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Acid-Catalyzed Homogeneous Esterification Reaction for Biodiesel Production from Palm Fatty Acids

**Donato A. G. Aranda · Rafael T. P. Santos ·
Neyda C. O. Tapanes · André Luis Dantas Ramos ·
Octavio Auqusto C. Antunes**

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Abstract This work deals with esterification of palm fatty acids to produce biodiesel in a batch reactor, using homogeneous acid catalysts, evaluating the effect of the alcohol used, presence of water, type and concentration of catalysts. Methanesulfonic and sulfuric acid were the best catalysts. Reaction with methanol showed greater yields. It was showed very clearly that the presence of water in the reaction medium showed a negative effect in the reaction velocity. Kinetic parameters were estimated and molecular modeling was performed. Protonation of the carboxylic moiety of the fatty acid were defined as rate determinant step for the reaction.

Keywords Esterification · Biodiesel · Fatty acid · Homogeneous catalysis

D. A. G. Aranda (✉) · R. T. P. Santos · N. C. O. Tapanes
Greentec, Laboratório de Tecnologias Verdes, Escola de Química, Universidade Federal do Rio de Janeiro—UFRJ, Centro de Tecnologia, Bloco E, Sala 211, Cidade Universitária, Ilha do Fundão, CEP 21945-970, Rio de Janeiro, RJ, Brazil
e-mail: donato@eq.ufrj.br

A. L. D. Ramos
LCAT/ITP, Laboratório de Catálise, Instituto de Tecnologia e Pesquisa, Av. Murilo Dantas, 300—Prédio do ITP, Farolândia, CEP 49032-490, Aracaju, Sergipe, Brazil

A. L. D. Ramos
PEP/UNIT, Programa de Pós-Graduação em Engenharia de Processos, Universidade Tiradentes, Av. Murilo Dantas, 300, Farolândia, CEP 49032-490, Aracaju, Sergipe, Brazil

O. A. C. Antunes
Instituto de Química, Universidade Federal do Rio de Janeiro, CT Bloco A, Sala 641, Cidade Universitária, Ilha do Fundão, CEP 21949-900, Rio de Janeiro, RJ, Brazil

1 Introduction

Biodiesel is a fuel comprised of alkyl esters of long chain fatty acids [1]. It is an alternative to petroleum diesel for reducing emissions of gaseous pollutants such as CO, SO_x, particulate matter and organic compounds [2, 3]. Considering that it is made from renewable resources, its production provides a mean to recycle CO_2 [4, 5]. Its properties are similar to petroleum-based diesel, allowing its use either as a substitute for diesel fuel or more commonly in fuel blends [3, 6, 7]. Besides, this fuel has an important social impact in countries with agricultural vocation like Brazil, the fifth oil crops producer in the world, responsible for 8.2% of oil crops production in 2006 [8].

There are several routes to obtain biodiesel using oilseeds, edible oils, animal fats and waste oils and greases as feedstock. Transesterification of triglycerides with low molecular weight alcohols catalyzed by homogeneous catalysts is the most used one [9–13]. This route has some advantages, like low cost and mild reaction conditions. Since alkali-catalyzed transesterification is much faster—about 4,000 times—than acid-catalyzed transesterification [2, 9, 10], basic catalysts as alkaline hydroxides, methoxides and carbonates are more often used to promote the reaction. However, the overall base-catalyzed process suffers from serious limitations concerning strict feedstock specifications [2], especially the content of free fatty acids (FFA) and water. Saponification reaction is an undesired reaction which may be promoted, depending on the reaction conditions and the free acid content of the vegetable oil used. The soap decreases selectivity toward biodiesel, inhibits separation of the alkyl esters and glycerol and contributes to emulsion formation during the water wash [1, 11, 14].

Esterification of FFA with low molecular weight alcohols is another route to produce biodiesel and can be used as a pretreatment for basic transesterification reaction to convert the FFA into methyl esters and avoid saponification, especially when FFA content is higher than 1% w/w [2, 9, 10, 12]. The reaction may be represented by the following scheme:

$$\underset{\text{fatty acid}}{\text{R}{-}\text{COOH}} + \underset{\text{alcohol}}{\text{R}'{-}\text{OH}} \rightarrow \underset{\text{biodiesel}}{\text{R}{-}\text{COOR}'} + \text{H}_2\text{O}$$

Some authors have shown that alkyl esterification of fatty acids is faster than transesterification of triglycerides [15, 16]. This observation was assigned to the fact that alkyl esterification is a kind of one step reaction, while transesterification of triglycerides consists of three stepwise reactions, with diglycerides and monoglycerides as intermediates, and the presence of glycerol. The much higher solubility of fatty acids in low chain alcohols may also be related to this observation.

In some cases, fatty acids are by-products of the food processing, like in the edible Palm Oil-based oleochemical industry, which produces 4–8% of FFA of total crude Palm Oil in the physical refining. The recovery of fatty acids residue is difficult and not economically feasible [17]. Therefore, its alternative usage as feedstock for biodiesel production looks promising. The present work aims to study the esterification of palm fatty acids, by-products of edible Palm Oil production, to produce biodiesel, using homogeneous acid catalysts.

2 Experimental

2.1 Reactants and Catalysts

Fatty acid mixture used in this work was a palm oil extraction residue provided by Agropalma, a Palm Oil producer in Brazil. Table 1 displays the composition of fatty acid mixture residue, showing the predominance of palmitic and oleic acids. Anhydrous methanol and ethanol used were supplied by Tedia do Brasil (+99.9% purity). Commercial hydrated ethanol used in the present work showed not more than 4% wt/wt water content (ethanol/water azeotropic mixture).

Table 1 Composition of fatty acid mixture residue

Fatty acid	Percentage
Lauric (C12:0)	1.2
Myristic (C14:0)	0.1
Palmitic (C16:0)	46.4
Oleic (C18:1)	41.2
Linoleic (C18:2)	11.1

The following homogeneous catalysts were used: sulfuric acid (98%); phosphoric acid (85%); trichloroacetic acid (98%) and methanesulfonic acid (95%).

2.2 Esterification Reaction

Reactions were performed in a stainless steel 600 mL batch reactor (PARR 4842), maximum pressure of 10,000 psi and equipped with a sample withdrawal, stirring and heating system. Stirring velocity was kept constant (500 rpm). Reaction mixture has consisted of 307 g of fatty acid mixture, 149 mL methanol or 215 mL ethanol, providing an alcohol/fatty acid molar ratio (A/FA) of 3. Reactants were introduced together with the appropriated catalyst mass (generally 0.1% wt/wt) and time of reaction was considered when desired temperature (generally 130 °C) was reached. Samples were withdrawn at 5, 10, 15, 20, 25, 30, 45 and 60 min. Reaction conversion was estimated from the FFA content of the medium by NaOH titration.

2.3 Kinetic and Quantum Chemistry Studies

Reaction rate constants and reaction orders were estimated using conversion x reaction time curves for methanesulfonic and sulfuric acids catalyzed reactions, using the following modeling: $(-rA) = k\, C_{\mathrm{FA}}^{\alpha}\, C_{\mathrm{ALC}}^{\beta}$, where FA is fatty acid and ALC is alcohol

Activation energies were obtained from reaction rate constant (also estimated using conversion x reaction time data) at 130, 145 and 160 °C, for sulfuric acid catalyzed reaction.

Molecular modeling was performed using Titan 1.0 software (Wavefunction Inc.) for the two most abundant fatty acids in the raw material: palmitic and oleic acids. BP density function method with 6–31 G** base was applied.

Fatty acids protonation energies were calculated by:

$$E_{\mathrm{proton}} = \left|E_{\mathrm{protonspecies}} - E_{\mathrm{neutralspecies}}\right|$$

Atomic charges were extracted from the molecular properties file.

Energy profiles of the esterification of palmitic and oleic acids were performed using Gaussian 03 W (Gaussian Inc. 2004) molecular orbital package [18, 19]. Semi-empirical calculations are widely used in homogeneous catalysis [20–22].

3 Results and Discussion

3.1 Esterification Reaction

Figure 1 presents kinetic curves of the esterification reaction using anhydrous methanol as reactant. It can be

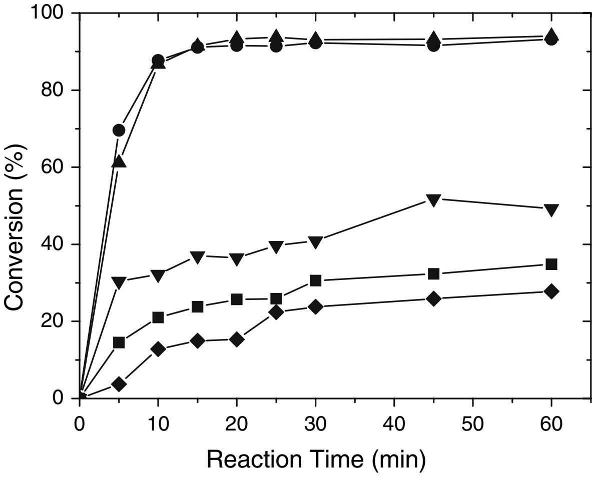

Fig. 1 Esterification of fatty acids with anhydrous methanol, $T = 130$ °C, A/FA = 3, 0.1% w/w catalyst. (■) Non-catalytic; (●) Sulfuric acid; (▲) Methanesulfonic acid; (▼) Phosphoric acid; (◆) Trichloroacetic acid

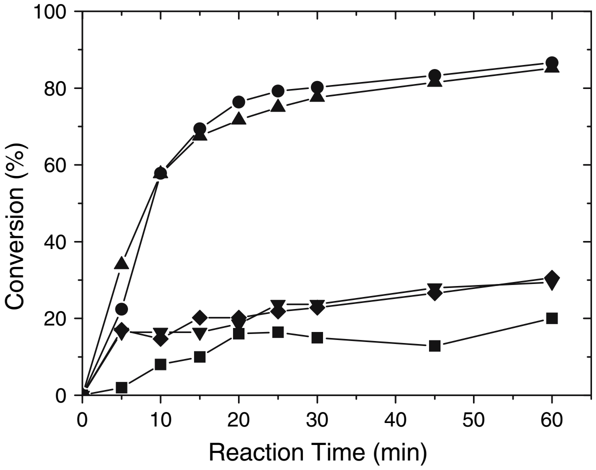

Fig. 2 Esterification of fatty acids with anhydrous ethanol, $T = 130$ °C, A/FA = 3, 0.1% w/w catalyst. (■) Non-catalytic; (●) Sulfuric acid; (▲) Methanesulfonic acid; (▼) Phosphoric acid; (◆) Trichloroacetic acid

observed that the reaction occurs in the absence of catalysts, with a conversion near 35% at 1 h. Trichloroacetic acid did not accelerate the reaction, and phosphoric acid has yielded minor improvements in conversion. Sulfuric and methanesulfonic acids were the best catalysts, with conversions higher than 90% at 1 h of reaction. The result may be assigned to the higher acid strength of these two acids compared to phosphoric and trichloroacetic acids. Higher acid strength means more H^+ species been released to protonate the carboxylic moiety of the fatty acid, increasing the electrophilicity of the carbonyl carbon atom and facilitating the second step, which is the nucleophilic attack of the alcohol, forming a tetrahedral intermediate. Last steps include proton migration and breakdown of the intermediate [2].

Kinetic curves of the esterification reaction using anhydrous ethanol are displayed in Fig. 2. Similar results were obtained concerning catalyst efficiency, showing the best performance of sulfuric and methanesulfonic acid. However, methanol reaction was faster than ethanol. Some authors have also observed the same behavior [15, 23, 24], which may be attributed to the shorter chain of methanol and its higher polarity. Steric hindrance inherent to both the carboxylic acid and the alcohol species seems to be important in the step of the nucleophilic attack of the alcohol, making reaction with methanol (a smaller molecule) faster [2].

Figure 3 shows the effect of sulfuric acid concentration on the kinetic curves. A small amount of catalyst (0.01% w/w) is enough to promote the reaction. Increases in catalyst concentration accelerate the reaction progressively. Similar result was obtained for methanesulfonic acid, as can be seen in Fig. 4.

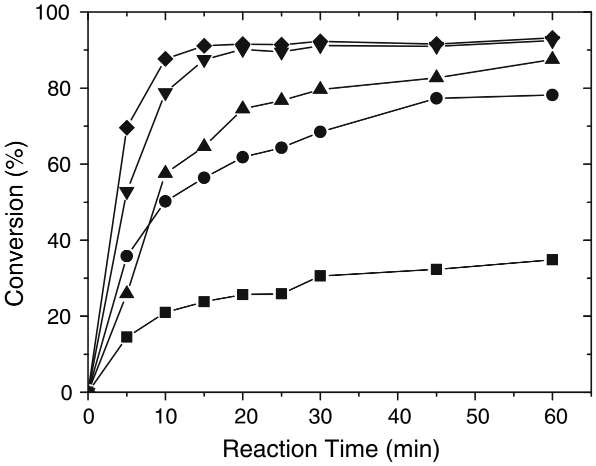

Fig. 3 Esterification of fatty acids with anhydrous methanol catalyzed by sulfuric acid—effect of catalyst concentration (w/w); $T = 130$ °C, A/FA = 3 (■) Non-catalytic; (●) 0.01%; (▲) 0.03%; (▼) 0.05%; (◆) 0.1%

The effect of water in the reaction medium can be seen in Fig. 5. Inhibition effect can be observed mainly in ethanol reaction. Reaction inhibition by the presence of water is commonly reported in transesterification reaction, being attributed to the formation of soap, which lowers the yield of esters and renders the separation of ester and glycerol and water washing difficult, besides favoring the hydrolysis of triglycerides and FFA [1, 9, 23]. In the case of acid-catalyzed esterification, soap formation is not expected, but inhibition effect was also observed [25], which may be attributed to equilibrium constraints, that is, esterification reaction has been shifted to the left, favoring the hydrolysis of the ester. Higher inhibition of ethanol reaction may be related to phase miscibility and emulsion formation.

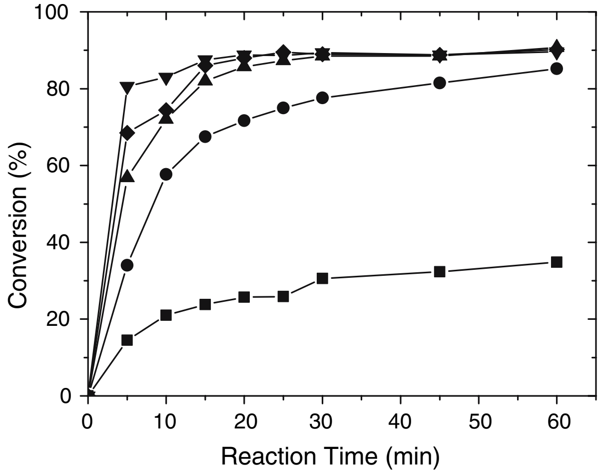

Fig. 4 Esterification of fatty acids with anhydrous methanol catalyzed by methanesulfonic acid—effect of catalyst concentration (w/w). (■) Non-catalytic; (●) 0.1%; (▲) 0.25%; (▼) 0.5%; (◆) 1%

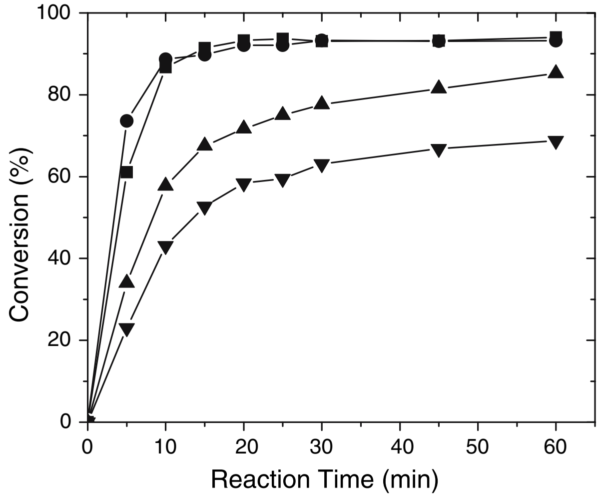

Fig. 5 Esterification of fatty acids catalyzed by methanesulfonic acid—effect of water; $T = 130$ °C, A/FA = 3, 0.1% w/w catalyst. (■) Anhydrous methanol; (●) Hydrated methanol; (▲) Anhydrous ethanol; (▼) Hydrated ethanol

Table 2 Kinetic parameters for the fatty acids esterification reaction with anhydrous methanol catalyzed by sulfuric acid

Catalyst	Kinetic parameters		
Concentration (%)	K[a]	α	β
0	1.418	1.294	4.70×10^{-4}
0.01	0.720	1.212	5.01×10^{-5}
0.03	0.832	1.186	2.16×10^{-5}
0.05	0.981	1.144	2.29×10^{-4}
0.1	1.591	1.142	5.86×10^{-4}

[a] $[M^{(1-\alpha-\beta)}\ \mathrm{min}^{-1}]$

$T = 130$ °C, A/FA = 3

Table 3 Kinetic parameters for the fatty acids esterification reaction with anhydrous methanol catalyzed by methanesulfonic acid

Catalyst	Kinetic parameters		
Concentration (%)	K[a]	α	β
0	1.418	1.294	4.70×10^{-4}
0.1	1.372	1.193	2.70×10^{-5}
0.25	1.614	1.166	1.00×10^{-4}
0.5	1.237	1.403	4.30×10^{-4}
1	1.773	1.159	2.00×10^{-4}

[a] $[M^{(1-\alpha-\beta)}\ \mathrm{min}^{-1}]$

$T = 130$ °C, A/FA = 3

Table 4 Kinetic parameter k (min^{-1}) for the fatty acids esterification reaction with anhydrous methanol catalyzed by sulfuric and methanesulfonic acid at different temperatures

Temperature (°C)	Sulfuric acid			Methanesulfonic acid		
	0.01%	0.03%	0.05%	0.01%	0.03%	0.05%
130	0.492	0.750	1.008	0.938	1.455	1.972
145	1.150	1.319	1.488	1.596	2.024	2.452
160	1.801	1.785	1.769	2.247	2.490	2.733

A/FA = 3

3.2 Kinetic Study

Tables 2 and 3 summarize kinetic parameters obtained for the fatty acid esterification reaction catalyzed by sulfuric and methanesulfonic acid, respectively. Similar results were obtained for both catalysts (sulfuric and methanesulfonic acid), independent of catalyst concentration: similar rate constants, first order with respect to fatty acid and zero order with respect to alcohol. The later result may be explained by the excess of alcohol used. The former result has been reported before in the literature for transesterification reaction [2, 16, 26, 27], which confirms that both reactions have the same rate determinant step (probably the protonation of the carboxylic moiety) and similar mechanisms.

Table 4 presents rate constant values for different temperatures and concentrations in reaction with methanol. These data were plotted using linearized Arrhenius equation, as seen in Figs. 6 and 7, while Table 5 summarize activation energies obtained using Arrhenius equation. Good correlations ($R^2 > 0.980$) were obtained for both catalysts. As expected, activation energy decreases as catalyst concentration increases. Besides, activation energy values obtained are very similar comparing both catalysts and smaller than the ones reported for transesterification reaction [26], which is expected given the higher complexity of triglyceride molecule compared to fatty acid.

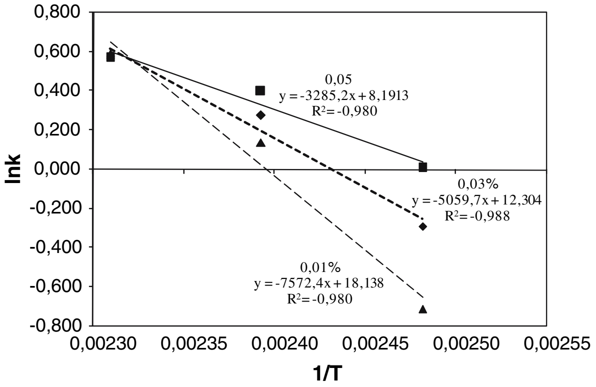

Fig. 6 Temperature dependence of the reaction rate constants k with anhydrous methanol, catalyzed by sulfuric acid, A/FA = 3, *T* = 130 °C (▲) 0.01% w/w catalyst; (◆) 0.03% w/w catalyst; (■) 0.05% w/w catalyst

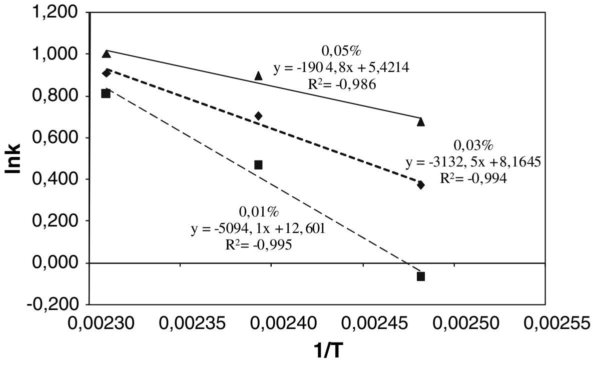

Fig. 7 Temperature dependence of the reaction rate constants k with anhydrous methanol, catalyzed by methanesulfonic acid, A/FA = 3, *T* = 130 °C (▲) 0.01% w/w catalyst; (◆) 0.03% w/w catalyst; (■) 0.05% w/w catalyst

Table 5 Activation energies for the sulfuric and methanesulfonic acid catalyzed fatty acids esterification reaction with anhydrous methanol

Catalyst concentration (%)	Activation energy (kcal/mol)	
	Sulfuric acid	Methanesulfonic acid
0.01	15.046	10.122
0.03	10.054	6.224
0.05	6.528	3.785

A/FA = 3

Table 6 Mulliken charges of species in carbonyl moiety (100 × electron charge)

Palmitic acid				Oleic acid			
Neutral species		Protonated species		Neutral species		Protonated species	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C	0.785	C	0.869	C	0.781	C	0.845
O1	−0.572	O1	−0.599	O1	−0.569	O1	−0.607
O2	−0.692	O2	−0.569	O2	−0.695	O2	−0.577
H	0.494	H1	0.554	H	0.494	H1	0.550
		H2	0.548			H2	0.544

Table 7 Calculated protonation energies of fatty acids

Acid	Protonation energy (kcal/mol)
Oleic	215.6
Palmitic	212.2

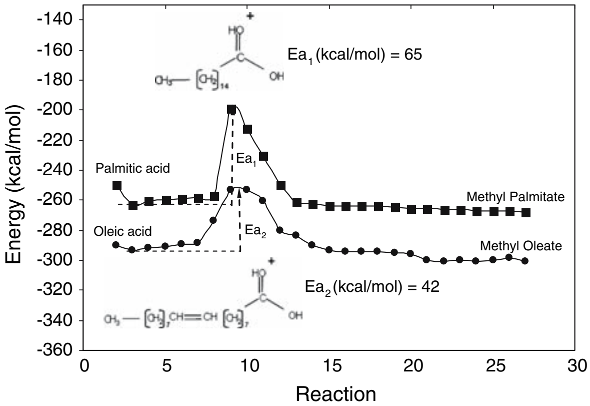

Fig. 8 Energy profiles for the esterification of palmitic acid (■) and oleic acid (●) with anhydrous methanol

3.3 Quantum Chemistry Study

Mulliken charges distribution of palmitic and oleic acid species are presented in Table 5, while Table 6 shows protonation energy values. No great intrinsic reactivity differences between fatty acids were observed, which means that both acids and probably all the others presented in the fatty acid mixture should have similar conversions in esterification reaction. This result may be explained by the fact that both esterification and transesterification reactivities are related to the carboxyl moiety and not in the alkyl chain (Table 7).

Activation energies were determined by semi-empirical simulations of each step of the reaction. Energy profiles along the fully optimized esterification of palmitic and oleic acid are illustrated in Fig. 8, and the transition states were defined for each reaction. These transition states corresponds to the protonated species, confirming that protonation of the carboxylic moiety of the fatty acid is the rate determinant step.

Activation energy can be determined by energy of these transition states (Ea_1 and Ea_2). Although the similar protonation energy of both fatty acids, the energy profiles indicated that esterification of oleic acid is faster than esterification of palmitic acid ($Ea_1 > Ea_2$). This result may be assigned to the polarity of the double bond of oleic acid, which increases the reactivity of carboxylic moiety of the fatty acid.

4 Conclusions

Acid-catalyzed homogeneous esterification reaction from palm fatty acids was studied using a batch reactor. Small amount of catalyst (0.01% w/w) is enough to promote the reaction, with the conversion increasing with higher amounts of catalyst. Acid strength of the catalyst was responsible for the higher activity of sulfuric and methanesulfonic acids, releasing more H^+ species to protonate the carboxylic moiety of the fatty acid (rate determinant step). Shorter chain and higher polarity of methanol has resulted in higher activity than ethanol, which presents steric hindrance in the reaction and shows higher water inhibition, attributed to phase miscibility and emulsion formation. Kinetic parameters obtained were similar to the ones reported for transesterification reaction, indicating a similar rate determinant step. Lower activation energy was the exception. Quantum chemistry studies have shown that despite the similar protonation energy of fatty acid, the double bond of oleic acid increase the reactivity of carboxylic moiety of the fatty acid.

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