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Research Article

Heterogeneously Catalyzed Esterification of FFAs in Vegetable Oils

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The production of methyl esters (biodiesel) from free fatty acids (FFAs) contained in vegetable oils was studied using a heterogeneous acid catalyst. The feedstock was a by-product of a vegetable oil refinery. The experiments were performed in a batch reactor, in a temperature range of 363.15–393.15 K, with an initial molar ratio of methanol to FFAs of 6.6/1, while the catalyst mass was fixed at 2 wt % of the total vegetable oil mass. A technical kinetic model has been developed which accounts for the reversible esterification reaction. Kinetic parameters were determined by fitting experimental data to the model.

Keywords: Biofuels, Catalysts, Esterification, Oils

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1 Introduction

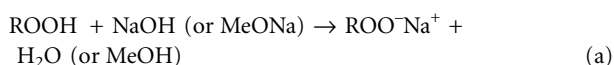
Humanity shows an unsatisfied thirst for energy. As a consequence, an amount of energy almost equivalent to 10 000 million tons of oil is spent every day. Although society has based its future on energy, most of the energy used derives from fossil fuels such as coal, natural gas, and especially petroleum. The use of these sources contributes to the increase of greenhouse gas emissions and global warming. Therefore, fulfillment of the requirements set by Kyoto targets has become a crucial factor. To this end, the European Community has decided to replace by the year 2010, at least 5.75 % of the yearly consumed fossil fuels by biofuels, the use of which does not contribute to the growth of greenhouse gases (2003/30/EC directive). Among these biofuels, biodiesel – consisting of fatty acid methyl esters (FAME) – has been widely recognized as a promising biofuel and its market is growing fast.

Biodiesel can be produced from a variety of feedstock such as vegetable oils, animal fats, and waste grease, through the transesterification reaction of triglycerides (TGs) [1, 2] or the esterification of free fatty acids (FFAs) present in the feed, with low molecular weight alcohols. Biodiesel has similar physical properties to diesel and therefore it can be used as a substitute for diesel fuel, either in neat form or in blends with it. Compared to petroleum-based diesel, biodiesel is more rapidly biodegradable and less toxic, with a higher flash point than diesel and an ultra-low sulfur content [3]. In addition, biodiesel in-

creases the lubricity of diesel fuel in their mixtures. The deep desulfurization process for the production of low sulfur-content diesel has a negative effect on fuel lubricity [4], while an addition of 1 % biodiesel, or even less, restores the required fuel lubricity [5]. Furthermore, biodiesel is an oxygenated fuel (oxygen content about 10 %) with low particulate emissions when it burns. Particulate matter emissions can be reduced up to 45–50 % when biodiesel is used instead of diesel in conventional engines, while the reduction can reach 75–83 % for the engines with the latest technology [6].

Nowadays, refined vegetable oils such as Soybean, Rapeseed, Sunflower, and Palm oils are the major feedstocks for biodiesel production, worldwide. Refined oils can be easily converted to biodiesel with the current industrial technology of basic homogeneous catalysis. The main disadvantage of using refined oils as raw material for biodiesel production is their high cost, which has a major effect on the final product price. However, waste grease such as yellow grease from used cooking oils and animal fats, are attractive alternatives for biodiesel production due to their low cost. Production of biodiesel from used oils and fats also contributes to waste recycling. However, the conversion of feedstocks with high FFA content to biodiesel requires a more complicated process.

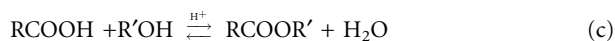
When a basic homogeneous catalyst is used for the transesterification of feeds with FFAs, soaps are produced as by-products through the unwanted saponification reaction [7] of carboxylic acids, with the base (e.g., KOH, NaOH, and CH₃ONa) as shown below (see reaction (a)):



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The water produced hydrolyses an amount of the esters to form more FFAs (reaction b) that consume the base catalyst and produce soap, according to reaction (a).

To overcome this problem, an acid catalyst can be used instead. Homogeneous acid catalysts, e.g., H₂SO₄, although effective, even with much lower reaction rates than basic catalysts reaction rates, lead to serious contamination problems [8]. The product must be thoroughly cleaned of catalyst residues, which are extremely corrosive and unhealthy if they are burned with the fuel. For these reasons, acid catalysis is not widely used in the industrial praxis. However, this method has the advantage that it converts FFAs to biodiesel, promoting esterification:



Esterification is a reversible reaction and the production of methyl esters is controlled by the equilibrium of the reaction. A route of first converting FFAs to esters and then attempting transesterification of the triglycerides with the conventional basic catalysis method appears very attractive. In this way, the well established and widely used transesterification process can be used, avoiding all the problems associated with the presence of FFAs. The very promising process – which is under development – for FFA conversion to esters prior to transesterification reaction is based on the use of heterogeneous catalysts. A number of studies on solid catalysts performance for FFAs esterification have appeared recently. The majority of these studies use strong acidic anion-exchange resins such as Amberlyst 15 [9], acidic cation-exchange resins such as Dowex 50Wx8-100 [10], or acid sulfonic resins such as Relite [11]. All these types of catalysts appear to be effective in esterification reactions of free fatty acids with methanol in the temperature range from 308.15 to 363.15 K. For the esterification reaction, methanol has been mainly used as alcohol. Aafaqi et al. [12] used a ZnA/SG catalyst for the esterification reaction of palmitic acid with isopropanol, achieving promising results. Finally, the fibrous polymer-supported sulfonic acid catalyst, Smopex-101, has been tested by Lilja et al. [13] with a variety of acid reactants such as acetic, propanoic and pentanoic acid, and various alcohols such as methanol, ethanol, 1-propanol, 2-propanol, butanol, and 2-butanol. However, in all the studies available, model compounds have been used as acid reagents. In this study, we present esterification results for a real feedstock with high FFA content, for an expanded experimentation temperature range, for the stability of a super acidic catalyst as well as for the verification of the developed kinetic model with two different feeds of very high FFA content.

2 Experimental Section

2.1 Materials

A high-acidity vegetable oil was used as base feedstock in this study. The acidity (AD) of the feedstock was 38.1 wt % (acid value: AV = 75.57). The water content was 1250 mg/kg while the total mineral content (K, Na, Ca, and Mg) was less than 10 mg/kg. The feedstock was a by-product of a vegetable oil

refinery and it is representative of a low price material with high FFA content. As an alcohol for the esterification reaction, analytic grade (purity 99.9%) methanol (Sds) was used. For the promotion of the reaction, an acidic solid catalyst was used. The catalyst was the commercial super acidic resin Purolite CT-275. The physical properties of the catalyst are shown in Tab. 1. Furthermore, two other by-products with high FFA content were used to verify both the applicability of the model and the derived kinetic parameters in real feeds.

Table 1. Physical properties of the catalyst.

Commercial name and provider	PUROLITE by Purolite International Limited
Chemical Name	Polystyrenesulphonic acid
Specific gravity	1.20–1.30 (in water)
Solubility	in water: insoluble in oil: insoluble
Acidity [eq H ⁺ kg ⁻¹]	5.20
S _g [m ² kg ⁻¹] ^a	31·10 ⁻³
V _g [m ³ kg ⁻¹] ^b	0.29·10 ⁻³
T _{max} [K]	418.15

^aBET method.

^bDetermined by adsorption – desorption of N₂ at 77 K.

2.2 Batch Reactor Experiments

The reaction was carried out in a Series 4560 Bench Top Mini Batch Reactor (Parr Instrument Company, Illinois, USA). The reaction mixture was formed with an initial molar ratio of methanol to FFAs equal to 6.6/1 mol/mol, while the catalyst was fixed at 2 wt % of the total vegetable oil mass.

To avoid oxidation of the reactants during reaction, the reacting mixture was stripped with nitrogen before the reaction. All the experiments were performed in the temperature range from 363.15 to 393.15 K, while the initial pressure was monitored between 350 and 650 kPa. During experimentation, samples were manually collected. The samples collected from the reactor were allowed to settle in a ventilator.

2.3 Method of Analysis

Prior to the acidity analysis, the samples were first centrifuged to separate any cracked parts of the catalyst and then the liquid mixture was stripped with N₂ at about 323.15 K for 1800 s to remove the excess methanol and the amount of water produced during reaction.

After preparation, the samples were analyzed by a standard titration procedure. A weighted amount of sample was dissolved into ethanol (purity 99.9%) and diethyl ether (purity 99.9%). To identify the pH change, some drops of phenolphthalein indicator were added into the solution. The titration was performed with a 1 kmol m⁻³ KOH water solution.

The acidity (AD) of the oil was calculated from the following equation:

$$AD = \frac{C_{\text{sol,KOH}} V_{\text{sol,KOH}} MB_{\text{OAc}}}{m_{\text{oil}} 1000} 100 \text{ (wt\%)} \quad (1)$$

The acid value (AV) of the oil was calculated as follows:

$$AV = \frac{C_{\text{sol,KOH}} V_{\text{sol,KOH}} MB_{\text{KOH}}}{m_{\text{oil}}} \text{ (mg}_{\text{KOH}}/\text{gr}_{\text{oil}}) \quad (2)$$

3 Mathematical Model

The process in the batch reactor used is at the transition state, since the concentration of reactants and products are changing with time. The consideration of total mixing due to strong agitation of the reacting mass allows the postulation of uniform reaction temperature and concentration in the reacting mass. In its general form, the mass balance is described by the following equation:

$$\text{Accumulation} = \{\text{input} + \text{production} - \text{output} - \text{consumption}\} \quad (3)$$

In the case of our experiments, there were no inputs and outputs. Only the production of methyl esters and water with the corresponding consumption of FFAs and methanol, according to the esterification reaction, took place.



This reaction can be considered as a second order reversible reaction. Therefore, the consumption rate of FFAs can be depicted by the following equation:

$$(-r_{\text{FFAs}}) = -\frac{dC_{\text{FFAs}}}{dt} = \left\{ \begin{array}{l} k_{\text{FFAs}} C_{\text{FFAs}} C_{\text{MeOH}} \\ -k_{-\text{FFAs}} C_{\text{MEs}} C_{\text{H}_2\text{O}} \end{array} \right\} \quad (4)$$

while the equilibrium constant, K_e , can be calculated from:

$$\frac{dC_{\text{FFAs}}}{dt} = 0 \Rightarrow K_e = \frac{k_{\text{FFAs}}}{k_{-\text{FFAs}}} = \frac{C_{\text{MEs}(e)} C_{\text{H}_2\text{O}(e)}}{C_{\text{FFAs}(e)} C_{\text{MeOH}(e)}} \quad (5)$$

Applying the mass balance of Eq. (3) for the FFAs production in the batch reactor, we obtain:

$$\text{Accumulation} = -\text{Consumption} \quad (6)$$

or:

$$M_{\text{mix}} \frac{dC_{\text{FFAs}}}{dt} = -(-r_{\text{FFAs}}) m_{\text{cat}} \quad (7)$$

and from Eq. (4):

$$M_{\text{mix}} \frac{dC_{\text{FFAs}}}{dt} = -\left\{ \begin{array}{l} k_{\text{FFAs}} C_{\text{FFAs}} C_{\text{MeOH}} \\ -k_{-\text{FFAs}} C_{\text{MEs}} C_{\text{H}_2\text{O}} \end{array} \right\} m_{\text{cat}} \quad (8)$$

Moreover, the reactant and product concentrations in the mixture are related by the following equations:

$$C_{\text{FFAs}} = \frac{N_{\text{FFAs}}}{M_{\text{mix}}} \quad (9)$$

$$C_{\text{MeOH}} = \frac{N_{\text{MeOH},0} - N_{\text{MeOH,react}}}{M_{\text{mix}}} = \frac{N_{\text{MeOH},0} - (N_{\text{FFAs},0} - N_{\text{FFAs}})}{M_{\text{mix}}} \quad (10)$$

$$C_{\text{H}_2\text{O}} = \frac{N_{\text{H}_2\text{O}}}{M_{\text{mix}}} = \frac{N_{\text{H}_2\text{O},0} + N_{\text{H}_2\text{O,react}}}{M_{\text{mix}}} = \frac{N_{\text{H}_2\text{O},0} + (N_{\text{FFAs},0} - N_{\text{FFAs}})}{M_{\text{mix}}} \quad (11)$$

$$C_{\text{MEs}} = \frac{N_{\text{MEs}}}{M_{\text{mix}}} = \frac{N_{\text{FFAs},0} - N_{\text{FFAs}}}{M_{\text{mix}}} \quad (12)$$

With replacement of the product and reactant concentrations in the mass balance, Eq. (8), by their equivalents from Eqs. (9–12), a first order non-linear differential equation is derived in which the time appears as the independent variable and the free fatty acids content (N_{FFAs}) as the dependent variable. By solving this equation, the evolution of N_{FFAs} with time can be described.

3.1 Estimation of the Kinetic Parameters

In the differential equation, Eq. (8), the two reaction constants k_{FFAs} and $k_{-\text{FFAs}}$, are unknown and must be determined. These two reaction constants are interrelated by the equilibrium constant K_e ($K_e = k_{\text{FFAs}}/k_{-\text{FFAs}}$). The solution of the non-linear differential equation, Eq. (8), was attempted with the use of the second order Runge-Kutta code [14]. The amount of the reactants and products withdrawn from the reactor at each sampling has been taken into account for the calculation of the corresponding concentrations and the numerical solution of the relevant differential equation. With the target to determine the best values of the reaction constants and the equilibrium constant so that the calculated mass of the acid in the reactor ($N_{\text{FFAs,calc}}$) is as close as possible to the experimentally determined value ($N_{\text{FFAs,exp}}$), an optimization procedure was adopted. With this procedure, minimization of the differences between calculated and experimental values was attempted, by minimizing the value of the following objective function:

$$F = \sum_{t=0}^{t_{\text{end}}} \left(1 - \frac{N_{\text{FFAs,calc},t}}{N_{\text{FFAs,exp},t}} \right)^2 \quad (13)$$

The minimization of the objective function was attempted with the Newton method [15].

4 Results and Discussion

4.1 Estimation of the Equilibrium Constants

As mentioned in the experimental section, experiments were performed at 393.15, 383.15, 373.15, and 363.15 K, respectively. The reaction time was kept as long as about 180000 s (50 h) until the system reached equilibrium. For each temper-

ature, the equilibrium constant (K_c) can be calculated from Eq. (5) knowing the final value of AD or AV at equilibrium, from which $N_{\text{FFAs}(e)}$ can be calculated. The results from these calculations are shown in Tab. 2.

From the values in Tab. 2, it is observed that the equilibrium constant increases with temperature.

Table 2. Estimated values of the equilibrium constant.

Temperature T [K]	Initial AD [%]	Final AD [%]	K_c [-]
393.15	38.1	4.59	1.1994
383.15	38.1	4.78	1.1091
373.15	38.1	5.58	0.8638
363.15	38.1	7.44	0.5269

4.2 Reaction Constants

During the heating period of the reactor, which was about 900 s, an amount of free fatty acids reacted with methanol to produce methyl esters and water. To minimize the experimental error due to the preheating time, a sample was withdrawn from the reactor at the time the reaction mixture reached the desirable temperature and the real amounts of FFAs, MEs, MeOH, and H₂O in the mixture were calculated. Tab. 3 shows the initial masses of the reactants and the real masses when the desired temperature was achieved for a representative experiment.

By solving the model and optimizing the objective function, the kinetic parameters for each experiment were determined. These values along with the corresponding value of the objective function are shown in Tab. 4.

Table 3. Initial mass of the reactants and the corresponding masses at the beginning of the experiment when the desirable temperature (393.15 K) was reached.

Temperature [K]	MeOH [$\text{kg} \times 10^3$]	FFAs [$\text{kg} \times 10^3$]	MEs [$\text{kg} \times 10^3$]	H ₂ O [$\text{kg} \times 10^3$]	TGs [$\text{kg} \times 10^3$]
298.15	56.86	76.11	0.00	0.39	123.65
393.15	56.07	69.11	7.34	0.84	123.65

Table 4. Estimated values of the reaction constant and the corresponding values of the objective function.

Temperature [K]	k_{FFAs} [$\text{kg}^2 \text{kg}_{\text{cat}}^{-1} \text{mol}^{-1} \text{s}^{-1}$]	$k_{-\text{FFAs}}$ [$\text{kg}^2 \text{kg}_{\text{cat}}^{-1} \text{mol}^{-1} \text{s}^{-1}$]	F [-]
363.15	$1.40 \cdot 10^{-4}$	$2.65 \cdot 10^{-4}$	0.0141
373.15	$2.73 \cdot 10^{-4}$	$3.16 \cdot 10^{-4}$	0.0249
383.15	$4.76 \cdot 10^{-4}$	$4.32 \cdot 10^{-4}$	0.0456
393.15	$8.37 \cdot 10^{-4}$	$6.98 \cdot 10^{-4}$	0.0391

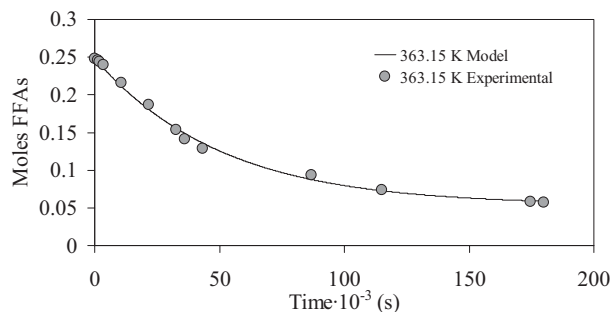


Figure 1. Evolution of the catalytic esterification of FFAs in the high acidity oil (38.1 wt% AD). Methanol-to-FFAs molar ratio: 6.6/1. Reaction temperature: 363.15 K.

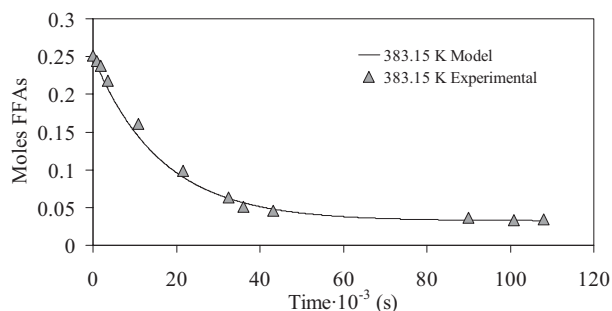


Figure 2. Evolution of the catalytic esterification of FFAs in the high acidity oil (38.1 wt% AD). Methanol-to-FFAs molar ratio: 6.6/1. Reaction temperature: 383.15 K.

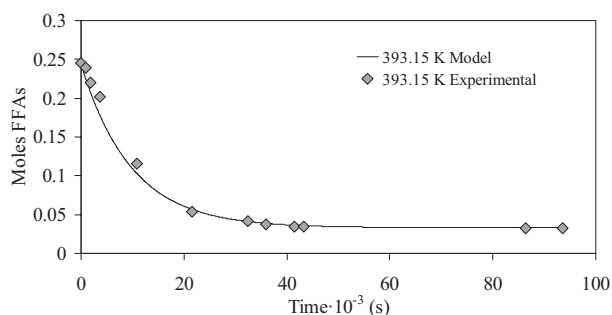


Figure 3. Evolution of the catalytic esterification of FFAs in the high acidity oil (38.1 wt% AD). Methanol-to-FFAs molar ratio: 6.6/1. Reaction temperature: 393.15 K.

The evolution of the reaction as well as the fitting of the kinetic model to the experimental values is shown in Figs. (1–3).

In Fig. 4, the predicted values of the FFAs mass in the reacting mixture are compared with the experimental ones for all the experimental runs carried out in the temperature range between 363.15 and 393.15 K.

A good agreement between the experimental and the calculated values is observed for all the experimental points. This implies that the proposed technical kinetic model can be used for reliable calculations and design of relevant reactors.

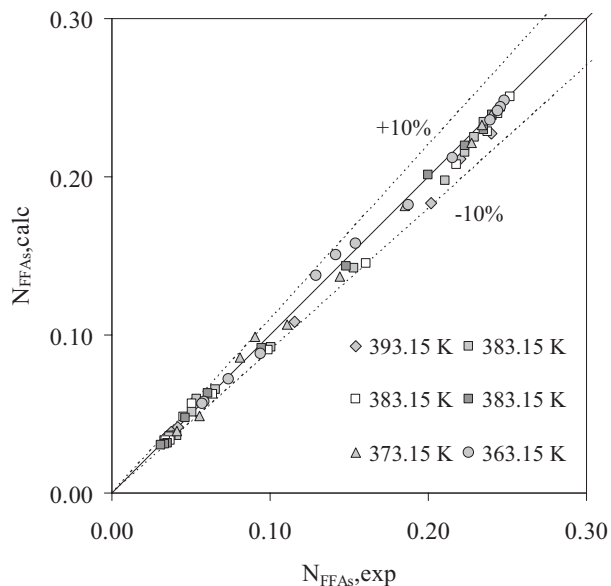


Figure 4. Plot of the predicted FFAs mass in the reacting mixture against the experimental values. Reaction temperatures are from 363.15 to 393.15 K.

4.3 Calculation of the Activation Energy

The dependence of the reaction constant of a chemical reaction on reaction temperature is described by the Arrhenius Law, as given in Eq. (14):

$$k = A_0 e^{-E_a/RT} \quad (14)$$

Therefore, the activation energy, E_a , is calculated from the Arrhenius-Van't Hoff plot (see Fig. 5) by using the calculated values of the reaction constants. Values of the activation energy as well as the pro-exponential factors of the direct (esterification) and reverse (hydrolysis) reactions are shown in Tab. 5.

In Fig. 5, the change in the equilibrium constant, along with the change of the reaction constants, with temperature is presented.

Comparing the activation energy of the esterification reaction calculated from our data, $E_{FFAs} = 70.34 \text{ kJmol}^{-1}$, and the corresponding value for the esterification of decanoic acid with methanol presented by Steinigeweg and Gmehling [9] (72.23 kJmol^{-1} calculated from the modified LH-HW model and 68.71 kJmol^{-1} calculated from the pseudo homogeneous kinetic model), it is observed that they do not differ significantly.

The heat of reaction (ΔH_r) calculated from our equilibrium data in the temperature range between 363.15 and 393.15 K has a value of $\Delta H_r = 31.30 \text{ kJmol}^{-1}$ ($\Delta H_r = 7.47 \text{ kcalmol}^{-1}$). Tesser et al. [11] determined a lower value ($2.68 \text{ kcalmol}^{-1}$) using data collected in the temperature range from 323.15 to 373.15 K for an oleic acid-methanol system which was studied in a batchwise-operated reactor. Steinigeweg and Gmehling [9] determined an even smaller heat of reaction ($0.92 \text{ kcalmol}^{-1}$)

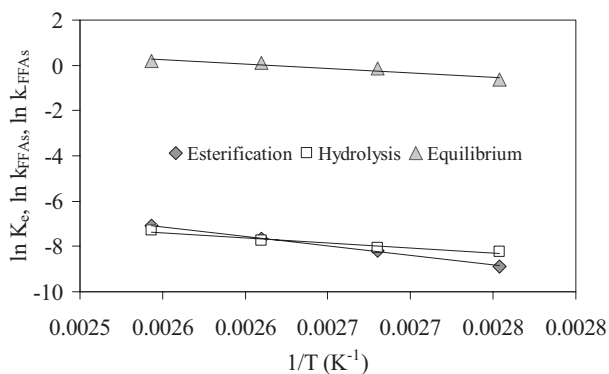


Figure 5. Arrhenius-Van't Hoff plot of equilibrium and reaction constants in the temperature range of 363.15 to 393.15 K.

Table 5. Activation energy and the pro-exponential factor for esterification and hydrolysis reactions.

Reaction	E_a [kJmol ⁻¹]	A [kg ² kg _{cat} ⁻¹ mol ⁻¹ s ⁻¹]	R^2 [-]
Esterification	70.34	$1.12 \cdot 10^{11}$	0.999
Hydrolysis	37.93	$4.19 \cdot 10^6$	0.947

from data collected in the temperature range from 309 to 338 K. From these values, it is obvious that the effect of temperature on the equilibrium constant increases as the reaction temperature increases.

4.4 Model Verification

In order to verify the applicability of our model in the case of vegetable oils with high FFAs content, two equilibrium experiments were conducted at 393.15 K with different feedstocks and methanol-to-oil molar ratios. The first experiment took place using a vegetable oil by-product with AD = 58 wt % and molar ratio, methanol to FFAs, equal to 6/1. For the second, a vegetable oil by-product with AD = 100 wt % was used with the methanol-to-FFAs molar ratio equal to 3/1. In both experiments, the catalyst mass was fixed to 2 wt % of the total oil mass. In Tabs. 6 and 7, the experimental values at equilibrium are shown and compared with the values calculated from the equilibrium constants derived from the data of this study (1st stage of equilibrium).

In order to further study the model prediction for mixtures with random compositions (FFAs, MEs, Water, TGs), the rest of the methanol and produced water were stripped off the mixture after the 1st equilibrium stage. Then, a measured quantity of methanol was added to the mixture (FFAs, MEs, and TGs) and esterification proceeded until the 2nd equilibrium stage was reached. For the first experiment (see Tab. 6), this step was repeated for one more time in order to achieve very low free fatty acid concentration in the final product.

Table 6. Experimental values and model predictions for conversion at equilibrium of the feedstock with AD = 58 wt% ($T = 393.15$ K).

	Experimental		Model prediction	
	Acidity [wt %]	Acidity [wt %]	MEs [wt %]	MEs [wt %]
Initial	58.00	58.00	0.00	0.00
1 st Eq. Stage	6.13	7.62	51.40	51.40
2 nd Eq. Stage	2.23	2.13	57.00	57.00
End	1.02	0.80	58.36	58.36

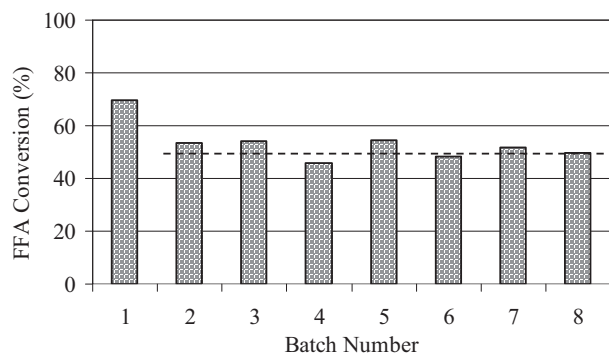
Table 7. Experimental values and model predictions for conversion at equilibrium of the feedstock with AD = 100 wt% ($T = 393.15$ K).

	Experimental		Model prediction	
	Acidity [wt %]	Acidity [wt %]	MEs [wt %]	MEs [wt %]
Initial	100.00	100.00	0.00	0.00
1 st Eq. Stage	20.94	22.32	77.68	77.68
End	4.23	4.68	95.32	95.32

In the case of the second experiment (see Tab. 7), there were no TGs in the reaction mixture because the feedstock consisted of FFAs only. A very good agreement between the experimental points and the calculated ones is observed in Tab. 7, even at very high FFAs conversions. From this data, it can be deduced that efficient pre-treatment of vegetable oils with very high FFAs content can be achieved.

4.5 Catalyst Deactivation

An important factor in catalytic applications is the catalyst stability and decay with time. The catalyst stability was checked with a number of experiments performed at 383.15 K, with the same feedstock used to derive the kinetic parameters, methanol-to-FFAs molar ratio equal to 6.6/1, and 2 wt % cata-

**Figure 6.** Catalyst activation for 8 batches at 383.15 K.

lyst. The results are shown in Fig. 6. After each experiment, the catalyst was filtered and separated from the reaction mixture and then it was used for the next experiment with fresh reactants. The reaction time was kept at 43200 s (12 h) for each experiment. The catalyst was not washed after separation but it was left overnight to drain.

As it is observed, no deactivation occurs after the first batch and a steady catalyst performance for 302400 s (84 h) during the operation was assured with these experiments.

5 Conclusions

A commercial super acidic catalyst was used to esterify the FFAs in a vegetable oil based feedstock. By-products of vegetable oil refining processes with high FFA content can be used effectively to produce biodiesel. The resulting oils can be fed to conventional units to be processed and produce biodiesel by transesterifying the existing triglycerides. The esterification kinetic model developed predicted the esterification extent of two other oils with much higher FFA content very well.

Symbols used

A	$[\text{kg}^2\text{kg}_{\text{cat}}^{-1}\text{mol}^{-1}\text{s}^{-1}]$	pro-exponential factor
AD	$[\text{mg}_{\text{OA}}/\text{mg}_{\text{oil}}]$	acidity
AV	$[\text{mg}_{\text{KOH}}/\text{gr}_{\text{oil}}]$	acid value
C_i	$[\text{molkg}^{-1}]$	concentration of substance i in the reaction mixture
ΔH_r	$[\text{kJmol}^{-1}]$	heat of reaction
E_a	$[\text{kJmol}^{-1}]$	activation energy
E_{FFAs}	$[\text{kJmol}^{-1}]$	activation energy for esterification
F	$[-]$	objective function
FFAs	$[-]$	free fatty acids
K_e	$[-]$	equilibrium constant
k_{FFAs}	$[\text{kg}^2\text{kg}_{\text{cat}}^{-1}\text{mol}^{-1}\text{s}^{-1}]$	reaction constant of esterification
$k_{-\text{FFAs}}$	$[\text{kg}^2\text{kg}_{\text{cat}}^{-1}\text{mol}^{-1}\text{s}^{-1}]$	reaction constant of hydrolysis
m_{cat}	$[\text{kg}]$	mass of catalyst
M_{mix}	$[\text{kg}]$	mass of reaction mixture
m_{oil}	$[\text{kg}]$	mass of oil phase which includes TGs, MEs, FFAs
N_i	$[\text{moles}]$	moles of substance i in the reacting mixture
r_i	$[\text{molkg}_{\text{cat}}^{-1}\text{s}^{-1}]$	reaction rate of substance i
S_g	$[\text{m}^2\text{kg}^{-1}]$	specific area
t	$[\text{s}]$	reaction time
t_{end}	$[\text{s}]$	reaction end time
V_g	$[\text{m}^3\text{kg}^{-1}]$	specific volume

Subscripts

calc	calculated values
exp	experimental values
i	substance of reaction mixture $i = \text{FFAs, MEs, MeOH, and H}_2\text{O}$, respectively

MEs	methyl esters
OA	oleic acid
sol	solution
TGs	triglycerides
react	reacted
mix	reaction mixture

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