0.5 ml) were taken from the reaction mixture, and immediately dissolved in 25 ml of THF and filtered through a 0.45 μm Millipore filter. All samples were analyzed by High Pressure Size Exclusion Chromatography (HPSEC).

The composition of the samples, in terms of triacylglycerols (*TG*), diacylglycerols (*DG*), monoacylglycerols (*MG*), ethyl esters (*EE*), ethanol (*ET)* and glycerol (*GL*), was determined by HPSEC. The methodology was adapted from Schoenfelder[23], however the columns proposed by this method were replaced by three Phenogel columns 50A, 100 A and 500 A, (300 mm x 7.8 mm).

The quantification was carried out on a Shimadzu VP series HPLC equipped with two LC–10ADVP solvent delivery units for binary gradient elution, a model RID10A differential refractometer, an automatic injector with an injection volume of 20 µL, a model CTO−10ASVP column oven for precision temperature control even at sub−ambient temperatures, a model SCL–10AVP system controller and LC–Solution 2.1 software for remote management.

The results obtained in the chromatograms were converted to molar concentrations of each component based on calibration curves expressed in mass concentration (g.L^{-1}). The molar concentrations $[C_i]$(mol.L^{-1}) were calculated from the mass concentrations using molar mass of the components or the average molar mass of the class of components.

The same analytical procedure described above was used for evaluating the refined oils composition in terms of *TG*, *DG* and *MG*. Based on these results and on the probable triacylglycerol compositions (Table 2), the average molar masses of *TG*, *DG* and *MG* fractions of the vegetable oils were calculated. These calculations were performed considering the stoichiometry relating the *TG* fraction to the *DG* and *MG* fractions. The oil composition in terms of *TG*, *DG* and *MG* and the corresponding average molar masses are given in Table 3.

The oil conversion degree, X (in %), was calculated from the content of acylglycerols in the mixture at the beginning and the end of the reaction process by the following (1):

$$X = \frac{(w_{TG0} + w_{DG0} + w_{MG0}) - (w_{TG} + w_{DG} + w_{TG})}{(w_{TG0} + w_{DG0} + w_{MG0})}.100$$

Where w_{TGO}, w_{DGO} and w_{MGO} are the mass fractions of *TG*, *DG* and *MG* at the initial reaction time, respectively, and w_{TG}, w_{DG} and w_{MG} are the corresponding fractions at the final time.

The kinetic model assumed for the transesterification process has been fitted with the aid of a program written in FORTRAN software. The integration of the model ordinary differential equations was performed using the Runge-Kutta 4th order method. To estimate the kinetic parameters, an optimization technique based on genetic algorithm (GA) was used [24]. The optimizer algorithm developed by Carroll [25] was adapted, as indicated in prior works reported in the literature [26, 27], for minimizing the differences between the kinetic model predictions and the experimental data, using the following objective function (2):

$$F_{OBJ} = \sum_{i=1}^{I}\sum_{k=1}^{K}\left(\frac{C_{sim\,i,k} - C_{\exp\,i,k}}{C_{exp_{max}}}\right)^2$$

With$i$ varying over time and C_k referring to the molar concentrations of the reaction components or class of components (TG, DG, MG).

The kinetic model was based on the approach proposed by Noureddini & Zhu [16], in which the following reactions are considered (3):

$$TG + ET \underset{k_2}{\overset{k_1}{\rightleftarrows}} DG + EE$$

$$DG + ET \underset{k_4}{\overset{k_3}{\rightleftarrows}} MG + EE$$

$$MG + ET \underset{k_6}{\overset{k_5}{\rightleftarrows}} GL + EE$$

The set of differential equations characterizing the stepwise reaction for oil transesterification is shown below (4), (5), (6), (7), (8), and (9):

$$\frac{d[C_{TG}]}{dt} = -k_1[C_{TG}][C_{ET}] + k_2[C_{DG}][C_{ET}]$$

$$\frac{d[C_{DG}]}{dt} = k_1[C_{TG}][C_{ET}] - k_2[C_{DG}][C_{EE}] - k_3[C_{DG}][C_{ET}] + k_4[C_{MG}][C_{EE}]$$

$$\frac{d[C_{MG}]}{dt} = k_3[C_{DG}][C_{ET}] - k_4[C_{MG}][C_{EE}] - k_5[C_{MG}][C_{ET}] + k_6[C_{GL}][C_{EE}]$$

$$\frac{d[C_{EE}]}{dt} = k_1[C_{TG}][C_{ET}] - k_2[C_{DG}][C_{EE}] + k_3[C_{DG}][C_{ET}] - k_4[C_{MG}][C_{EE}] + k_5[C_{MG}][C_{ET}] - k_6[C_{GL}][C_{EE}]$$

$$\frac{d[C_{GL}]}{dt} = k_5[C_{MG}][C_{ET}] - k_6[C_{GL}][C_{EE}]$$

$$\frac{d[C_{ET}]}{dt} = -\frac{d[C_{EE}]}{dt}$$

Where k_1 to k_6 are reaction rate constants; *TG, DG, MG, GL, ET,* and *EE* are the concentrations of the components in the reaction mixture. Note that the rate constants associated with the overall reaction were not considered since, as indicated by Noureddini & Zhu [16], their effects are negligible.

The initial values of the kinetic constants of reaction (k_i) were estimated by linear regression of the concentrations of reactants and products over time obtained experimentally and subsequently adjusted using the genetic algorithm optimization method. Having the values of the kinetic constants (k_i), the activation energies (E_a) and pre-exponential factors(A) were determined by linearization of the Arrhenius(10).

$$ln(k) = -\left(\frac{E_a}{R}\right) \times \frac{1}{T} + ln(A)$$

Where A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant.

III. RESULTS AND DISCUSSION

Typical concentration curves for the transesterification of soybean oil at 308.15 K and sunflower oil at 338.15 K are presented in Fig. 1 and 2, respectively. These figures show the rate of consumption of triacylglycerol's and formation of ethyl esters and glycerol as well as of the intermediate compounds.

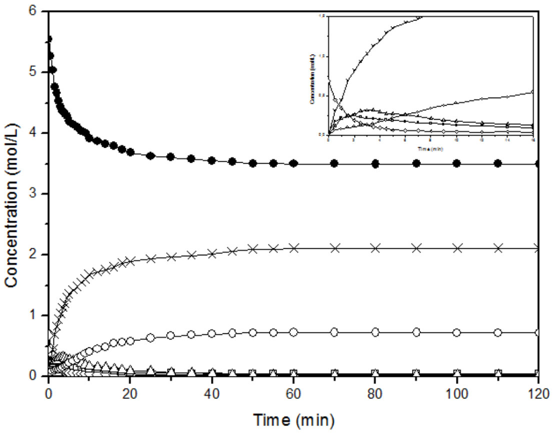

FIG. 1 –THE COMPOSITION OF THE REACTION MIXTURE DURING THE TRANSESTERIFICATION OF SOYBEAN OIL AT 308.15 K. EXPERIMENTAL DATA: (–◊–) TRIACYLGLYCEROL; (–□–) DIACYLGLYCEROL; (–Δ–) MONOACYLGLYCEROL; (–×–) ETHYL ESTER; (–○–) GLYCEROL AND (–●–) ETHANOL.

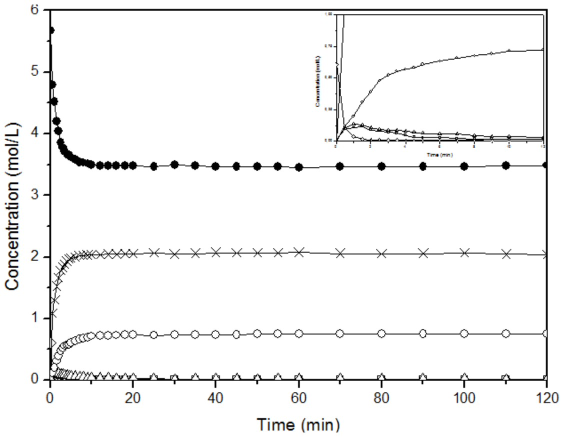

FIG. 2 – THE COMPOSITION OF THE REACTION MIXTURE DURING THE TRANSESTERIFICATION OF SUNFLOWER OIL AT 338.15 K. EXPERIMENTAL DATA: : (–◊–) TRIACYLGLYCEROL; (–□–) DIACYLGLYCEROL; (–Δ–) MONOACYLGLYCEROL; (–×–) ETHYL ESTER; (–○–) GLYCEROL AND (–●–) ETHANOL.

The first stage of the transesterification of triacylglycerols may be controlled by mass transfer. Due to the fact that the oil is not fully miscible with alcohol, this stage might be characterized by slow reaction rates, hence the importance of a good stirring at this stage in order to avoid any mass transfer constraint. In general, the first step is faster when the reaction is ethanolysis, instead of the methanolysis, due to the difference in the oil solubility in both. The second stepis rapidand is controlled byreaction kinetics, while the latter is dominated by the reaction chemical equilibrium [28,29].

The production rate of ethyl esters in Fig. 1 and 2 starts with a sudden increase followed by a lower production rate when the reaction approaches equilibrium. Darnako and Cheryan [14] and Noureddine and Zhu [16] have observed a sigmoidal pattern for production of methyl esters. This pattern consists of a slow rate at the beginning, followed by a sudden surge and finally a slow rate again, especially at low temperatures. These authors explained that the initial mass transfer-controlled region could be eliminated if sufficient mixing is provided.

Fig. 1 and 2 show that no period controlled by mass transfer occurs in the present study, being the reaction path controlled only by its kinetics. Ahiekpor and Kuwornoo [13] also observed the same behavior in the study of palm oil ethanolysis.

The assays were performed at three different temperatures (308.15, 323.15, and 338.15 K) and the kinetic rate constants were estimated for these temperatures. The calculated values are shown in Table 4. Fig. 3 and 4 show the concentration profiles of experimental and simulated data for the transesterification process of soybean and sunflower oils, respectively, at 323.15 K.

TABLE 4
THE RATE CONSTANTS AT DIFFERENT TEMPERATURES

	Rate constants (L.mol^{-1}.min^{-1})					
Temperature (K)	k_1	k_2	k_3	k_4	k_5	k_6
Soybean oil						
308.15	0.1019	0.0236	0.1254	0.2554	0.0578	0.0042
323.15	0.2720	0.0593	0.3586	0.2671	0.0525	0.0125
338.15	0.3312	0.0615	0.4374	0.2844	0.0927	0.0128
Sunflower oil						
308.15	0.1067	0.0286	0.1334	0.2533	0.0464	0.0078
323.15	0.2381	0.0674	0.4693	0.9456	0.1287	0.0197
338.15	0.3483	0.1414	0.9286	1.0942	0.2498	0.0230

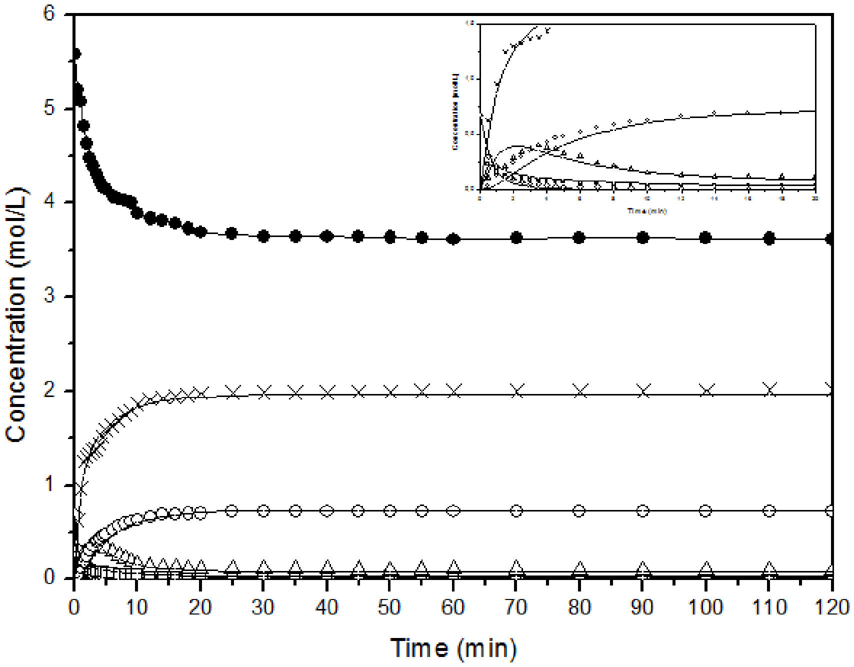

FIG. 3 –THE COMPOSITION OF THE REACTION MIXTURE DURING THE TRANSESTERIFICATION OF SOYBEAN OIL AT 323.15 K. (——) SIMULATION RESULTS AND EXPERIMENTAL DATA : (◊) TRIACYLGLYCEROL; (□) DIACYLGLYCEROL; (Δ) MONOACYLGLYCEROL; (×) ETHYL ESTER; (○) GLYCEROL AND (●) ETHANOL.

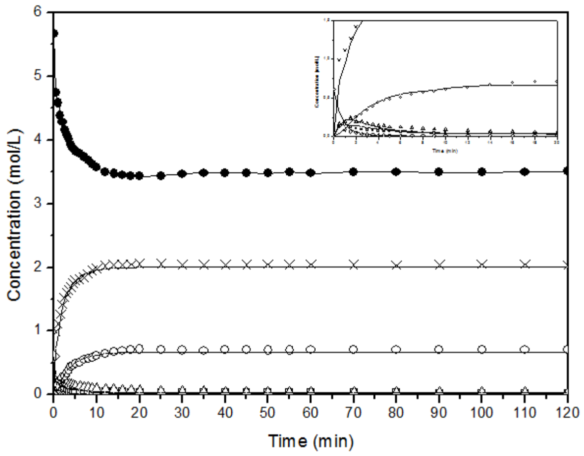

FIG. 4 – THE COMPOSITION OF THE REACTION MIXTURE DURING THE TRANSESTERIFICATION OF SUNFLOWER OIL AT 323.15 K. (——) SIMULATION RESULTS AND EXPERIMENTAL DATA (◊) TRIACYLGLYCEROL; (□) DIACYLGLYCEROL; (Δ) MONOACYLGLYCEROL; (×) ETHYL ESTER; (○) GLYCEROL AND (●) ETHANOL.

The dependence of the overall conversion in relation to the temperature is presented in Fig. 5 (A) and (B) for soybean and sunflower oils, respectively. In accordance with these Figures, the tests conducted at higher temperatures resulted in faster and higher conversion rates. These Figures also show that, over the temperature range of 308.15-323.15 K, approximately forty minutes of reaction time are sufficient to achieve maximum oil conversion to ethyl esters. We can also observe that for the temperature of 338.15K the maximum conversion was already achieved after approximately twenty minutes.

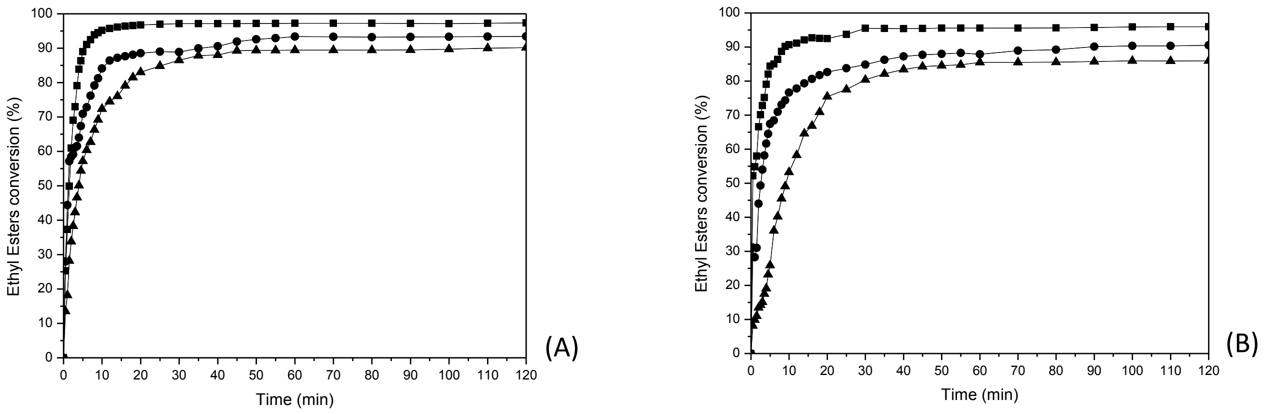

FIG. 5 – THE EFFECT OF THE TEMPERATURE AND TIME ON THE OVERALL CONVERSION TO ETHYL ESTERS FOR SOYBEAN OIL (A) AND SUNFLOWER OIL (B). (▲) 308.15 K; (●) 323.15 K; (■) 338.15 K.

The Arrhenius (6) was applied for determining the activation energies and pre-exponential factors for the ethanolysis reactions of soybean and sunflower oils, respectively, and the values obtained are shown in Table 5.

TABLE 5
ACTIVATION ENERGIES AND PRE-EXPONENTIAL FACTORS FOR THE REACTION STEPS OF ETHANOLYSIS OF SOYBEAN AND SUNFLOWER OILS.

Reaction	Soybean oil		Sunflower oil	
	Activation energy (cal.mol^{-1})	Pre-exponential factor (L.mol^{-1}.min^{-1})	Activation energy (cal.mol^{-1})	Pre-exponential factor (L.mol^{-1}.min^{-1})
$TG \rightarrow DG$	8203.426	$7.59\text{x}10^{4}$	8197.167	$7.42 \text{ x } 10^{4}$
$DG \rightarrow TG$	6698.938	$1.53\text{x}10^{3}$	11023.56	$1.91 \text{ x } 10^{6}$
$DG \rightarrow MG$	8702.558	$2.13\text{x}10^{5}$	13429.72	$4.89 \text{ x } 10^{8}$
$MG \rightarrow DG$	739.559	$8.52\text{x}10^{-1}$	10206.87	$5.28 \text{ x } 10^{6}$
$MG \rightarrow GL$	3183.908	9.42	11637.45	$8.79 \text{ x } 10^{6}$
$GL \rightarrow MG$	7791.455	$1.67\text{x}10^{3}$	7498.372	$1.84 \text{ x } 10^{3}$

As it can be seen, for soybean oil the first two reactions (TG↔DG and DG↔MG) are favored by high temperatures. However, for the third step (MG↔GL) the forward reaction has lower activation energy than the reverse reaction, indicating a more favorable reverse reaction at higher temperatures. This same behavior was observed by Noureddini & Zhu [16], although the calculated activation energies for the three-step reactions in the present case are slightly lower than the corresponding values obtained by these authors for the methanolysis of soybean oil.

In case of sunflower oil the observed behavior is different, since the last two reactions (DG↔MG and MG↔GL) are favored by high temperatures. On the other hand, in the first step (TG↔MG) the forward reaction has lower activation energy than the reverse reaction, indicating a more favorable reverse reaction at higher temperatures. Values obtained in the present work are within an acceptable range according to data reported in the literature[30,31].

IV. CONCLUSION

The experimental data of concentration versus time showed that the production rate of ethyl esters started with a sudden surge followed by a lower production rate when the reaction approaches equilibrium, and the concentration profiles did not followed the sigmoidal behavior observed in the methanolysis.

The reaction rate constants, the corresponding activation energies, and pre-exponential factors reproduced very satisfactorily the process studied, showing that the developed kinetic model can be used to describe the ethanolysis process of soybean and sunflower oils adequately.

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