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# Comparison of Different Reactor Configurations for the Reduction of Free Acidity in Raw Materials for Biodiesel Production

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Waste oils used in biodiesel production contain high concentrations of free fatty acids. We studied the esterification of oleic acid, dissolved in soybean oil, with methanol in order to simulate its behavior. We used sulfonic exchange acid resin as the catalyst in two different reactors: a well-stirred slurry reactor (WSSR) and a spray tower loop reactor (STLR) both working at atmospheric pressure. Methanol was fed continuously to both the reactors with very low feed rates in order to minimize the amount of methanol emerging from the reactor outlet. This methanol removed the water produced in the reaction thereby favoring esterification. The WSSR and STLR had very similar performance in that were both better than that of a plug flow reactor (PFR) working in the same conditions of atmospheric pressure and low methanol feed rate. Both the WSSR and STLR showed liquid–solid phase mass transfer limitations. All the kinetic runs have been interpreted with a mathematical model adopting the kinetics previously developed by the authors using a well-stirred batch reactor. For both the reactors, the feasibility of a pseudocontinuous operation has also been successfully tested.

## Introduction

Biodiesel is a fuel made from renewable materials such as vegetable oils or animal fats. It is biodegradable and nontoxic and produces, when burned, significantly fewer emissions than petroleum-based diesel. Biodiesel can be used in current diesel engines and is a possible candidate to partially replace fossil fuels as the world's primary transport energy source. Biodiesel is produced nowadays mainly by the transesterification of vegetable oils in the presence of basic homogeneous catalysts (NaOH, KOH, or related alkoxides). In order to decrease the cost of biodiesel production, it would be preferable to use cheaper raw materials such as waste oils and fats, but in these materials, the contents of free fatty acid (FFA) can be higher than 0.5–1% by weight (bw) which is the limit tolerated when using the above-mentioned basic catalysts. When biodiesel is produced from oils containing high amounts of FFA, pretreatment is necessary to reduce the acidity to below the threshold limit. This is possible by an esterification reaction of FFAs with methanol, catalyzed by acid exchange resins, for example. This can be carried out in a well-stirred batch reactor<sup>1</sup> or in a tubular packed bed reactor<sup>2</sup> both working under pressure. The operation in both cases requires a large amount of methanol, and so, the separation of the unreacted methanol from stripped water becomes onerous. One of the goals of the present work is to investigate the possibility to reduce the amount of methanol used in the process by carrying out the esterification reaction at atmospheric pressure.<sup>3</sup> A set of preliminary experimental runs, done in a plug flow reactor at atmospheric pressure by using a soybean oil/oleic acid mixture, provides low conversions of the oleic acid (about 16%). This value is lower than the one obtained with the experimental runs carried out under pressure, in which the conversion values reached a maximum of about 90%.<sup>2</sup> Even though the operation at atmospheric pressure has the advantage

of stripping water well, the lower amount of methanol dissolved in the oily phase and the possible formation of methanol bubbles, which changes the fluidodynamics of the system, make this kind of configuration less suitable for the esterification unit, since the final acidity is very far from the required specification. For this reason, other reactor configurations have been investigated and this is the main goal of this work. In particular, the reaction has been carried out in a well-stirred slurry reactor (WSSR) and in a spray tower loop reactor (STLR) both working at atmospheric pressure. The STLR configuration has already provided satisfactory results for reactions requiring fast gas–liquid mass transfer rates<sup>4–6</sup> with a gaseous reagent of relatively high solubility.

In both the reactors, the oily phase was precharged into the reactor, while a low flow rate of methanol was fed continuously. Some experimental runs were also carried out in which continuous behavior of the liquid phase was simulated. Initially, a fixed amount of acid oil was treated, and when the value of the acidity reached a prefixed low value, an amount of fresh acid oil was pulsed into the reactor and an equivalent amount of product withdrawn.

All the obtained results were interpreted with a mathematical model considering the effect of both kinetics and mass transfer. The fact that the methanol flow rates adopted were quite low limits the reaction rates in both cases, but we have the advantage of a smaller volume of collected unreacted methanol to be purified from the reaction water.

The two reactors tested showed comparable performances, but the STLR has the advantage of there being no moving parts in the reactor.

## Experimental Section

**Apparatus, Methods, and Reagents.** As mentioned above, two different reactors have been used to study the esterification of oleic acid dissolved in soybean oil catalyzed by a sulfonic acid exchange resin: a well-stirred slurry reactor (WSSR) and a spray tower loop reactor (STLR). The properties of the catalyst

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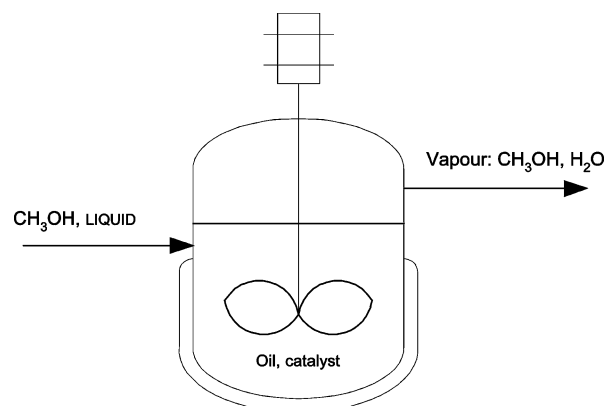
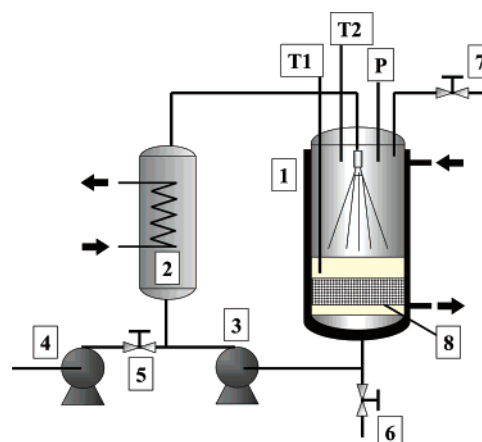
**Table 1. Properties of Catalyst**

commercial name and producer	Relite CFS by Resindion
matrix	porous copolymer styrene–DVB
functional groups	sulfonics
acidity	3.6 mequiv/g
particles mean diameter	0.7 mm
particles size range	0.3–1.18 mm
total exchange capacity	2.0 equiv/L
maximum operating temperature	140 °C
bulk density	0.840 g/cm <sup>3</sup>
pellet porosity	0.4

are summarized in Table 1. Simplified schemes of the tested reactors are respectively reported in Figures 1 and 2. The WSSR is a stainless steel jacketed reactor with a capacity of 900 cm<sup>3</sup>, equipped with a stirrer that is very efficient in recirculating the vapors inside the liquid at 1200–1500 rpm. This stirrer is driven by a high-torque magnetic coupling able to obtain a good mixing also with high viscosity fluids. Both liquid and suspended catalyst are well-stirred in this case. The STLRL has an overall volume of 4000 cm<sup>3</sup> and is equipped with a recirculating pump, normally operating with a liquid flow rate of about 2600 cm<sup>3</sup>/min. Here the catalyst was confined in a stainless steel screen and the reactor operated as a fixed bed. In both cases, the oil containing dissolved oleic acid was loaded into the reactor and heated by using a thermostat bath. When the oil reached the reaction temperature, liquid methanol was fed with a micropump to the reactor. The methanol in contact with the oil flashed promptly. In the case of the STLRL, a mixture of methanol and oil was sprayed into the reactor giving rise to a very fast gas–liquid mass transfer. Liquid drops of oil saturated with methanol fall at the top of a liquid column which contacts the catalytic bed during recirculation.

The amounts of acid oil normally introduced in the WSSR equipment were 200–400 g, while in the STLRL system there were 400–500 g. More details about the runs performed and the adopted operative conditions are reported in Table 2. As can be seen, the methanol flow rates were kept in the 0.5–1 cm<sup>3</sup>/min range, the initial acidities were kept between 29.5 and 50.1% bw, the amounts of catalyst between 5 and 41.1 g, and the temperatures from 100 to 115 °C. It is important to point out that in some STLRL runs some stainless steel springs were mixed with the catalyst to evaluate the effect on performance and also to provide a comparison with a packed bed reactor (PFR).<sup>2</sup> As a matter of fact, in the PFR, this type of catalyst dilution is fundamental to avoid an excessive increase in the pressure drop due to the resin exchange swelling.

Kinetic runs consist in withdrawing small samples of the oil containing FFA, at different reaction times, and measuring the residual acidity by titration.

**Figure 1.** Scheme of the well-stirred slurry reactor (WSSR).**Figure 2.** Scheme of the spray tower loop reactor (STLRL): (1) spray reactor, (2) exchanger, (3–4) pumps, (5–7) valves, (8) catalytic bed, (T1–T2) thermocouples, (P) transducer.

Pseudocontinuous runs were performed on both the WSSR and STLRL with the following procedure: at the end of a normal run such as the WSSR3 and the STLRL1, the acidity was reduced to a very low level of about 1%, then 100 cm<sup>3</sup> of the reaction mixture was discharged from the reactor, and 100 cm<sup>3</sup> of a fresh solution was rapidly added. The acidity obviously increased and then slowly decreased as a consequence of the reaction. When the acidity again reached the prefixed value of about 1%, the procedure was repeated exactly in the same way. The operation was repeated 6–7 times for the runs as can be seen in Table 3.

The refined soybean oil used in the runs was purchased from a local food store, while all the other reagents were furnished by the Aldrich Co at the maximum level of purity available.

**Table 2. Summary of the Experimental Runs Performed with the Laboratory Well-Stirred Slurry Reactor (WSSR) and Laboratory Spray Tower Loop Reactor (STLRL)<sup>a</sup>**

no of run	$Q_{\text{MeOH}}$ (cm <sup>3</sup> /min)	oil initial acidity (% bw)	$W_{\text{oil}}$ (g)	$T$ (°C)	$P$ (bar)	$W_{\text{cat}}$ (g)	$W_{\text{spring}}$ (g)	rpm	$\beta_M$ (1/min)	$k_s$ (cm/min)
WSSR1 <sup>b</sup>	0.5	47.8	200.16	110	1	5.0		400	0.00863	
WSSR1 <sup>c</sup>	0.5	47.8	200.16	110	1	5.0		1200	0.03462	0.0217
WSSR2	0.5	47.8	200.08	110	1	5.0		1200	0.02384	0.0157
WSSR3	1	34.6	400.58	115	1	41.1		1200	0.07557	0.0124
STLRL1	1	50.1	500.00	100	1	30.0				0.001773
STLRL2	1	48.2	500.00	100	1	30.0				0.000586
STLRL3	1	45.4	500.00	110	1	30.0	50			0.001691
STLRL4	1	44.2	500.00	110	1	30.0	150			0.002980
STLRL5	1	29.5	400.58	115	1	41.1				0.001124
PFR1	0.6	48.6	8.6 (cm <sup>3</sup> /min)	100	1	196.0	356		conversion 0.16	

<sup>a</sup> WSSR reactor volume = 900 cm<sup>3</sup>. STLRL reactor volume = 4000 cm<sup>3</sup>. PFR (continuous packed bed reactor) empty reactor volume = 500 cm<sup>3</sup>. <sup>b</sup> First part of the run. <sup>c</sup> Second part of the run.

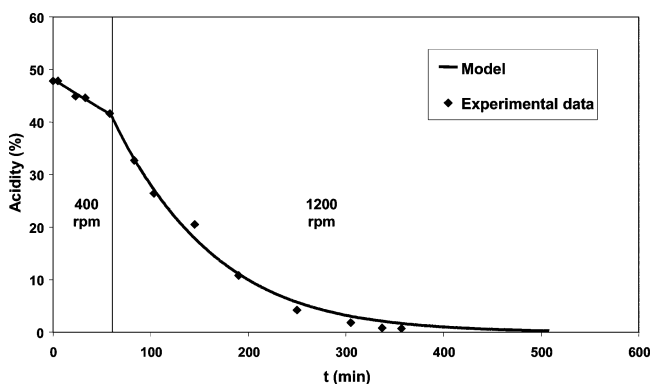
**Table 3.** Experimental Data of Evolution with Time of Oil Acidity for Several Runs

run WSSR1		run WSSR2		run STLR2		run STLR3		run STLR4		run STLR5		run STLR1-PC <sup>a</sup>		run WSSR3-PC <sup>a</sup>	
time (min)	acid (%)	time (min)	acid (%)	time (min)	acid (%)	time (min)	acid (%)	time (min)	acid (%)	time (min)	acid (%)	time (min)	acid (%)	time (min)	acid (%)
0	47.8	0	47.8	0	48.2	0	45.4	0	44.2	0	29.5	0	50.1	0	34.6
5	47.8	15	38.5	17	39.8	15	41.6	15	42.7	37	19.1	10	42.7	10	28.8
23	44.9	42	38.3	51	33.9	30	37.2	30	40.9	70	10.7	22	40.7	20	23.9
33	44.6	72	31.3	99	20.3	50	29.7	45	31.2	103	5.6	35	41.6	40	16.9
58	41.6	102	23.4	125	13.1	70	23.4	75	24.4	126	3.1	50	39.2	60	10.1
83	32.7	145	16.7	194	5.9	100	18.8	110	15.8	180	1.05	90	22.7	80	7.2
103	26.4	190	10.5	260	3.7	135	11.7	150	10.2	226	0.7	120	14.3	110	4.1
145	20.5	250	4.4	329	3.7	175	5.8	180	6.3			150	8.5	140	2.5
190	10.8	305	2.1			220	2.8	245	2.3			185	4.9	205	1.7
250	4.2	337	1.2			237	1.1	305	0.8			215	2.7	235	1.2
305	1.8	366	0.8			265	0.6					245	1.5	250	4.7
337	0.8	400	0.8									290	0.9	270	3.4
												290	4.2	300	1.9
												338	2.4	330	1.4
												375	1.4	350	1.3
												387	10.8	365	1
												470	3.1	375	5.3
												495	1.8	395	2.8
												525	1	415	1.5
												525	8.9	435	1
												558	6.3	445	4.3
												588	4.3	460	3.6
												625	2.5	475	2
												625	9	490	1.4
												675	6.3	500	1.2
												715	4.3	510	4.5
												783	1.9	540	2.2
												795	11.2	550	1.5
												855	5.6	560	4.5
												915	2.6	590	2.3
												975	1.4	620	1
														636	4.4
														651	3.3
														671	1.5
														686	0.9

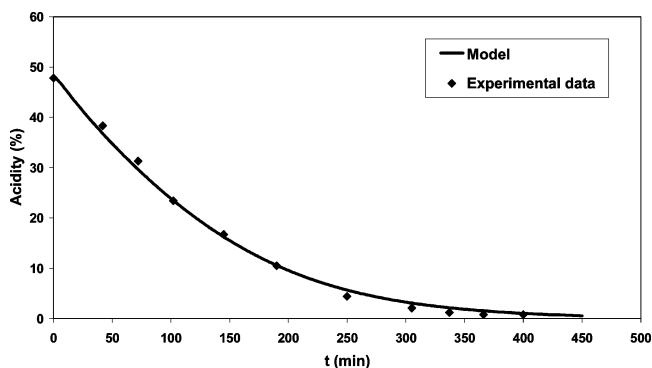
<sup>a</sup> PC: pseudocontinuous conditions.

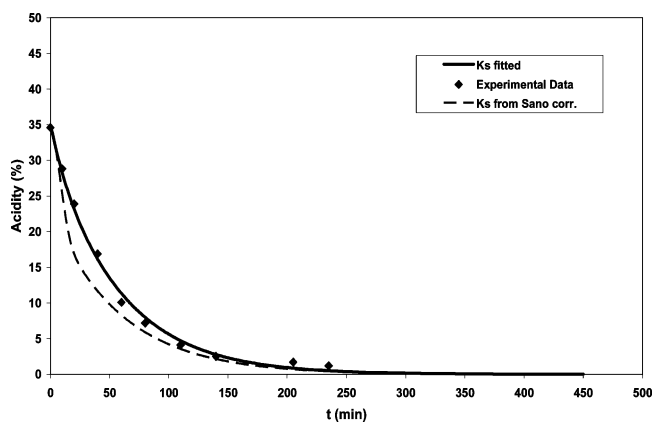
## Results and Discussion

As previously mentioned, kinetic runs were performed in the conditions reported in Table 2 by using the two reactors described. The same table contains the performance of a packed bed reactor for comparison. The changes of acidity for selected runs over time are included in Table 3 and plotted, as experimental points, in Figures 3–8. It is interesting to observe that the two reactors display a quite similar kinetic behavior despite the different devices used. As further confirmation, an experimental run was carried out in similar operative conditions for both reactors. Both reactors were charged with 41.1 g of catalyst and 400 g of acid oil (acidity about 30%). The methanol feed rate was 1 cm<sup>3</sup>/min, and the temperature was 115 °C in

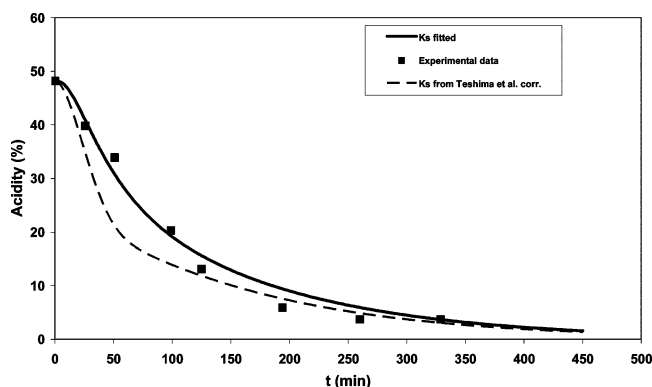
**Figure 3.** Comparison between the experimental data and model simulation for the run WSSR1.

both cases. After a reaction time of about 4 h, a final acidity value of about 1% bw was reached for both the reactors, corresponding to a conversion of about 98%. This similarity in behavior can easily be explained by considering the high recirculation rate of the liquid phase in the STLR which therefore can be considered like a well-stirred reactor. However, in both cases, the results are significantly improved compared with plug flow reactors working at low methanol pressure (see Table 2). However, both reactors are rate limited as a consequence of the low methanol flow rate. A compromise was reached between the advantage of working at high reaction rates (high-pressure operation) and that of minimizing the volume of the unreacted methanol containing water produced by the reaction (low-pressure operation). In Figure 9 (curve 2), it is

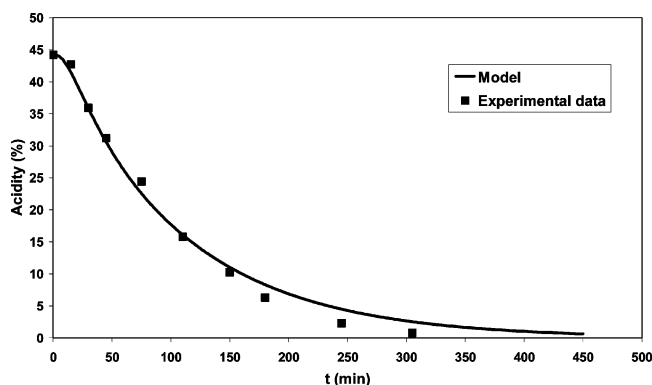
**Figure 4.** Comparison between the experimental data and model simulation for the run WSSR2.



**Figure 5.** Comparison between the experimental data and model simulation for the run WSSR3.



**Figure 6.** Comparison between the experimental data and model simulation for the run STLR2.



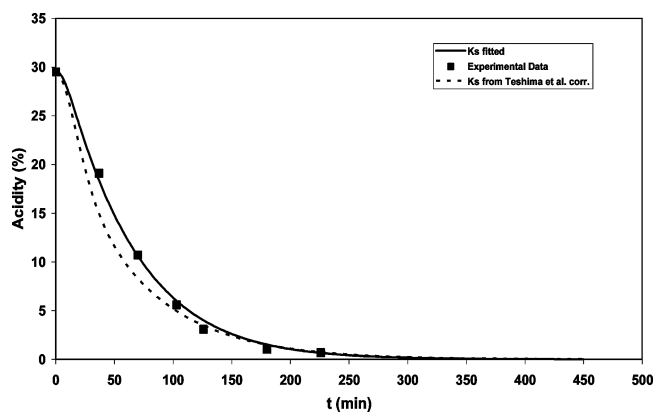
**Figure 7.** Comparison between the experimental data and model simulation for the STLR4.

possible to see the calculated kinetic behavior in the absence of any type of mass transfer limitation.

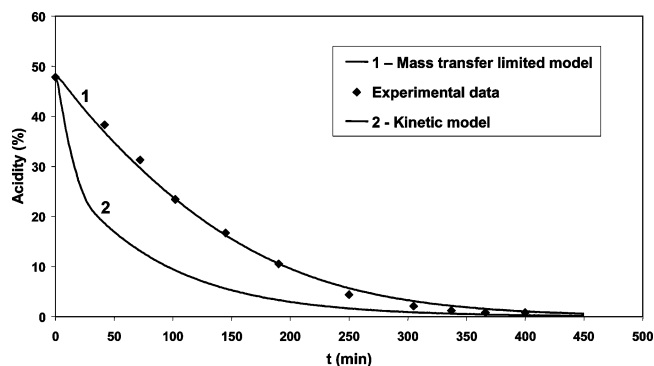
Simulations of all the kinetic runs performed in the WSSR were performed by solving the following system of ordinary differential equations related to the mass balance in the liquid phase:

$$\frac{dn_{A,l}}{dt} = -rW_{cat} \quad (1)$$

$$\frac{dn_{M,l}}{dt} = -rW_{cat} + \beta_M(x_M^* - x_M)n_{TOT,l} \quad (2)$$



**Figure 8.** Comparison between the experimental data and model simulation for the run STLR5.



**Figure 9.** Comparison between kinetic behavior without mass-transfer limitation and the experimental run WSSR2.

$$\frac{dn_{E,l}}{dt} = rW_{cat} \quad (3)$$

$$\frac{dn_{W,l}}{dt} = rW_{cat} - \beta_W(x_W - x_W^*)n_{TOT,l} \quad (4)$$

These equations have been integrated together with the ones related to mass balance in the gas phase:

$$\frac{dy_{N_2}}{dt} = -F_v(1 - y_w - y_M)\frac{1}{n_{TOT,v}} \quad (5)$$

$$\frac{dy_M}{dt} = (F_l - F_v y_M - \beta_M(x_M^* - x_M)n_{TOT,l})\frac{1}{n_{TOT,v}} \quad (6)$$

$$\frac{dy_W}{dt} = (-F_v y_W + \beta_W(x_W - x_W^*)n_{TOT,l})\frac{1}{n_{TOT,v}} \quad (7)$$

The set of equations related to the gas phase also takes into account for the transient effects due to the presence of nitrogen in the empty part of the reactor. Nitrogen is gradually removed by the unreacted methanol and water produced as a consequence of the reaction. We have then to solve many other algebraic equations after each integration step. In particular, we can write an overall mass balance for the reactor:

$$F_v = F_l - J_M + J_W \quad (8)$$

where

$$J_M = \beta_M(x_M^* - x_M)n_{TOT,l} \quad (9)$$

$$J_W = \beta_W(x_W - x_W^*)n_{TOT,I} \quad (10)$$

$$r = k_1 x_A x_M \left( 1 - \frac{1}{K_{eq}} \frac{x_E x_W}{x_A x_M} \right) c_{cat} \quad (11)$$

$$x_i = \frac{n_{i,l}}{n_{TOT,I}} \quad \text{where } i = M, A, E, W, T \quad (12)$$

$$n_{TOT,I} = n_{A,I} + n_{M,I} + n_{W,I} + n_{E,I} + n_{T,I} \quad (13)$$

$$V_l = \sum_i \frac{n_{i,l} PM_i}{\rho_i} \quad (14)$$

$$n_{TOT,v} = \frac{P}{RT} (V_R - V_l) \quad (15)$$

$$x_W^* = \frac{y_W P}{P_W^0 \gamma_W} \quad (16)$$

$$x_M^* = \frac{y_M P}{P_M^0 \gamma_M} \quad (17)$$

The oleic acid conversion has been calculated as

$$X = \frac{n_{A,I}^0 - n_{A,I}}{n_{A,I}^0} \quad (18)$$

while acidities expressed in percent bw of oleic acid have been calculated as follows:

$$A_c = \frac{n_{A,I} PM_A}{n_{A,I} PM_A + n_{E,I} PM_E + n_{T,I} PM_T} \times 100 \quad (19)$$

As a first approximation we have assumed ideal solutions in all cases, i.e.,  $\gamma_M = \gamma_W = 1$ .

The mathematical model for simulating the runs performed in the STLR is quite similar to the one described for the WSSR. In both cases, the possible effects of gas–liquid and liquid–solid mass transfer were considered.

As a matter of fact, in the case of the STLR, gas–liquid mass transfer is very fast (as already observed in a previous work related to another reaction performed in the same device<sup>4</sup>), while the liquid–solid mass transfer rate slows down due to the low linear velocity of the fluid (as occurs in PFR reactors<sup>2</sup>). Therefore, we have to modify the reaction rate (11) expressed as follows:

$$r = k_1 x_A x_{M,s} \left( 1 - \frac{1}{K_{eq}} \frac{x_E x_{W,s}}{x_A x_{M,s}} \right) c_{cat} \quad (20)$$

In order to evaluate surface concentrations of both methanol and water, we need to introduce the two steady-state assumptions:

$$rW_{cat} = k_S a_S (x_M - x_{M,s}) c_{TOT,I} V_l \quad (21)$$

$$rW_{cat} = k_S a_S (x_{W,s} - x_W) c_{TOT,I} V_l \quad (22)$$

Another modification regards eq 9. In this case, the gas–liquid mass transfer coefficient is assumed to be very high, while the value of  $x_M^*$  has been multiplied by a factor  $\alpha$  (varying from 0 to 1) corresponding to the spray nozzle device efficiency in

**Table 4. Kinetic Parameters Used in the Model<sup>a</sup>**

Kinetic Equation			
reaction: oleic acid + methanol $\leftrightarrow$ methyl oleate + water			
$r = k_1 x_A x_M \left( 1 - \frac{1}{K_{eq}} \frac{x_E x_W}{x_A x_M} \right) c_{cat}$			
parameters	pre-exp factor ( $k_0$ )	activ energy ( $E_a$ ) (kcal/mol)	heat of rctn ( $\Delta H_r$ ) (kcal/mol)
$k_1$ (mol·cm <sup>3</sup> /g·cat <sup>2</sup> ·min)	12.93 ± 2.87	14.00 ± 0.99	
$k_{eq}$	4.17 ± 0.04		2.68 ± 0.05

<sup>a</sup> Subscripts: A = oleic acid; M = methanol; E = methyl oleate; W = water.

saturating the reacting oil with methanol. The resulting equation is as follows:

$$J_M = \beta_M (\alpha x_M^* - x_M) n_{TOT,I} \quad (23)$$

This factor was submitted to mathematical regression analysis giving a value very close to 1 for all the examined runs, showing that, as expected, the droplets emerging from the spray nozzle were always completely saturated.

In the case of the WSSR runs, both the mass transfer resistances, that is, gas–liquid and liquid–solid resistances, were initially considered. For this purpose, in Figure 3, it is possible to observe the effect of the gas–liquid mass transfer limitation in the initial part of the run, when a low stirring rate was adopted (400 rpm). In the second part of the run, performed at 1200 rpm of the stirrer, a more active mass transfer is operative, but it is still limiting as can be deduced by the kinetic behavior reported in Figure 9 (curve 2). It is not clear, just by observing the kinetic runs, what is the limiting effect. For this reason, we have simulated the WSSR runs by assuming alternatively the gas–liquid or liquid–solid mass transfer limitation. The parameters obtained by regression analysis were, then, compared with the ones estimated by the literature correlations in order to discriminate between the two mentioned alternatives.

The system of ordinary differential equations coupled with the algebraic equations was solved by using the Berkeley Madonna software.<sup>7</sup> The method used for solving the ordinary differential equations was the fourth order Runge Kutta method. The mathematical regression analysis was made by adopting the simplex method.

The kinetic parameters used in the model are the same as those determined in a previous work.<sup>1</sup> These parameters were obtained by interpreting several kinetic runs performed under pressure in a batch reactor<sup>1</sup> and are reported in Table 4 together with their confidence limits at 95% of probability. The internal diffusion resistance was excluded on the basis of two runs reported in ref 1, where the behavior of 1 mm catalytic particles was compared with that of powdered catalysts. Being that the two runs were quite similar, the intervention of the internal diffusion limitation can be neglected. The adjustable parameters introduced in the present model that could be significant in fitting the experimental results are the gas–liquid mass transfer parameter  $\beta_M$  or the liquid–solid mass transfer coefficient  $k_S$  for the WSSR runs and only the liquid–solid mass transfer coefficient  $k_S$  for the STLR ones. As mentioned before, for the WSSR reactor, it was not possible to identify exactly the type of resistance, gas–liquid or liquid–solid, so both the types of model fitting were performed. On the contrary the STLR runs



were limited only by liquid–solid resistance and, consequently, only  $k_S$  values were calculated by fitting.

Both the values of mass transfer parameters  $\beta_M$  and  $k_S$ , obtained by fitting the WSSR runs, were compared with those obtained from suitable literature correlations. If we assume for these runs the gas–liquid limitation, it is possible to evaluate from the literature<sup>8</sup> values of  $\beta_M$  in the range 3–18 min<sup>-1</sup> that are much higher than those reported in Table 2, obtained by fitting. On the contrary, by adopting the control of liquid–solid mass transfer resistance, the widely used correlation suggested by Sano et al.<sup>9</sup> for agitated vessels gives a value of  $k_S = 0.039$  cm/min that is in satisfactory agreement with the values obtained by fitting. Therefore, we can conclude that WSSR and STLR runs are both dominated by the liquid–solid mass transfer limitation, and in Table 2, the values of  $k_S$  obtained by mathematical regression on the experimental data of each run are reported.

In Figures 3–8 are shown examples of the obtained fittings by using the  $k_S$  values reported in Table 2. In Figure 5 is also reported, for a useful comparison, a simulation in which the value of  $k_S = 0.039$  cm/min derived from the Sano et al. correlation has been used. The obtained agreement is quite satisfactory, by considering the high uncertainty usually associated with this kind of correlation, with the physicochemical parameters used in the calculations changing with the extent of the reaction.

It is known, for example, that the viscosity consistently changes during the reaction, and this has an effect on the mass transfer coefficient.

The liquid–solid mass transfer coefficients  $k_S$  for each STLR run are also reported in Table 2. As can be seen, the effect of the springs as a catalyst diluent seems to be positive in increasing the mass transfer performance probably because the springs have the effect of locally increasing the flow turbulence. With the aim to compare the fitted  $k_S$  values with values estimated from literature correlations, the Coeuret correlation<sup>10</sup> was initially used to estimate the liquid–solid mass transfer coefficient. This correlation, developed for a laminar flow regime with very low Reynolds numbers, appears as follows:

$$Sh_{\text{part}} = 5.4 Re_{\text{part}}^{1/3} Sc^{1/4} \quad (24)$$

In this relation, an effective diffusivity<sup>2</sup> has been introduced for the calculation of  $Sh_{\text{part}}$ , defined by the following equation:

$$D_{\text{eff}} = D \frac{\epsilon_B \sigma}{\tau} \quad \text{with } \epsilon_B = 0.4, \sigma = 0.8, \text{ and } \tau = 3 \quad (25)$$

In relation 25, some parameters introduced were taken from the literature<sup>11</sup> as approximated values. A value of  $k_S = 0.0956$  cm/min has been obtained from relation 24, that is much higher than the fitted values. Also, other literature correlations for packed beds have been considered, but still, the values obtained for  $k_S$  were too high (0.0563 cm/min for the correlation of Wakao and Funazkri<sup>12</sup> and 0.0570 cm/min for the Sherwood correlation<sup>13</sup>). Finally, the correlation of Teshima and Ohashi,<sup>8</sup> developed for catalyst enclosed in rotating baskets, was tested, and the resulting  $k_S$  value was 0.0231 cm/min. The use of a correlation developed for a rotating basket, instead that for a packed bed, can be justified by considering that the catalyst, inside the chamber of the STLR, is enclosed in a basket with low packing density. This configuration seems to be better approximated than a packed bed as the basket rotation is simulated by the flowing fluid. The  $k_S$  value obtained by the Teshima and Ohashi<sup>8</sup> correlation had been used for simulating

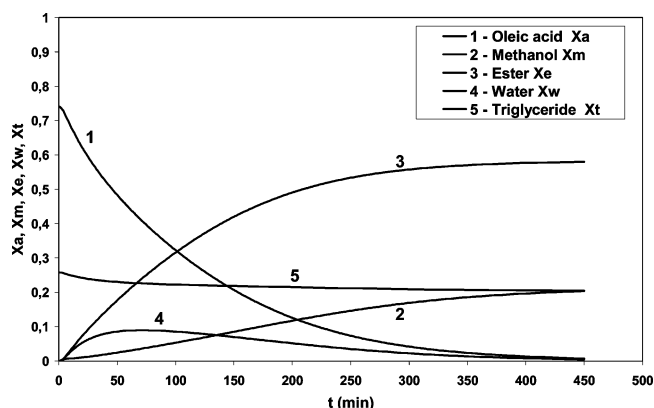


Figure 10. Evolution with time of liquid molar fractions (run WSSR2).

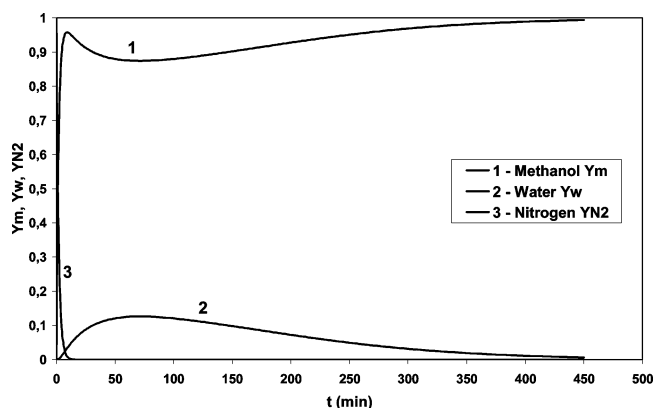


Figure 11. Evolution with time of molar fractions in the vapor phase (run WSSR2).

all the experimental runs, and in Figures 6 and 8, examples of the model behavior are reported and compared with the fitted experimental runs. As can be appreciated, although the  $k_S$  values obtained from the Teshima and Ohashi correlation are somewhat higher than the ones estimated by fitting, they can be considered comparable.

The difference of an order of magnitude in the  $k_S$  values respectively determined for the WSSR and STLR is due to the assumption of different values of catalyst concentration  $c_{\text{cat}}$  and external catalyst specific surface  $a_s$ . In the case of the WSSR, these values are referred to the liquid volume that is present in the reactor, while, for the STLR, they are referred to the basket volume where the reaction takes place.

The mathematical model developed gives not only the amount of reacted oleic acid, as a function of time, but also the evolution with time of the liquid and vapor phase composition and the amount of both methanol and water collected at the reactor outlet at any instant of the reaction. This is shown in Figures 10 and 11 that are both related to the WSSR2 run in which the evolution with time of respectively the composition of both the liquid and vapor phase are reported.

Finally, Figure 12 reports the pseudocontinuous behavior observed in the WSSR3 run. This behavior was simulated by using the same mathematical model for the first three steps of the pseudocontinuous operation. The progressive loss in fitting agreement is due to the different times adopted for withdrawing the reacted solution and adding the fresh one, respectively. A very similar behavior was also obtained for the STLR1 run in the spray reactor. In conclusion, with this run, we have demonstrated the feasibility of the continuous operation also for the oily liquid phase in both reactors.

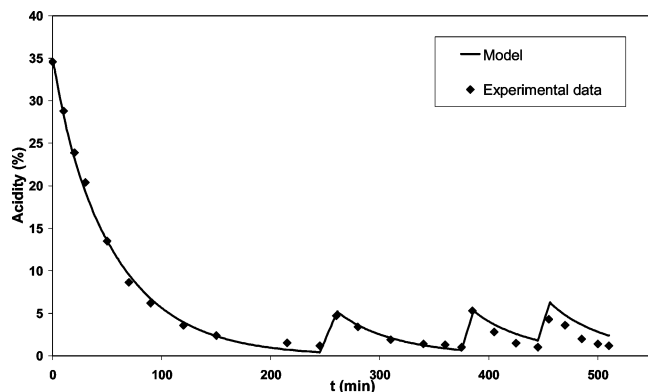


Figure 12. Simulated pseudocontinuous behavior starting at about 250 min of the WSSR2 run.

## Conclusions

Two different reactors, operating at atmospheric pressure, were used to explore the possibility of reducing free fatty acids in waste oils, by esterification with methanol, in biodiesel production. Oleic acid was used as a model molecule for studying the reaction, catalyzed by acid exchange resins, and very low methanol flow rates were adopted to reduce the amount of methanol to a quantity slightly higher than the stoichiometric. This would allow reduction of the cost of methanol separation from the water formed during the reaction.

The two reactors, the well-stirred slurry reactor and spray tower loop reactor, have shown similar behavior with performances that are better than those obtainable in a PFR working at atmospheric pressure for similar methanol flow rates. The improved performances are due to the efficiency in stripping water shifting the equilibrium of the reaction to the right. These reactors are, therefore, more suitable for the reduction of free fatty acids in biodiesel production. Moreover, the STLRL has the advantage of no moving parts inside the reactor and, therefore, avoids catalyst crushing by mechanical attrition.

All the runs performed were interpreted by using a mathematical model containing a kinetic expression, derived from a previous work performed in a batch reactor,<sup>1</sup> with related parameters. The internal particle mass transfer limitation was excluded in both cases on the basis of a previous evaluation on powdered catalyst. As a consequence of the low amount of methanol feed, mass transfer limitations occur in both the reactors and the limitation occurred in both cases at the liquid–solid interphase. Moreover, the liquid–solid mass transfer coefficients, determined by regression on the experimental data, have been compared with the values obtained by appropriate correlations reported by the literature confirming their suitability. Finally, the feasibility of a completely continuous operation for methanol and oil in both types of reactors was demonstrated.

## List of Symbols

$A_c$  = acidity of the oily phase in percent bw of oleic acid  
 $a_s$  = solid particle external surface ( $\text{cm}^2/\text{cm}^3$ )  
 $c_{\text{cat}}$  = catalyst concentration in the reactor ( $\text{g}/\text{cm}^3$ )  
 $E_a$  = activation energy ( $\text{kcal}/\text{mol}$ )  
 $F_l$  = liquid feed flow rate of methanol ( $\text{mol}/\text{min}$ )  
 $F_v$  = overall vapor flow rate ( $\text{mol}/\text{min}$ )  
 $J_M, J_W$  = methanol and water gas–liquid mass transfer fluxes ( $\text{mol}/\text{min}$ )

$k_1, k_{\text{eq}}$  = kinetic and equilibrium parameters ( $k_1 = \text{mol}\cdot\text{cm}^3/\text{g}^2\cdot\text{min}$ )  
 $k_s$  = liquid–solid mass transfer parameter ( $\text{cm}/\text{min}$ )  
 $k_0$  = pre-exponential factor ( $\text{mol}\cdot\text{cm}^3/\text{g}^2\cdot\text{min}$ )  
 $n_{i,l}$  = mols of the  $i$  components in the liquid phase (with M = methanol, W = water, A = oleic acid, E = ester, T = triglyceride)  
 $n_{\text{TOT},l}, n_{\text{TOT},v}$  = total mols respectively in liquid and vapor phase  
 $P_M^0, P_W^0$  = vapor pressure of methanol and water (atm)  
 $PM_i$  = molecular weight of  $i$ th component ( $\text{g}/\text{mol}$ )  
 $P$  = pressure (atm)  
 $R$  = gas constant ( $\text{cm}^3\cdot\text{atm}/\text{mol}\cdot\text{K}$ )  
 $r$  = reaction rate ( $\text{mol}/\text{min}\cdot\text{g}_{\text{cat}}$ )  
 $t$  = time (min)  
 $T$  = temperature (K)  
 $V_l$  = liquid phase volume ( $\text{cm}^3$ )  
 $V_R$  = overall reactor volume ( $\text{cm}^3$ )  
 $W_{\text{cat}}$  = catalyst weight (g)  
 $X$  = oleic acid conversion  
 $x_i$  = liquid phase molar fractions for M = methanol, W = water, A = oleic acid, E = ester, T = triglyceride  
 $x_M^*, x_{W,l}^*$  = interphase molar fractions of methanol and water, respectively  
 $x_{M,s}, x_{W,s}$  = surface molar fractions of methanol and water, respectively  
 $y_M, y_W, y_{N_2}$  = vapor phase molar fractions of methanol, water and nitrogen  
 $\beta_M, \beta_W$  = gas–liquid mass transfer coefficients ( $\text{mol}/\text{min}$ )  
 $\Delta H_r$  = reaction enthalpy ( $\text{kcal}/\text{mol}$ )  
 $\gamma_M, \gamma_W$  = activities coefficients parameters  
 $\rho_i$  = density of the  $i$ th component ( $\text{g}/\text{cm}^3$ )  
 $\alpha$  = saturation efficiency of spray nozzle  
 $\epsilon_B$  = bed porosity  
 $\sigma$  = bed constriction factor  
 $\tau$  = bed tortuosity

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**Note Added after ASAP Publication.** This article was released ASAP on March 24, 2007, with incorrect units for  $k_1$  in Table 4, along with a minor text addition to the Runge Kutta method. The correct version was posted on June 4, 2007.

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