Robust kinetic modeling of heterogeneously catalyzed free fatty acids esterification in monophasic liquid/solid packed bed reactor: rival model discrimination

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Introduction

In order to make more sustainable the production of energy, new kinds of fuels were studied in recent years (Iglinski et al. 2014). Several studies were conducted in order to quantify the biomass potential as new and sustainable energetic feedstock (Christoforous and Fokaides 2015). Among different biofuels, one of the most promising is biodiesel (BD), that is, a fatty acid methyl esters (FAME) mixture and can be obtained by transesterification of highly refined vegetable oils with methanol in homogeneous-based catalyzed processes (Ng et al. 2010). The oils are mainly constituted by triglycerides (about 90–98 % of total mass) and free fatty acids (FFA), linear carboxylic acids in the C14–C22 range, with different instauration levels (Ma and Hanna 1999). However, the commercialization of biodiesel is difficult due to its final cost, that is, strongly dependent by the feedstock used (Haas et al. 2006). Intensive studies were dedicated to find possible solutions to this problem. One of the proposed solutions is the use of raw oils, i.e., unrefined or waste oils as feedstock (Liew et al. 2014). Some examples of low-cost raw mate-rials for biodiesel production are crude vegetable oils (Pinto et al. 2005), waste cooking oils (Boffito et al. 2012), and animal fats (Bianchi et al. 2009). However, these types of low-cost feedstock show some drawbacks. One critical point is represented by their high content of free fatty acids that during the transesterification reaction, catalyzed by a

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homogeneous base catalyst, leads to the formation of soaps, which prevent the separation of glycerol. Another important drawback is represented by a loss in the product yield due to the not conversion of FFA in methyl esters, i.e., biodiesel.

The esterification of FFA with methanol in the presence of either homogeneous or heterogeneous acid catalysts allows, at the same time, to lower the acid content and to obtain methyl esters, already in this preliminary step. Different studies on the esterification reaction were carried out, using different acid catalysts, for example, sulfuric acid (Berrios et al. 2007) and different heterogeneous solid catalysts, like sulfated zirconia (Lu et al. 2010) or ion-exchange resins (Tesser et al. 2009). The results obtained in these studies demonstrate the possibility to perform this reaction with heterogeneous catalysis using non-severe operative conditions, i.e., temperature lower than the boiling point of methanol and room pressure. The final concentration of FFA in the oil after some hours of reactions reaches the level considered as suitable for the successive transesterification reaction (FFA < 0.5 %w), as reported for example from Caetano et al. (2014) in a study concerning the conversion of spent coffee grounds in biodiesel. A crucial parameter to be considered is the amount of methanol added to the oil. In fact, although the stoichiometric alcohol/FFA molar ratio is one for this reaction, a higher amount of alcohol is convenient in order to shift the reaction toward the desired products. For this reason, in the typical reaction conditions (Santacesaria et al. 2007), there are two liquid phases, being the methanol soluble in oil up to about 6–8 % by weight, depending on the operative conditions and on the oil type. The presence of a double liquid phase (plus the solid catalyst) makes much more difficult design and operation of the different types of reactors, either batch or continuous, for the fol-lowing aspects: (1) extraction of FFA dissolved in the oil by the methanol-rich phase with consequent loss of FFA conversion to BD; (2) in continuous reactors, in particular packed bed reactors, the part of the catalyst particles surrounded by the methanol phase is not physically in contact with the FFA of the vegetable oil, and cannot therefore exert its action; and (3) a liquid–liquid–solid system is more complex from a diffusional point of view, being highly mass transfer limited.

A recent study by the authors (Pirola et al. 2014a) demonstrated that the use of limited amount of methanol avoids the formation of a double liquid phase inside the reactor without limiting in a considerable way the final conversion of FFA by esterification, for both batch and packed bed continuous reactor. On the basis of these positive results, the aim of the present paper is the modelization of this monophasic liquid/solid system, where the liquid is the reacting media in which the methanol is

dissolved in the vegetable oil and the solid is the catalyst. A commercial solid acid resin (Amberlyst 46) was used as catalyst. The choice of this resin was based on its peculiar properties (Pirola et al. 2010); in fact, unlike all other Amberlyst type resins, this catalyst is not internally sulfonated but it only has surface acid groups (Chakrabarti and Sharma 1993). Consequently, it is not subject to any internal adsorption–desorption phenomena for both reactants and products. Moreover, the minimized water adsorption leads to a slower catalyst deactivation. A continuous packed bed reactor (Pirola et al. 2014b) was used to collect experimental data using different operative conditions (temperature and residence times, in particular) and a kinetic modelization was developed.

The esterification reaction of FFA in vegetable oils using this kind of solid catalyst was also modelized by different groups (for example Tesser et al. 2005 and Omota et al. 2003) and by Popken et al. (2000) for the system acetic acid/methanol. Nevertheless, the modelization proposed in the present work presents relevant novelties with respect to these previous works. In particular, it was demonstrated (Pirola et al. 2014a) that, when using ion-exchange resins as catalyst, the first four experimental runs give progressive different results in terms of FFA conversion, i.e., the performance of the catalyst decreases from the first to the fourth run and then remains stable. This particular behavior is due to the products (especially water) adsorption onto the resin surface. For this peculiar characteristic of this kind of heterogeneous catalysts, it is better to use experimental data gathered after the achievement of stable catalytic performance as sound basis for the numerical regression of the kinetic parameters of any model. In fact, using the experimental data obtained with fresh catalysts (not equilibrated), the final model cannot properly represent the behavior of the continuous esterification reactor. Another key point of our interpretation is the choice to consider the liquid system inside the reactor as non-ideal by calculating the activity and not the concentration of each compound. This aspect is not common in literature, where usually the bulk concentrations of reagents and products are considered. We used the UNIQUAC model for the calculation of the activity coefficients. The great advantage of this not-ideal approach is a more realistic representation of the system, with the possibility to calculate the methanol and water liquid phase separation. Finally, as already discussed, this study was developed only considering data collected in system without demixing of methanol and oil.

More in detail, two different kinetic models were considered, a pseudo-homogeneous and an adsorption based one which accounts for the different affinities toward the polymeric matrix of all the species involved in the reaction and the solvent (triglycerides), following the same approach proposed by Popken et al. (2000) for similar

catalytic systems. For both the models, the ideal and not-ideal behaviors of the mixture were considered, and the results were compared. The identification of the better kinetic interpretation able to represent the reactor behavior in different operative configurations is a crucial step for the optimization and simulation of the proposed technology (Myint and El-Halwagi 2009).

The non-linear regression program belonging to the BzzMath C++ (Manenti and Buzzi-Ferraris 2009) optimizer library was used for regressing the kinetic parameter.

Experimental

Chemicals

Sunflower oil was purchased from TopAgri (Verona, Italy). Methanol (>99.8 %) was purchased from Sigma Aldrich, and KOH 0.1 mol L^{-1} in ethanol was purchased from Fluka.

Amberlyst 46 (A46) catalyst was used for all the experiments. It was kindly provided by Dow Chemicals. Table 1 (Chakrabarti and Sharma 1993) summarizes the main features of this resin. Before its use, Amberlyst 46 was dried at 80 °C in an oven for 14–16 h. Higher temperatures in air atmosphere are not recommended, due to the risk of losing the sulfonic acid sites in the form of

–SO$_3$H (desulfurization of the polystyrene matrix of the catalyst).

The exchange capacity of the catalyst in its wet form was evaluated by total ion exchange with sodium chloride solution and subsequent titration (Boffito et al. 2012). A value of 0.43 ± 0.01 meq H$^+$ g^{-1} was obtained, which is consistent with the manufacturer data.

Experimental data

As previously introduced, the experimental data used for the regression of the kinetic parameters were gathered using a continuous packed bed reactor (PBR), as shown in Fig. 1. The PBR reactor is an iron cylinder 20.3 cm long and with an internal diameter of 4.7 cm with 2 intermediate samplings. The catalytic bed is placed at 7.4 cm from the bottom of the reactor, and it has a volume of 86 cm^3. Other experimental details are reported in previous paper (Pirola et al. 2014b). In order to be sure that the experimental results were not affected from the initial resin equilibration, only data after 40 h of reaction were considered, in accordance with the results previously collected (Pirola et al. 2014a).

The esterification reaction was carried out at different operative temperatures at 6 bar. The main advantage of this reactor configuration is the possibility to perform deacidification reactions above the methanol normal

Table 1 Catalyst A 46 main physical–chemical features

Catalyst	Surface area (m^2 g^{-1})	Average pore diameter (Å)	Total pore volume (mL g^{-1})	Acidity (meq H$^+$ g^{-1})	Max working temperature (°C)
Amberlyst 46	75	235	15	>0.4	120

Fig. 1 Scheme of the experimental apparatus and picture of the PBR reactor
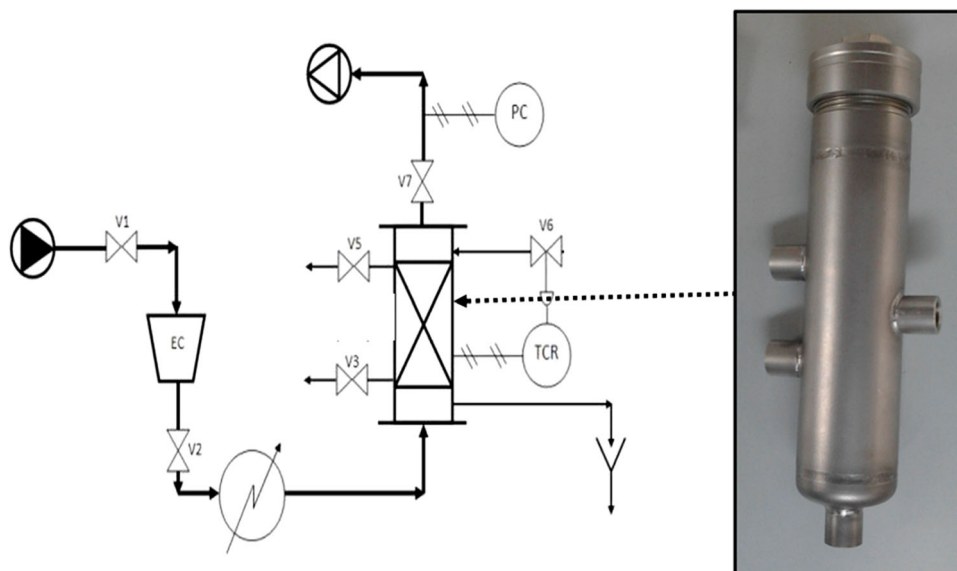
Table 2 PBR reactor main characteristics

Reactor volume (cm^3)	Void fraction	Catalyst density (kg/dm^3)	Catalyst charged (g)
0.180	0.36	0.60	51.6

boiling point (64.70 °C) because the system is under pressure. In Table 2, the main reactor characteristics are reported.

The determination of the FFA weight percentage was carried out using a colorimetric titration on samples collected from the reactor. 20 mL of 2-propanol was added to each sample to dissolve FFA and facilitate the titration. KOH 0.1 mol L^{-1} was used as titrant and phenolphthalein as indicator. FFA weight percentage was calculated using the following equation:

$$\text{FFA } (\%_W) = \frac{\text{Volume}_{\text{titrant}}(\text{L}) \times 0.1 \ (\text{mol/L})^{-1} \times \overline{\text{MW}}_{\text{FFA}}(\text{g/mol})}{\text{Sample mass (g)}}, \tag{1}$$

where $\overline{\text{MW}}_{\text{FFA}}$ was calculated considering both the original FFA composition of sunflower oil and the initial addiction of oleic acid used to increase the FFA concentration to a standard initial value of 5 %. The value of residual acidity is compared to the initial value, and the acidity conversion % was calculated as follows:

$$\text{FFA}_{\text{conversion}}(\%) = \frac{\text{FFA}_0 - \text{FFA}_t}{\text{FFA}_0} \times 100, \tag{2}$$

where FFA_0 is the initial acid value, and FFA_t is the acid value at time t.

C++ BzzMath non-linear regression

The kinetic parameters regression on experimental data was performed by means of the set of very robust optimizers belonging to the BzzMath library (Buzzi-Ferraris and Manenti 2012). Such optimizers are based on the object-oriented programming and parallel computing so as to reduce the computational time (Buzzi-Ferraris and Manenti 2010a), and they have implemented special numerical methods able to simultaneously handle the so-called nar-row-valley problem, which typically arise in the estimation of kinetic and thermodynamic parameters (Buzzi-Ferraris and Manenti 2009). The possible multicollinearities of the parameters, which could be due to coupled chemical–physical phenomena, and the possible presence of bad-quality measures with the identification of possible outliers (Buzzi-Ferraris and Manenti 2010b). Actually, the mistake made by many strategies is to adopt search directions oriented along the bottom of the valley for the one-dimensional minimum.

Such a search will prove ineffective, usually because the direction is inexact and the valley is non-linear. To exploit the search direction that inaccurately detects the bottom of the valley, it is necessary to change the point of view: (1) any optimization algorithm can find the bottom of the valley by starting from a point outside the same valley; (2) the line joining two points on the bottom of the valley is a reasonable valley direction; therefore, there is a good probability that a point projected along such a direction will be close to the valley; (3) nevertheless, this valley direction must not be used as the one-dimensional search direction, but rather as a direction along which a new point projection must be carried out; (4) this new point should not be discarded even though it is worse than the previous one, rather it is the new starting point for a new search; and (5) this search must be performed in the sub-space orthogonal to the valley direction to prevent the issue of small steps arising. This philosophy is particularly simple in object-oriented programming. The optimization problem is split into two different levels: the first (outer optimizer) is managed by a single object that exploits the above-mentioned procedure to find a certain number of points to initialize an even number of objects. In the second (inner optimizer), each object uses a program to search for the minimum with a limited number of iterations starting from the point assigned by the outer optimizer. This philosophy is useful in solving all problems demanding algorithm robustness: (1) when the function has many minima and we need to search for the global minimum; (2) when the function has very narrow valleys (or steep walls); and (3) when the function is undefined anywhere. All these problems arise in the estimation of thermodynamic parameters. The performance in terms of estimation accuracy and computational effort as well of the proposed approach has been proven with respect to the tools available in the commercial suites.

Kinetic models

All the experimental data above mentioned were used for the regression of the esterification reaction kinetic parameters. Two different models are proposed. The first one is the pseudo-homogeneous one, in which even though a heterogeneous catalyst is used, the reaction rate is considered dependent on the bulk activities of the components. This model is simple and depends on few parameters. The particular characteristics of the selected catalyst Amberlyst 46, i.e., the possibility to not consider the internal diffusional aspects, are on the basis to study the possibility that this simply model should properly represent our system. The expression of the reaction rate according to this model is shown in the following equation:

$$r = \frac{d}{dt} \times \overset{\circ}{c}_{FFA} = \left(\overset{\circ}{k_1} \times \exp\left(-\frac{E_{a1}}{RT}\right) \times a_{FFA} \times a_{MeOH} \right.$$
$$\left. - \overset{\circ}{k_{-1}} \times \exp\left(-\frac{E_{a-1}}{RT}\right) \times a_{FAME} \times a_{H_2O} \right), \tag{3}$$

where $\overset{\circ}{k_1}$ and E_{a1} are the adjustable Arrhenius kinetic parameters for the direct reaction (esterification), while $\overset{\circ}{k_{-1}}$ and E_{a-1} are the ones for the inverse reaction (hydrolysis), a_i are the component activities, and T is the absolute temperature. Instead of considering all the fatty acids molecules, the oleic acid was chosen to represent all the oil FFA. Consequently, FAME are represented by methyl oleate and oil by triolein, a triglyceride constituted by three molecules of oleic acid.

The second model considered is an adsorption-based one, shown in the following equation with similar symbols of Eq. (3):

$$r = \frac{d\xi}{dt} \times \overset{\circ}{c}_{FFA} = \left(\frac{\overset{\circ}{k_1} \times \exp(-\frac{E_{a1}}{RT}) \times a'_{FFA} \times a'_{MeOH} - \overset{\circ}{k_{-1}} \times \exp(-\frac{E_{a-1}}{RT}) \times a'_{FAME} \times a'_{H_2O}}{\left(a'_{FFA} + a'_{MeOH} + a'_{FAME} + a'_{H_2O} \right)^2} \right). \tag{4}$$

Moreover,

$$a'_i = \frac{K_i \times a_i}{MW_i}. \tag{5}$$

This equation is derived (Song et al. 1998) from the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model by considering instead of a constant number of moles adsorbed onto the resin a constant mass, as explained by Popken et al. (2000). K_i is the adsorption affinity constants for the i-th molecule, shown in Table 3. Popken studied the adsorption on Amberlyst 15 of water, methanol, ethyl acetate, and acetic acid. Considering that the polymeric substrate of Amberlyst 46 is the same of Amberlyst 15, the constant of water and ethanol can be used. As suggested in a work by Rehfinger and Hoffmann (1990), the adsorption constant of methyl oleate (FAME) and oleic acid (FFA) could be calculated from the one of methanol (Eq. 6).

Table 3 Binary adsorption equilibrium constants taken from Popken et al. (2000)

Component (i)	Binary adsorption affinity (K_i)
Water	5.24
Methanol	5.64
FFA	1.61

Finally, the absorption of oil on the resin is neglected due to the high molecular weight and volume of the triolein molecule.

$$K_{FFA} = K_{FAME} = \frac{K_{MeOH}}{3.5} \tag{6}$$

As shown in Eq. (5) this model takes into account the adsorption onto the resin surface by means of the parameter K_i. MW_i is the molecular weight of the i substance.

The temperature dependence of the kinetic parameters was considered, as highlighted in Eq. 4, using the Arrhenius model.

The use of experimental adsorption equilibrium constants is proposed in order to limit the number of numerical parameters to be regressed in the kinetic model. In this way, the binary adsorption affinities were not regressed together with the kinetic parameters because their values are known (Table 3) and none of them needs to be included as adjustable parameters in the fitting of the kinetic data.

The kinetic models with either an ideal liquid phase, considering the activity coefficients equal to one, or the non-ideality of the mixture using the UNIQUAC equation model were considered. UNIQUAC interaction parameters τ_{ij} were calculated using the following equation:

$$\tau_{ij} = \exp\left(\frac{b_{i,j}}{T}\right), \tag{7}$$

where the binary b_{ij} parameters were taken from the AspenPlus™ database and reported in Table 4.

Results and discussion

Experimental esterification results

All the experimental data were collected in a monophasic liquid/solid system. The experimental decrease in FFA concentration obtained in the run performed at 85 °C versus the residence time in PBR reactor is reported in Fig. 2, as example. Correctly, only the slope of the first step is highly dependent on the temperature. It is noteworthy to observe that, also working with a quantity of methanol not so high to form a new liquid phase, the reaction conversion is satisfactory, being the final FFA content suitable for the

Table 4 UNIQUAC binary interaction parameters from the AspenPlus^{TM} database

i	FFA	H$_2$O	FFA	FFA	FFA	H$_2$O	H$_2$O	FAME	FAME	OIL
j	FAME	MeOH	H$_2$O	OIL	MeOH	FAME	OIL	OIL	MeOH	MeOH
$b_{i,j}$ (K)	83.44	−254.73	−377.09	80.52	−567.09	−252.11	−245.42	15.43	−579.71	−459.50
$b_{j,i}$ (K)	−106.26	165.26	−232.04	−90.43	112.63	−645.18	−435.31	−18.93	24.04	37.13
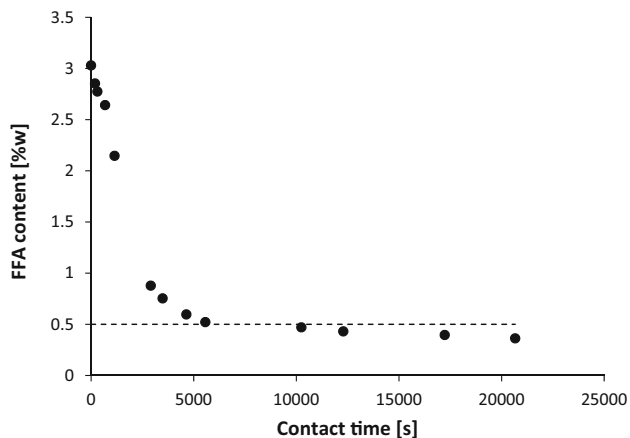
Fig. 2 FFA concentration versus residence time in PBR reactor. T = 85 ° C. The dotted line represents the FFA concentration considered suitable for the base catalyzed transesterification reaction (FFA % < 0.5)

successive transesterification reaction for the BD production. This agrees with the work of Ilgen (2014) in which, studying the deacidification of oleic acid using Amberlyst 46, an according result is reported. Even if in that reference the decrease in FFA conversion using a double phase system is attributed to the reduced concentration of FFA (since it remains constant in the oil-rich phase), it was evidenced that an increase in methanol amount leads to lower deacidification rate at the same reaction temperature.

The trends of the other runs, performed at different temperatures, are reported in Fig. 3, as FFA conversion vs. residence time in the reactor, together with the simulated corresponding curves, discussed in the next paragraph.

Kinetic regression results

On the basis of the experimental results, two different models, pseudo-homogeneous and adsorption-based, were proposed and the corresponding kinetic parameters were regressed. The optimized parameters for both models are reported below in Table 5 with the residual errors (SSE):

It is important to highlight that all the activation energies for the heterogeneously catalyzed reaction calculated in this work are apparent activation energies, not the true values for the chemical reaction. In fact, these energies correspond to the sum of all the micro-steps involved in the heterogeneous catalytic process. For this reason, the

negative value of the activation energies obtained for the inverse reaction should be considered not astonishing.

Even if the pseudo-homogeneous model does not consider the adsorption of both reactants and products, its use permits to better calculate the experimental trends, especially for the runs performed at high temperatures, respect to the more sophisticated adsorption-based model. This is probably due to the not-correct values of the adsorption constants, which were measured for the binary non-reactive mixtures at a fixed temperature (25 °C), far from the experimental operative conditions. Moreover, these numerical values were obtained for a similar, but different, catalyst, i.e., Amberlyst 15.

For these reasons, we performed a regression of the adsorption-based model kinetic parameters together with the binary adsorption constants of water and methanol (assuming valid the constraints of Eq. (6) and $K_{oil} = 0$). The final optimized parameters are reported in Table 6.

By giving the optimizer two more degrees of freedom, the SSE sensibly decreased, showing that a better fit could be obtained using the adsorption-based model. This finding is also reported in the work of Popken et al. (2000), in which a better fit was obtained for the acetic acid esterifi-cation reaction adopting the UNIQUAC model for the ac-tivities calculation and the adsorption-based model here used.

A comparison between some experimental data and the calculated behavior is shown in Fig. 3. From this Figure, it is clear how an adsorption-based model better fits the experimental data reported, that is particularly true near the equilibrium condition. The calculation of the activities considering the UNIQUAC model does not influence the overall SSE probably because the experimental amount of methanol used was chosen in order to have only a monophasic liquid mixture and then corresponding to mixture compositions only lightly non-ideal. Nevertheless, being the system oil/FFA/FAME/methanol/water highly non-ideal for others several compositions, a possible formation of two liquid phases can be calculated only using this more realistic thermodynamic approach, and thus its use is preferable.

The concentration of water produced and methanol consumed from the reaction calculated by the adsorption-based model considering as non-ideal the liquid mixture in function of the residence time inside the reactor are
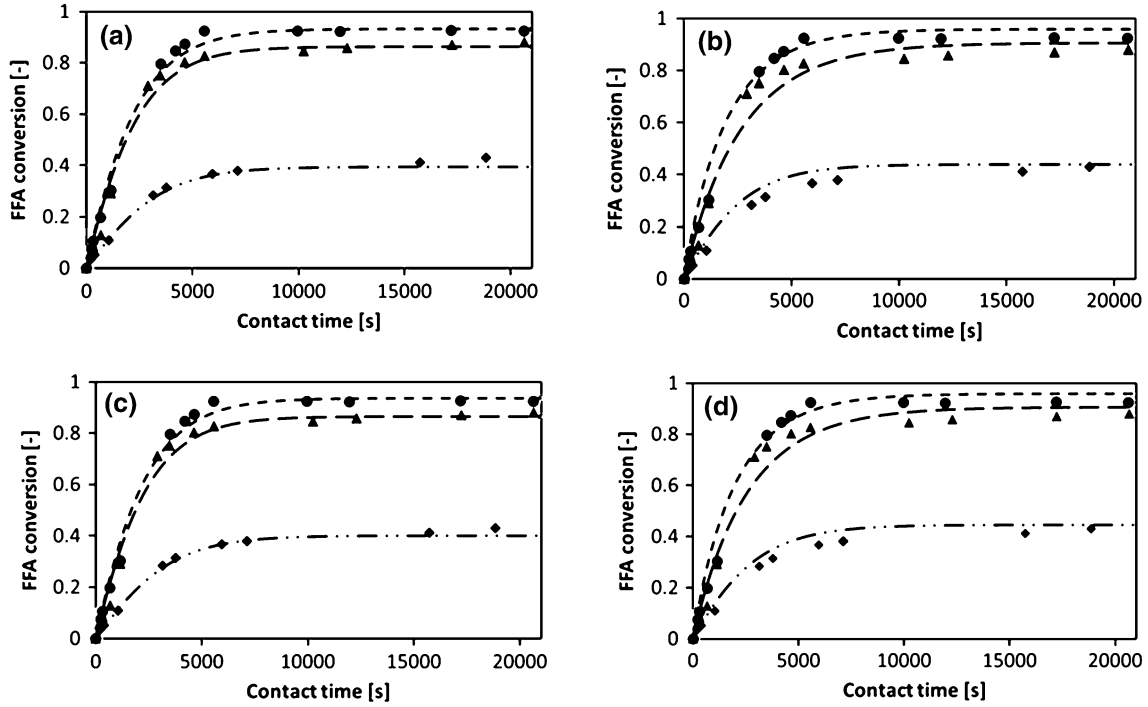
Fig. 3 Experimental FFA esterification, experimental data (*points*) at 95 °C (*circles*), 85 °C (*triangles*), and 54 °C (*diamonds*) and simulated curves using **a** the adsorption-based model with UNIQUAC, **b** the pseudo-homogeneous model with UNIQUAC, **c** the adsorption-based model with IDEAL (activity coefficients = 1), **d** the pseudo-homogeneous model with IDEAL (activity coefficients = 1)

Table 5 Optimized kinetic parameters for the FFA esterification using pseudo-homogeneous and adsorption-based models

Model	SSE	k_1^0 (mol/sm^3)	k_{-1}^0 (mol/sm^3)	E_{a1} (kJ/mol)	E_{a-1} (kJ/mol)
Pseudo-homogeneous (IDEAL)	0.131	9.30×10^7	9.62×10^{-8}	32.268	−67.589
Pseudo-homogeneous (UNIQUAC)	0.137	2.12×10^8	1.13×10^{-7}	33.154	−64.343
Adsorption-based (IDEAL)	0.145	9.67×10^6	8.39×10^{-9}	43.152	−57.229
Adsorption-based (UNIQUAC)	0.291	1.34×10^7	9.09×10^{-10}	43.067	−65.658

Table 6 Adsorption-based model kinetic parameter, regressed together with the water and methanol adsorption equilibrium constants

Adsorption-based model	SSE	k_1^0 (mol/sm^3)	k_{-1}^0 (mol/sm^3)	E_{a1} (kJ/mol)	E_{a-1} (kJ/mol)	K_{H_2O}	K_{MeOH}
IDEAL	0.09	3.22×10^6	6.96×10^{-1}	40.467	−55.796	1.74×10^{-2}	8.04×10^5
UNIQUAC	0.09	5.52×10^5	1.20×10^2	35.398	−58.339	5.16×10^{-7}	4.03×10^5

reported in Fig. 4 for the temperatures $T = 54, 85,$ and 95 °C.

The quantity of water produced allows to maintain the liquid mixture inside the reactor below the solubility limit and for this reason also at the end of the reaction in the reactor, there is only one liquid phase. Obviously, this result is dependent from the initial FFA amount in the vegetable oil because at the same conversion, the water produced by the reaction increases by increasing the starting acidity. The use of UNIQUAC model in order to take into account the non-ideality of the liquid medium is consequently advantageous when using starting vegetable oils characterized by higher FFA content. In this case, with the UNIQUAC adsorption-based model, it is possible to predict the behavior of the system, and it is possible to design a series of PBRs each of which dimensioned in order to avoid the liquid demixing. Proper water separation procedures will be necessary between two consecutive reactors. A detailed optimization of this kind of process will be considered in future works.

Fig. 4 Calculated trends for **a** water produced from the reaction and **b** methanol consumed from the reaction
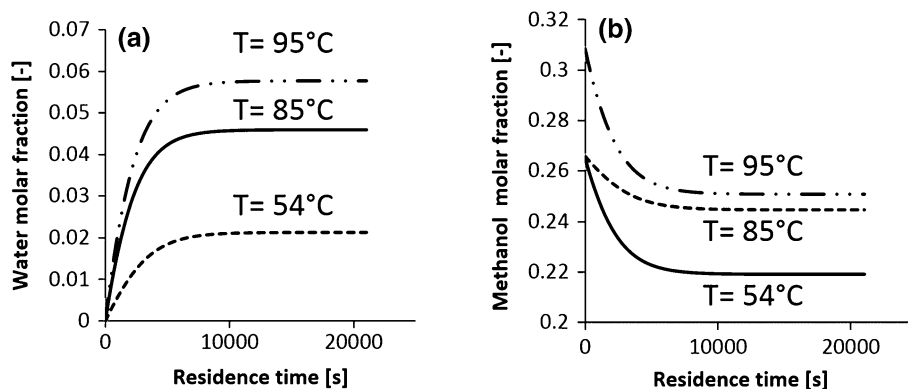
Conclusion

The esterification of FFA in sunflower oil with methanol was studied in a continuous packed bed reactor using an amount of methanol suitable to work in a monophasic liquid/solid system. The FFA conversion increases with temperature and residence time inside the reactor. Using proper residence time (2–4 h), it is possible to reach a conversion of FFA suitable for the successive transesterification reaction step for biodiesel production.

These experimental results allowed to regress the main kinetic parameters using a rigorous optimizer library, considering two different models and either an ideal or a non-ideal liquid phase behavior, using the UNIQUAC model for the calculation of the activity coefficients, that is not commonly found in literature.

From the regression results, it could be concluded that the adsorption-based model is better for fitting the experimental data and that, since the experimental data considered were obtained using a methanol amount such to have a monophasic liquid system, the calculation of the activity coefficient does not give a great advantage in this particular experimental situation. Nevertheless, considering the high non-ideality of the system oil/FFA/FAME/methanol/water, the use of the UNIQUAC model should be considered more convenient.

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