



SUSTAINABLE BIODIESEL: KINETIC STUDY AND MODELING OF CATALYTIC ESTERIFICATION OF USED VEGETABLE OILS AS THE FIRST STAGE OF THE PRODUCTION PROCESS

Verónica Rodríguez³, María F. Laborde^{1,2,3}, María C. Gely^{2,3}, Ana M. Pagano^{2,3,*}

¹Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET)

²Redes Interuniversitarias REDES VIII – Proy. 35-83-0096, Sec. de Pol. Universitarias (SPU), Min. de Educación de la Nación, Argentina

³Núcleo TECSE, Área de Procesos, Depto. Ing. Química, F. de Ingeniería, UNICEN, 7400 Olavarría, Argentina.

* Corresponding. Author: apagano@fio.unicen.edu.ar/anamariapagano@gmail.com

Received December 28th, 2016. Accepted in final form April 12th, 2017

Resumen

Con ánimo de contribuir a satisfacer las necesidades de producción sostenible de biocombustibles en procesos industriales, en el presente trabajo se ha estudiado la cinética de esterificación de aceites vegetales usados (UVOs) con etanol, empleando aceite de girasol acidificado. El proceso se llevó a cabo en un reactor discontinuo termostatzado con agitación magnética. Se ensayaron diferentes temperaturas (50, 60 y 70°C) y tiempos de reacción en el intervalo de 0-90 minutos. Se aplicó una relación molar de etanol / ácido oleico de 60: 1. El catalizador utilizado fue H₂SO₄ (5% p/p con respecto al contenido de ácidos grasos libres). Se determinó una conversión del 75,54% a 70°C. Estos datos cinéticos experimentales se utilizaron en la simulación del proceso completo de esterificación desarrollado en Aspen HYSYS[®] con resultados de conversión similares.

Abstract

In an attempt to satisfy the needs for sustainable production of biofuel in industrial processes, the present work develops the esterification kinetics of used vegetable oils (UVOs) with ethanol, employing acidified sunflower oil. The process was carried out in a thermostated batch reactor with magnetic stirring. Different temperatures (50°C, 60°C and 70°C) and reaction times in the range 0-90 minute were assayed. An ethanol/oleic acid molar ratio of 60:1 was applied. The catalyst used was H₂SO₄ (5% w / w relative to the free fatty acid). A conversion of 75.54% was determined at 70 °C. These experimental kinetic data were used in the simulation of the complete esterification process performed in Aspen HYSYS[™] with similar conversion results.

Palabras Clave: Biodiesel, esterificación catalítica, aceites vegetales usados, cinética de reacción.

Keywords: Biodiesel, catalytic esterification, used vegetable oils, reaction kinetics.

1. Introduction

Without doubt, the demand for biofuels has recently increased in response to the current energy crisis and concern for the environment. Biodiesel is a type of biofuel that can be added to diesel of fossil origin, which is used mainly in transport, in different percentages. In Argentina, from 2010 onwards, the minimum proportion evolved from 5% to 10% [1-4].

Biodiesel is an alternative fuel that represents a source of contamination-free energy, as it is derived from renewable raw materials and produces low toxic emissions [5-7]. It can be obtained from the catalytic transesterification of used vegetable oils (UVOs), helping to solve two current problems: reuse of residues and the production of sustainable biofuels from non-conventional raw materials, reducing the use of edible oils.

UVOs embody an economical source of raw material for the production of biodiesel [8-10]. However, it should be considered that during frying, the oil is subjected to high temperatures of 180-190 °C [11], which has a negative effect on the properties of the oil with the formation of free fatty acids (FFA). A high level of FFA in the transesterification can cause the deactivation of the alkaline catalyst and a saponification reaction that hinders the separation of the reaction products [9].

In order to reduce the acidity of the raw material to a level lower than 0.5% free fatty acids (% FFA) a pretreatment must be employed [12]. The esterification method of free fatty acids with a short chain alcohol is one of the best treatments for the final production of esters [13]. Predominantly, methanol has been used in the production of biodiesel. This short chain alcohol is derived from fossil resources so the produced biodiesel can not be termed as fully renewable. Therefore, it is interesting to analyze the possibility of using ethanol for the production of biodiesel, since this alcohol can be obtained by fermentation from various energy crops rich in carbohydrates (such as potatoes, sugarcane, corn grains and sorghum) or other Renewable resources (such as food industry waste) [14]. The application of renewable raw materials and their efficient processing is crucial in the development of sustainable processes [15].

In the literature, there are numerous studies in which different processes of biodiesel production on an industrial scale have been simulated with the Aspen HYSYS™ software [16-19], using different raw materials and catalysts. No reports have been found in which the study of the esterification process of UVOs with ethanol through acid catalysis has been approached. Neumann et al. [15] performed an experimental analysis of the kinetics of the esterification reaction of used vegetable

oils for the production of biodiesel, using oleic acid (as descriptor of the UVOs) and using ethanol in a reactive distillation column.

The economic and environmental interest of the use of UVOs, the need for a fully sustainable biodiesel production and the importance of the characterization of the kinetics of the reaction with ethanol to optimize the sizing of the esterification reactor required in a process plant, are the aspects that lead the present study. The general objective is to examine the influence of operational variables (temperature, time) on the FFA esterification reaction of UVOs with ethanol by acid catalysis. The aim is to optimize the process and to develop an experimentally validated kinetic model to introduce in the simulation model of the reactor that forms part of the esterification process previously developed by Laborde et al. [20].

2. Materials and Methods

The esterification reaction was carried out using commercial sunflower oil as raw material. This oil was selected as representative of UVOs, based on statistical data of edible oils consumption in Argentina [21].

The experiments were performed with commercial sunflower oil acidified artificially by adding an organic acid, as was proposed by several researchers [12, 22, 23].

Taking into account that triolein is one of the main components present in the triglyceride composition of traditional sunflower oils and the principal fraction in high oleic sunflower oils, oleic acid was selected to be added to commercial sunflower oil with the purpose of increasing its acid value. This decision was also supported by the evidence that oleic acid is the main constituent of residual and non-edible cooking oils [24].

The use of the synthetic "used vegetable oil" properly prepared by this procedure prevented avoiding the potential interferences of other possible components of the oil with the reaction kinetics focused on here.

The acid value of the samples was approximately 6.5 mg KOH / g oil, slightly higher than the levels typically found in frying oils [12, 24].

The acidity value, expressed as mg KOH / g oil, was determined by following the technique of AOCS Ca 5a-40 [29], after washing the sample with distilled water to remove the residual catalyst.

The esterification of the FFA was performed with anhydrous ethanol using an ethanol:oleic acid ratio of 60:1. The catalyst used was sulfuric acid at a concentration of 5% by weight with respect to the total acidity (represented as oleic acid). These conditions of molar ratio of reactants and catalyst

concentration were defined on the basis of the optimum operating conditions determined by Berrios et al. [12] in its esterification study, using methanol in order to obtain an acidity level lower than 0.5% FFA (equivalent to 1 mg KOH / g oil).

The effect of temperature (T) was studied by carrying out the reaction at 50, 60 and 70 °C. These experiments were performed in a batch reactor of 500 mL equipped with magnetic stirring and temperature control. The stirring speed varied between 300 and 400 rpm (although this variable does not produce a significant effect on the reaction rate [1]). The volume of reaction mixture was 360 mL.

The kinetics of the reaction was evaluated along 120 minutes by extracting 40 mL samples at regular intervals. These intervals were pre-established by means of preliminary testing of the experimental technique (not shown in this paper). These intervals were set at 15 minutes for the first 30 minutes of reaction, and then extended to 30 minutes until the end of the process.

After the sample was taken, the reaction was dropped by the addition of an excess of water [23, 25]. This procedure was performed in order to synchronize the residual acidity measurement of the different samples taken at a given time and temperature.

The extracted samples were quantified by titration using the AOCS standard Ca 5a-40 [29]. All experiments were performed in triplicate.

The experimental results were analyzed statistically with the software SYSTAT™ V12, by analysis of the variance (ANOVA) to evaluate the influence of temperature and time of reaction, and by means of regression of least squares to model the curves of reaction.

From the adjustment of the experimental data a kinetic model was developed, which was incorporated to the design of the stationary-state esterification reactor that participates in the complete flow diagram process previously developed in the Aspen HYSYS™ environment [20].

3. Results and Discussion

The experimental data of acid value (45 points) were obtained for the different temperature conditions and reaction times tested. The free acidity curves as a function of time decreased for all temperatures. Figure 1 shows the temporal results of acidity values grouped by temperature as triplicate average, with their corresponding standard error bars.

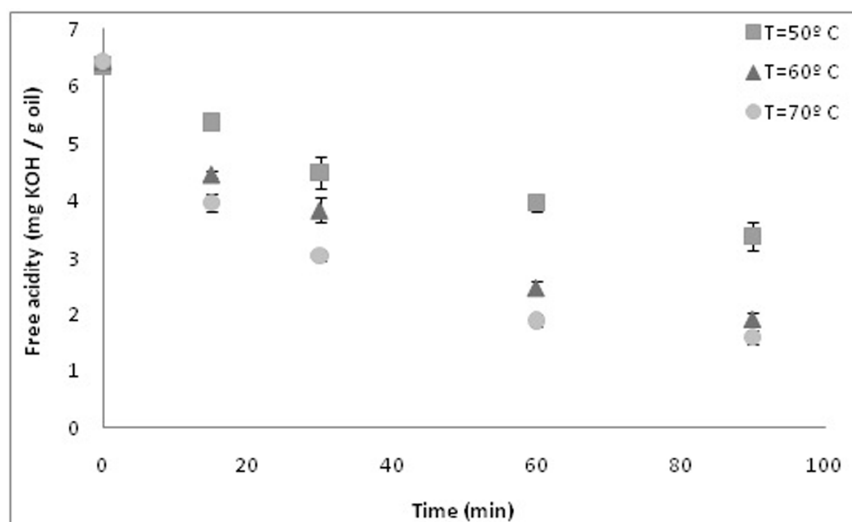


Fig.1. Variation of acidity value with temperature, using a sulfuric acid concentration of 5% w / w and an ethanol:oleic acid ratio of 60:1.

Effect of reaction temperature

The concentration of free fatty acids was measured throughout time. In the experimental trials, regardless the evaluated temporal range, it was observed that greater conversions of oleic acid were obtained at higher operating temperature, evidencing that the decrease in acidity was favored by the increase in temperature.

As an example, as shown in Fig. 1, at 30 min of reaction the acidity at 50 °C was 4.49 mg KOH / g oil while at 70 °C the acidity was 3.04 mg KOH / g oil, which demonstrates the above-mentioned statement.

The enthalpy of the esterification reaction at the reference temperature of 25 °C was theoretically calculated from the enthalpies of formation of the products and reagents. These enthalpies of formation were obtained from recognized databases (NIST, Chémeo, PubChem). As a result, a positive reaction heat value was obtained, which evidenced the endotherm of the reaction at 25 °C. Subsequently, from this result and specific heat-temperature correlations obtained from the Aspen HYSYS™ library for each reaction component, the enthalpy of reaction at each temperature was evaluated, always proving to be positive with which it can be assumed that the reaction is endothermic in the range of the study.

Moreover, other available tools, which are described below, were used to analyze the heat of reaction.

The equilibrium conversions in the 50-70 °C range were obtained by means of two procedures: i) asymptotic extrapolation of the kinetic model that adjusts the experimental data that has been developed in this work for each temperature; and ii) by experimental determination of the equilibrium conversion for each temperature of the experimental design at long reaction times (>120 minutes). The data determined by these two procedures yielded congruent.

Using the resulting values, the reaction equilibrium constants for each temperature were calculated and the enthalpy of reaction in the study range was obtained by means of the van't Hoff equation, showing positive sign, which again offered support to verify the endothermicity of the reaction.

Simultaneously, a decreasing evolution of the temperature of the reaction medium was experimentally recorded by means of a laboratory calorimeter (Dewar vessel).

The statistical analysis of the variance performed on the set of experimental results showed that there was a significant effect ($\alpha = 0.05$) of the time ($p < 7.177 \times 10^{-12}$), reaction temperature ($p < 1.237 \times 10^{-11}$) and its interaction ($p < 1.073 \times 10^{-11}$) on the acidity value of the samples.

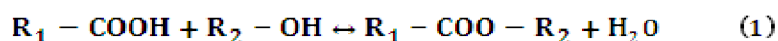
At 90-minutes reaction, different conversions of FAA, calculated as the ratio between remain moles and the initial moles of oleic acid [27, 23], were achieved at different working temperatures, as it can be seen in Table 1.

Table 1. Experimental conversions at 90 min of reaction

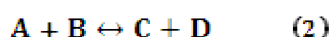
T (°C)	Conversion (%)
50	46.81
60	70.09
70	75.27

Development of the kinetic model

Using the experimental data obtained at different temperatures, a kinetic analysis of the esterification reaction of fatty acids with ethanol was carried out. The reaction of a fatty acid with an alcohol is as follows:



The reaction (1) expressed in generic form is:



The law of reaction velocity (2) [21] is presented in Equation (3):

$$\frac{-d[A]}{dt} = \mathbf{K_1 \cdot [A] \cdot [B] - K_2 \cdot [C] \cdot [D]} \quad (3)$$

where: K_1 , K_2 are kinetic constants of the direct and reverse reactions, respectively; $[A]$, $[B]$, $[C]$ and $[D]$ are de molar concentration of the reactants and products; t is the reaction time.

In the experiments performed, the ethanol-oleic acid molar ratio was high enough to assume a constant concentration of ethanol throughout the process.

With this premise, it can be established that $[B]$ is constant throughout the reaction, then:

$$K'_1 = K_1 \cdot [B] = \text{constant} \quad (4)$$

That is, the reaction becomes pseudo first order for the direct and second order reaction for the inverse reaction, as presented in Equation (5).

$$\frac{-d[A]}{dt} = K'_1 \cdot [A] - K_2 \cdot [C] \cdot [D] \quad (5)$$

As shown in Carberry [21], considering that $[C]$ and $[D]$ are zero at the beginning of the reaction and that $[A] = A_0 - E$, where E is the amount of $[A]$ that reacted (ie, acidity removed) and A_0 the initial acidity, then equation (5) can be expressed as:

$$\frac{dE}{dt} = K'_1 \cdot (A_0 - E) - K_2 \cdot E^2 \quad (6)$$

The integration of Equation (6) gives:

$$2 \cdot K_2 \cdot \alpha \cdot t = \frac{\ln[A_0 + E \cdot (\beta - 0.5)]}{[A_0 - E \cdot (\beta + 0.5)]} \quad (7)$$

$$\alpha = \sqrt{\left(\frac{K_{eq}^2}{4}\right) + K_{eq} \cdot A_0} \quad (8)$$

where:

$$\beta = \frac{\alpha}{K_{eq}} \quad \text{y} \quad K_{eq} = \frac{K_1}{K_2} \quad (9)$$

Explaining E from the expression (7) gives:

$$E = \frac{2 \cdot A_0 [e^{2K_2 t \alpha} - 1]}{e^{2K_2 t \alpha} \cdot (2\beta + 1) + 2\beta - 1} \quad (10)$$

The data experimentally obtained were adjusted by the statistical program SYSTAT™ V12 through Equations (7), (8) and (9). From this analysis, the kinetic constants were obtained for each experimental test (Table 2).

The influence of temperature on the constants of reaction rate can be determined by using Arrhenius's Equation (11):

$$K = A \cdot \exp\left[\frac{-\Delta E}{R \cdot T_a}\right] \quad (11)$$

where: A is the pre-exponential constant; ΔE is the activation energy of the reaction; R is the constant of ideal gases (8.314 J/(mol-K)); T_a is the absolute temperature.

Table 2. Kinetic constants for direct and reverse reactions of each experiment

Trial	T (°C)	K_1 (ASE*) (min^{-1})	K_2 (ASE*) (g oil / (min-mg KOH))
1	50	1.31×10^{-2} (2.14×10^{-3})	5.52×10^{-3} (1.25×10^{-3})
2	50	8.89×10^{-3} (8.60×10^{-4})	2.11×10^{-3} (8.00×10^{-4})
3	50	9.73×10^{-3} (4.90×10^{-4})	1.49×10^{-3} (3.70×10^{-4})
1	60	2.07×10^{-2} (6.00×10^{-4})	1.44×10^{-3} (1.00×10^{-4})
2	60	1.82×10^{-2} (1.44×10^{-3})	9.90×10^{-4} (2.90×10^{-4})
3	60	1.89×10^{-2} (1.27×10^{-3})	1.48×10^{-3} (2.60×10^{-4})
1	70	2.95×10^{-2} (1.12×10^{-3})	1.53×10^{-3} (1.00×10^{-4})
2	70	2.80×10^{-2} (4.40×10^{-4})	1.98×10^{-3} (5.00×10^{-5})
3	70	2.82×10^{-2} (1.23×10^{-3})	1.74×10^{-3} (1.20×10^{-4})

*ASE: standard error of the parameter (units of the parameter)

With the kinetic constants for each temperature and trial shown in Table 2, adjustment of Equation (11) was made with SYSTAT™ V12, from which it was possible to obtain the pre-exponential factor and the activation energy of the reaction, shown in Table 3.

Table 3. Activation energy and pre-exponential factor for direct and reverse reactions

Reaction	A (ASE*) (min^{-1})	ΔE (ASE*) (J/mol)
Direct	356817.60 (5.52)	46527.72 (4727.74)
Reverse	45.34 (157.18)	29008.51 (14213.50)

*ASE: standard error of the parameter (units of the parameter)

In Fig. 2 it is possible to observe that the reaction at 70 °C shows the best results in terms of decrease in acidity value in sunflower oil, due to the fact that it was performed at a higher temperature. However, these results reflect that it was not possible to obtain an acidity level lower than 1 mg KOH / g oil, which would be advisable to avoid the possible saponification reaction, the main disadvantage in biodiesel production.

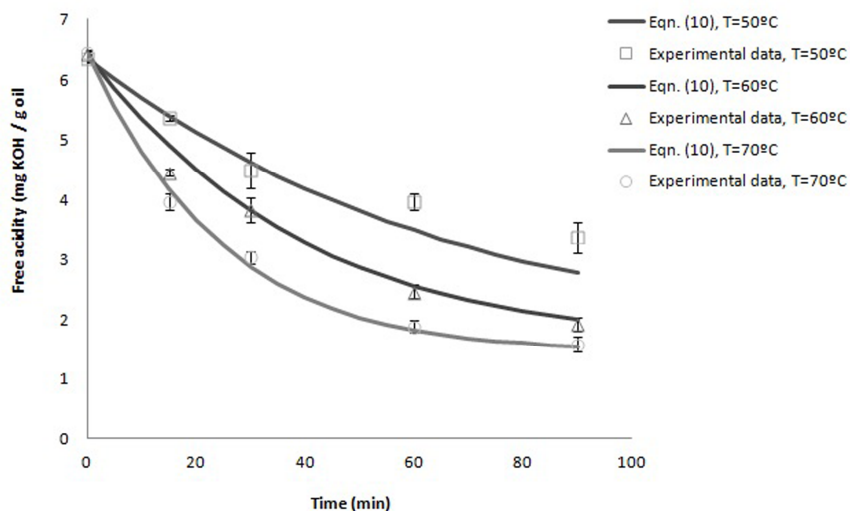


Fig. 2. Comparison between experimental data (points) and predicted curves of the kinetic model (lines).

In these experiments, the desired acidity of 1 mg KOH / g oil (equivalent to 0.5% FFA) resulted unattainable, obtaining an average final value in the experiment at 70 °C of 1.59 mg KOH / g oil to the 90-min reaction. This datum becomes the starting point to postulate that, through the modification of some variables of the reaction, as such as the increase of the catalyst concentration, it would be possible to obtain better results in the reduction of acidity.

Another possibility to obtain greater conversion in the reaction to be considered for further research work involves the esterification in two stages, eliminating the water produced in the first stage, as its presence impair the reaction [27].

Modeling in Aspen HYSYS™

On the bases of the complete esterification process developed by Laborde et al. [20] the esterification step in Aspen HYSYS™ (Figure 3) was simulated with a kinetic reactor by substituting the previously applied conversion reactor. The new reactor was defined using the activation energy and pre-exponential factor obtained in this work, an ethanol: oleic acid molar ratio of 60:1, atmospheric pressure and a temperature of 70 °C.

From the design equation of an isothermal CSTR reactor (continuous stirred tank reactor) [28] a required volume of 6.26 m³ was determined.

In the simulation of the process, a conversion was obtained in the kinetic reactor of 77.76% of the FFA at 70°C, only 2.7% higher than the experimentally obtained 75.54%.

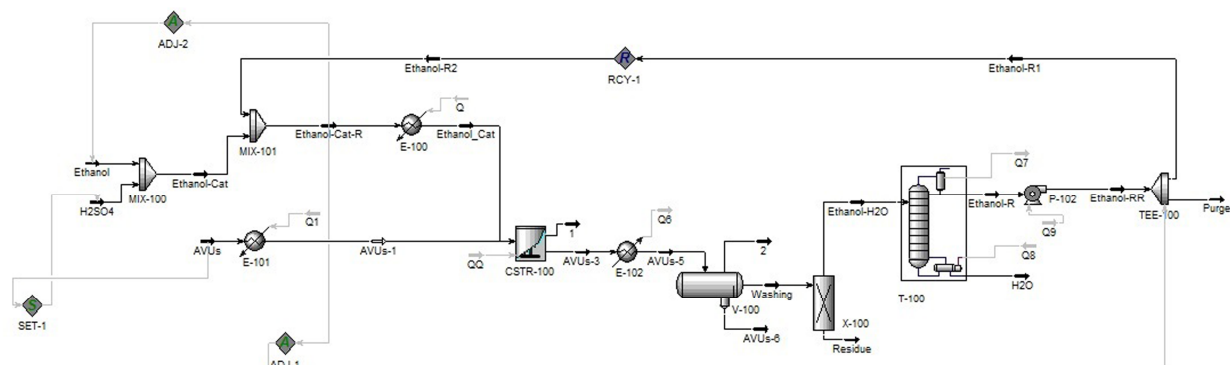


Fig. 3. Full esterification process of UVOs with ethanol

In order to compare the conversion of the reaction with ethanol and the results corresponding to methanol, the variation of the conversion of the FFA with the temperature was analyzed. For this purpose, Figure 4 was constructed by varying the temperature from ambient to the temperature near the boiling point of each alcohol (maximum working temperature at atmospheric pressure). The variation of the conversion as a function of T for esterification with ethanol was obtained by simulation, while the conversion of the reaction using methanol was calculated from the kinetics obtained by Berrios et al. [12].

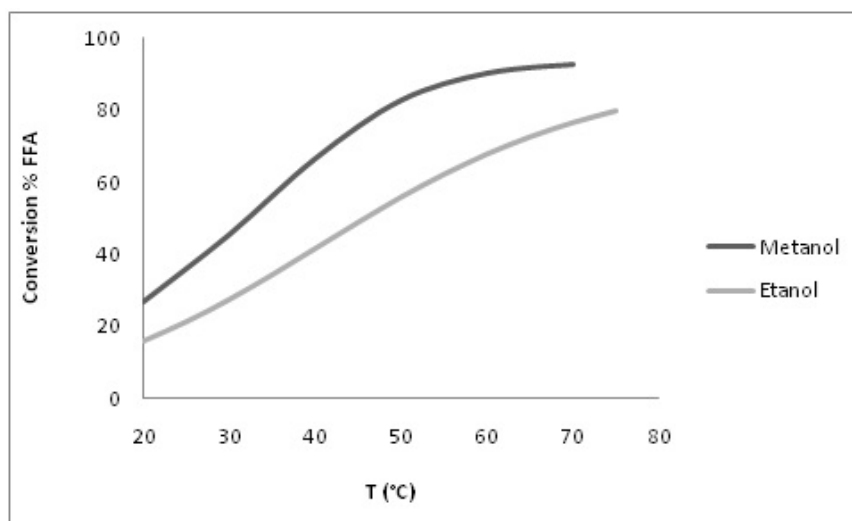


Fig. 4. Variation of FFA conversion as a function of reactor temperature for reaction with ethanol compared with that for methanol

It can be seen that the methanol conversion at the optimum process temperature (60 °C) is 13.46% greater than that obtained with ethanol at 70 °C (90.23%).

Despite the lower conversion of the reaction to ethanol under these working conditions, it is advisable to use ethanol instead of methanol. Ethanol is a renewable resource, and in addition, its handling is safer because it is less toxic than the latter. Besides, it improves the cold behavior properties of biodiesel, since the ethyl esters have a lower freezing point than the methyl esters.

4. Conclusions

The pre-exponential factor and the activation energy for the direct and reverse esterification reactions of UVOs with ethanol were determined from experimental data. The best working temperature for the esterification with ethanol catalyzed with 5% w / w H₂SO₄ was 70 °C, obtaining a conversion of 75.54%. This reflects that it was not possible to obtain an acidity below 1 mg KOH / g oil (0.5% FFA), which is normally recommended to avoid the saponification reaction during the subsequent transesterification. Thus, to achieve a decrease in the level of free fatty acids up to a recommended value, it is suggested for subsequent studies to implement increase in the concentration of catalyst or to perform the esterification in two stages, by eliminating the water produced in the first stage, as its presence impairs the reaction. The reaction with ethanol, despite its lower conversion in comparison with methanol, is recommended since, unlike methanol, ethanol is a renewable resource, its handling is safer as it is less toxic, and it improves the cold behavior properties of biodiesel, the ethyl esters having a lower freezing point than the methyl esters.

References

- [1] Resolución N° 660/2015: Acuerdo de Abastecimiento de Biodiesel para su Mezcla con Combustibles Fósiles en el Territorio Nacional. Ratificación., in Resolución 6602015, InfoLEG: República Argentina DOI: <http://servicios.infoleg.gob.ar/infolegInternet/anexos/250000-254999/251066/norma.htm>.
- [2] Resolución N° 1125/2013, in Resolución N° 11252013, InfoLEG: República Argentina, DOI: <http://servicios.infoleg.gob.ar/infolegInternet/anexos/220000-224999/224799/norma.htm>.
- [3] UNR, O.E.S. *Aceites & Grasas (A&G)* **2016**, *1*, 46.
- [4] Babazadeh, R.; Razmi, J.; Pishvae, M.S.; Rabbani, M. *Omega* **2017**, *66*, 258.
- [5] Hwang, J.; Bae, C.; Gupta, T. *Fuel* **2016**, *176*, 20.

- [6] Flores Velázquez, R.; Muñoz Ledo Carranza, R.; Villalb Valle, D. *Investigación. Ingeniería y Tecnología* **2010**, *10*, 35.
- [7] Nasir, N.F.; Daud, W.R.W.; Kamarudin, S.K.; Yaakob, Z. *Renewable and Sustainable Energy Reviews* **2013**, *22*, 631.
- [8] Banerjee, A.; Chakraborty, R. *Resources, Conservation and Recycling* **2009**, *53*, 490.
- [9] Wang, L.; Dong, X.; Jiang, H.; Li, G.; Zhang, M. *Bioresource Technology* **2014**, *158*, 392.
- [10] Yaakob, Z.; Mohammad, M.; Alherbawi, M.; Alam, Z.; Sopian, K. *Renewable and Sustainable Energy Reviews* **2013**, *18*, 184.
- [11] Hamilton, R.J.; Perkins, E.G. *A&G Magazine* **2002**, *3*, 292.
- [12] Berrios, M.; Siles, J.; Martín, M.A.; Martín, A. *Fuel* **2007**, *86*, 2383.
- [13] Boffito, D.C.; Pirola, C.; Galli, F.; Di Michele, A.; Bianchi, C.L. *Fuel* **2013**, *108*, 612.
- [14] Verma, P.; Sharma, M.P. *Fuel* **2016**, *180*, 164.
- [15] Neumann, K.; Werth, K.; Martín, A.; Górak, A. *Chemical Engineering Research and Design* **2016**, *107*, 52.
- [16] Zhang, Y.; Dubé, M.A.; Mclean, D.D.; Kates, M. *Bioresource Technology* **2003**, *89*, 1.
- [17] Zapata, C.D.; Martínez, I.D.; Castiblanco, E.A.; Henao Uribe, C.A. *Dyna* **2007**, *151*, 71.
- [18] Made in Argentina. 24/04/2014; DOI: <http://www.made-in-argentina.com/empresas/898/alimentos-y-bebidas-aceites-aceite-de-maiz>.
- [19] West, A.H.; Posarac, D.; Ellis, N. *Bioresource Technology* **2008**, *99*, 6587.
- [20] Laborde, M.F.; Serna Gonzalez, M.; Pagano, A.M.; Gely, M.C. CLICAP **2015** (Congreso Latinoamericano de Ingeniería y Ciencias Aplicadas), **2015**. San Rafael, Mendoza, Argentina
- [21] CIARA, Cámara de la Industria Aceitera de la República Argentina, **2017**.
- [22] Cardoso, A.L.; Gonzaga Neves S.C.; da Silva, M.J. *Energies* **2008**, *1*, 79.
- [23] Marchetti, M.; Pedernera M.N.; Schbib, N.S. *International Journal of Low-Carbon Technologies* **2011**, *6*, 38.
- [24] Neumann, K.; Werth, K.; Martín, A.; Górak, A. *Chemical Engineering Research and Design* **2016**, *107*, 52.
- [25] Ávila Gómez, A.E. Desarrollo de la cinética química de la reacción de transesterificación de la oleína de palma, Tesis Magister en Ingeniería Mecánica, Universidad del Norte, Barranquilla, Colombia, **2006**.
- [26] Carberry, J. *Chemical and Catalytic Reaction Engineering*, McGraw-Hill, Inc., **1976**.
- [27] Canakci, M.; Van Gerpen, J. *Trans. ASAE* **2001**, *44*, 1429.

[28] Levenspiel, O., *Ingeniería de las Reacciones Químicas*, Editorial Reverté, S.A, **1998**.

[29] AOCS Ca 5a-40, AOCS. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th edn., D. Firestone (Eds.), American Oil Chemists' Society, Champaign, **1989**.