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Biodiesel process intensification: the role of the liquid-liquid interface area in the achievement of a complete conversion in few seconds

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Abstract

Transesterification of vegetable oil with methanol, promoted by alkaline catalysts has been tested in many different reactors and surprisingly the reaction time, in some of these reactors, resulted very short, in the range of few seconds. In particular, by using static mixers, micro-reactors, oscillatory flow reactors, cavitational reactors, microwave reactors or centrifugal contactors, it is possible to obtain high biodiesel yields in a much shorter time than in stirred tank reactors. As the reaction occurs between two immiscible phases, a general conclusion could be that the higher the interface area the shorter the reaction time. In this paper, we will confirm this assumption because, by using a very efficient micro-mixer, followed by a void tube, very high conversions have been obtained in a few seconds of residence time. Another important observation is that passing from 1% to 2% b.w. of KOH catalyst concentration, a very high increase in the conversion is obtained. This means that the final conversion is not due to the chemical equilibrium but to the catalyst deactivation. For describing all the observed phenomena a new biphasic kinetic model based on a reliable mechanism has recently been developed and used here for quantitatively describing the performed runs.

Keywords: biodiesel; kinetics; micro-mixer; process intensification; transesterification.

1. Introduction

Biodiesel is produced in industry by reacting vegetable oils with methanol in the presence of a homogeneous catalyst such as NaOH, KOH or related alkoxides, at 60°C and atmospheric pressure. The reagents are immiscible liquids and recently we have shown that the interface surface area plays a fundamental role in promoting the transesterification reaction [1]. In another recently published paper and patent [2, 3], we have shown that a high activity can be obtained by performing the reaction in a continuous corrugated plates heat exchanger reactor. The high performances obtained in this case were due to a very active local micro-mixing operating in that type of reactor. It has been possible to conclude that all the reactors that increase the liquid-liquid interfacial area can give high performances in the transesterification reaction. This observation is confirmed by many results reported in the literature in which this reaction is performed in novel reactors [4] such as: reactors containing a static mixer, oscillatory flow reactors, microwave irradiated reactors, ultrasonic irradiated reactors, centrifugal contactors, rotating packed bed reactors and jet flow stirred reactors. In some of the used devices complete conversion has been obtained in 10–20 s of residence time [5]. It is also possible to increase the liquid-liquid interface area by using micro-reactors [6–8] as a consequence, again, of the high interfacial area developed by these systems. In other recently published papers [9, 10], we proposed the use of three different tubular reactors, respectively containing spheres of uniform size (2.5 mm of diameter) having micro-channels of approximately 1000 μm, spheres of two different sizes of 2.5 and 1 mm, respectively, of diameters having micro-channels of approximately 500 μm and two different sizes of 2.5 and 0.39 mm, respectively, of diameters having micro-channels of approximately 300 μm, for studying the methanol-soybean oil transesterification reaction. By using the unique or dual size distribution packing as static mixer elements we obtained very high transesterification conversions for residence times between 10 and 60 s. The same behavior has also been observed by using different static mixer elements such as: stainless steel ribbon wool and stainless steel threaded rods [10]. All these experimental observations confirm that the reaction rate is tremendously affected by the interfacial area. To quantitatively explain this behavior we have developed a liquid-liquid biphasic model based on a reliable reaction mechanism [10]. For this purpose, it is known that the most commonly used catalyst KOH reacts in methanol yielding to $KOCH_3$ according to the reaction:

$$K^+OH^- + CH_3OH \rightleftharpoons K^+OCH_3^- + H_2O \qquad (1)$$

Then, CH_3O^- reacts, at the liquid-liquid interface, with a molecule of triglyceride thus transferring the anion charge from the polar to the apolar phase in the form of di-acylglycerolate [11]. This justifies the experimental observation of a very fast reaction, in reactors developing very high interfacial area. The higher the initial interface area, the faster the CH_3O^- disappearance will be and the formation *in situ* of the true catalyst, that is, a mixture of di- and mono-acylglycerolate

[11]. Successively, the reaction rate rapidly declines because the ultimate formation of glycerolate anion that migrates in the polar phase, being insoluble in the apolar one thus subtracting catalyst to the reaction. The performances obtained in the already mentioned reactors, characterized by high interfacial area, were so high that none of the pseudo-homogeneous kinetic models proposed in the literature, derived from runs performed in batch conditions, was suitable to describe the observed kinetic behavior. Another aspect that the monophasic kinetic models were not able to describe the different plateau obtained by using different catalyst concentrations [10]. This difference has been observed in both batch and continuous runs, but in the last case the difference is dramatic and only a biphasic model can describe the observed behavior. By considering the suggested catalytic mechanism, it is clear that an intense local micro-mixing is very useful mainly in the initial phase of the reaction. For demonstrating this assumption, in this paper, we have made the reaction by using a very efficient commercial micro-mixer put before a void tube (MM+TR or MM+STTR). The micro-mixer gives place to an emulsion in which the reaction occurred completely in a few seconds. The biphasic kinetic model, developed in a previous work [10], has been applied to describe the obtained results. The kinetic parameters of the model are the same determined by mathematical regression analysis made on kinetic runs, taken from the literature [12, 13], related to batch runs, and the only adjustable parameters are the interface area and the mass transfer coefficient that are obviously different for the micro-mixer+empty tube reactor (MM+TR) with regard to a stirred batch reactor.

2. Experimental section

2.1. Reagents

Soybean oil used in the runs was purchased in a local food-store (Naples, Italy) (the fatty acid composition of the used soybean oil, determined by gas chromatographic analysis, was: (%, w/w): palmitic=11, stearic=4, oleic=23, linoleic=56, linolenic=5, others=1). All other employed reagents (when not specified) were supplied by Aldrich (St. Louis, MO, USA) at the highest level of purity available and were used as received without further purification.

2.2. Analytical method

The FAME (fatty acid methyl esters) yields, were determined by using ^{1}H NMR technique (GEMINI 200 Mz), measuring the area of the ^{1}H NMR signal related to methoxylic (A1, single signal at δ=3.7 ppm) and methylenic groups (A2, triplet signal δ=2.3 ppm), respectively. The FAME yields can be calculated by using the following equation:

$$yield_{FAME}=\left(\frac{2\times A1}{3\times A2}\right)\times 100 \tag{2}$$

The ^{1}H NMR spectra were obtained with GEMINI 200 equipment in deuterated chloroform [14].

In all cases, the conversion values were confirmed by gas chromatographic analysis (UNI 10946:2001), using a gas chromatograph (Perkin-Elmer model Clarus 500), equipped with a flame ionization detector (FID), an on-column injector, and employing a FS-HP5 column (10 m×0.32 mm, ID 0.1 μm film). Before analysis, the samples were derivatized by BSTFA [N,O-bis (trimethylsilyl) trifluoroacetamide with trimethylchlorosilane]. As internal standards, methyl-heptadecanoate was used for methyl ester and 1,2,4-butantriol was used for glycerol. The fluid dynamic tests were performed analyzing the samples by UV-visible measurements.

2.3. Description of the used reactor and related kinetic runs

A micro-mixer coupled with a void tubular reactor (MM+TR) was used to perform the kinetic runs. The void tubular reactor was a cylinder with internal diameter of 1 cm and length of 20 cm for a set of seven runs, whereas, in another set of eight runs a tube of the same diameter with a length of 10 cm was used. One run was performed at very low residence time by putting a Teflon tube with external diameter of 0.159 cm and 10 cm length (MM+STTR) after the micro-mixer. The micro-mixer was a Slit Interdigital Micro Mixer (SIMM-V2) of standard type with a 45 μm height of slit [15], kindly furnished by IMM (Institut fur Mikrotechnik Mainz GmbH). A picture of the Micro Mixer is shown in Figure 1 together with a scheme of the laboratory plant. Kinetics runs were made by feeding two different liquid flows to the reactors, one of methanol containing the dissolved catalyst (KOH, normally 1 or 2 wt% with regard to the oil) and another of refined soybean oil. The oil was preheated at the reaction temperature, whereas methanol was fed at room temperature. Two HPLC pumps were used for feeding the reagents. The typical experimental conditions of the performed runs were: molar ratio methanol/soybean oil=6:1, considering for soybean oil an average molecular weight of 885, a KOH catalyst concentration of 1 or 2% b.w. referred to the oil and a temperature of 60°C. All the kinetic runs performed and related operative conditions are reported in Table 1.

3. Mechanism and kinetic model

The biphasic kinetic model we proposed in a previous paper [10] began considering that methoxide anions formed with reaction (1) react, at the liquid-liquid interface, with triglycerides transferring the charge from the polar phase to the apolar phase as follows:

$$CH_3O^- + T \rightarrow D^- + E \qquad r_1=k_1\times a\times[CH_3O^-]_p\times[T]_a \tag{3}$$

(where D^- is di-acylglycerolate anion and a is the liquid-liquid interface area). The rate of this reaction was assumed proportional to the interface area, the catalyst concentration and the concentration of T at the interface (the last is assumed proportional to the bulk concentration). The effect of reaction (3) is that of transferring the catalyst from the polar to the apolar phase where the transesterification reaction occurs. As the rate

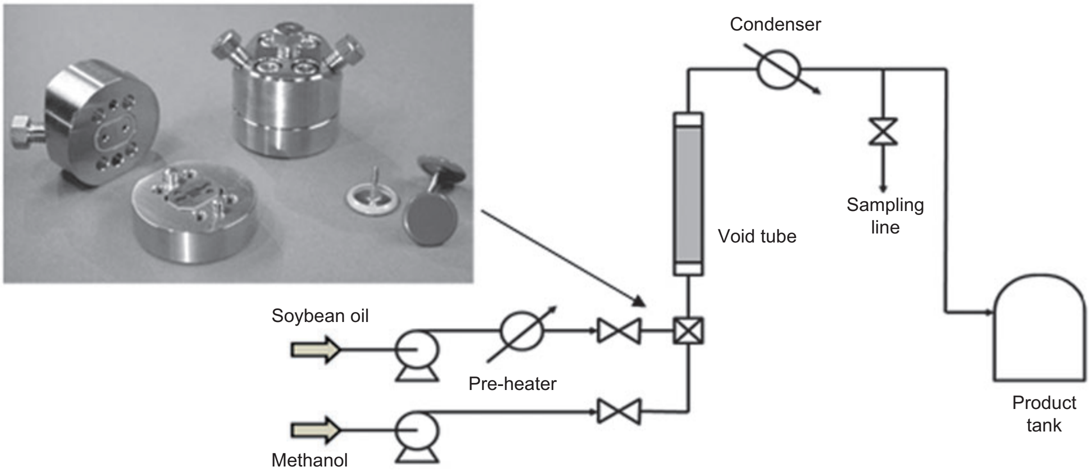

Figure 1 Slit Interdigital Micro Mixer Version 2 (SIMM-V2) produced by IMM (Institut fur Mikrotechnik Mainz GmbH). With the permission from IMM [15].

of CH_3O^- disappearance depends on the interface area, the limit of this rate will be the one corresponding to the contact of two monomolecular films. Another important observation is the dramatic change of the conversion in well-mixed continuous reactors obtained when the amount of used catalyst is increased, for example, by a factor of two, as previously observed in tubular reactors filled with different static mixers [9, 10] and also in the MM+TR reactor, as will be seen later. Therefore, the reached plateau is clearly a consequence of the catalyst deactivation and not of the chemical equilibrium. The deactivation occurs because the catalyst continues to change during the transesterification reaction according to the following simplified mechanism:

$$D^-+CH_3OH \rightarrow M^-+E \qquad r_2=k_2\times[D^-]^a\times[CH_3OH]_a \tag{4}$$

$$M^-+CH_3OH \rightarrow G^-+E \qquad r_3=k_3\times[M^-]^a\times[CH_3OH]_a \tag{5}$$

where M^-=mono-acylglycerolates anions and G^-=glycerolates anions.

G^-, formed in reaction (5) is not soluble in the oil phase and migrates, therefore, in the polar phase giving place to an equilibrium with methanol of the type:

$$CH_3OH+G^- \rightleftharpoons CH_3O^-+G$$

$$r_7=k_7\times\left\{\left[CH_3OH\right]_p\times\left[G^-\right]_p-\frac{1}{K_{eq,7}}\times\left[CH_3O^-\right]_p\times\left[G\right]_p\right\} \tag{6}$$

Thus, formed CH_3O^- can react again, at the interface, with residual T, D or M but with much lower rate being low CH_3O^- concentration. The occurring reactions would be:

$$CH_3O^-+D \rightarrow M^-+E \qquad r_1'=k_1\times a\times\left[CH_3O^-\right]_p\times\left[D\right]_a \tag{7}$$

$$CH_3O^-+M \rightarrow G^-+E \qquad r_1''=k_1\times a\times\left[CH_3O^-\right]_p\times\left[M\right]_a \tag{8}$$

We can conclude that G^- is much less active than D^- and M^-, which are the true catalysts initially formed *in situ*. To use more catalyst means to have a greater concentration of the

Table 1 List of the performed experimental runs.

Run	Q_{oil} (cm^3/min)	Q_{MeOH} (cm^3/min)	Q_{tot} (cm^3/min)	Vr (cm^3)	KOH (%)	τ (s)	Yield (%)
1	9.80	2.53	12.33	15.70	1.00	76	83.00
2	14.30	3.69	17.99	15.70	1.00	52	83.30
3	19.24	4.96	24.20	15.70	1.00	39	84.50
4	31.80	8.20	40.00	15.70	1.00	24	82.00
5	9.80	2.53	12.33	15.70	2.00	76	97.00
6	14.30	3.69	17.99	15.70	2.00	52	96.90
7	19.24	4.96	24.20	15.70	2.00	39	93.70
8	9.80	2.53	12.33	7.85	1.00	38	81.00
9	14.30	3.69	17.99	7.85	1.00	26	84.50
10	19.24	4.96	24.20	7.85	1.00	19	88.00
11	31.80	8.20	40.00	7.85	1.00	12	87.50
12	9.80	2.53	12.33	7.85	2.00	38	99.20
13	14.30	3.69	17.99	7.85	2.00	26	97.50
14	19.24	4.96	24.20	7.85	2.00	19	95.20
15	31.80	8.20	40.00	7.85	2.00	12	95.30
16	4.40	1.20	5.60	0.20	1.00	2	27.55

active components in any step of the reaction and also the deactivation is slowed as a consequence. Then the reaction occurs mainly in the oil phase in the three consecutive steps reported in the following scheme:

$$T+CH_3OH \overset{cat}{\Rightarrow} D+E \quad r_4=k_4\times\left[D^-+M^-\right]\times[T]_a\times\left[CH_3OH\right]_a \tag{9}$$

$$D+CH_3OH \overset{cat}{\Rightarrow} M+E \quad r_5=k_5\times\left[D^-+M^-\right]\times[D]_a\times\left[CH_3OH\right]_a \tag{10}$$

$$M+CH_3OH \overset{cat}{\Rightarrow} G+E \quad r_6=k_6\times\left[D^-+M^-\right]\times[M]\times\left[CH_3OH\right]_a \tag{11}$$

In any case, the dependence of the kinetic constants on the temperature is expressed with a modified Arrhenius law, whose expression is reported below:

$$k_i=k_i^{ref}\cdot\exp\left[\frac{Ea_i}{R}\cdot\left(\frac{1}{T^{ref}}-\frac{1}{T}\right)\right] \tag{12}$$

with T, expressed in Kelvin, and T^{ref} is a reference temperature chosen at 298 K. In particular, we have imposed, as a first approximation, three activation energy values which are:

- Ea_1: activation energy for the reactions (3), (7) and (8),
- Ea_2: activation energy for the reactions (4) and (5),
- Ea_3: activation energy for the reactions (9–11).

At last, reaction (6) is always near to the equilibrium.

The described mechanism is oversimplified because, according to Dijkstra et al. [11], di-acylglycerolate anion formed, at the interface, in the first catalytic reaction step (4), migrates to the apolar phase and promotes further transesterification steps through the formation of an enolate intermediate [10], that is, many intermediate anionic species are involved and we have introduced a lumped kinetic model for describing the kinetic runs.

It is not possible to exclude the possibility of the intervention or the contribution of an alternative mechanism, similar to the classical mechanism in which the first step is exactly the same, that is, methoxide anion attacks the carbon of the carbonyl group for yielding a glyceroxide anion, then glyceroxide removes a proton from dissolved methanol molecules restoring methoxide anion, but methoxide is not soluble in the apolar phase and is surrounded by many molecules of tri-, di- and mono-glycerides. Therefore, it promptly reacts before reaching the polar phase and its concentration always keeps very low. This means assuming that the proton abstraction from methanol is a rate determining step. The role of methoxide anion, in this regard, is similar to the one of enolates, neglected in our model, and the transesterification reaction rates are still dependent on the glycerolate anions concentration. In practice, the model remains unchanged although some intermediates are different.

Methanol is partitioned between the two liquid phases and, obviously, only the methanol dissolved in the oil is involved in the reaction. In some conditions, this last aspect can further slow the reaction as a consequence of the mass transfer limitation. The equations describing the mass transfer of methanol and glycerol from the two phases are, respectively:

Polar phase:

$$J^p_{CH_3OH}=k_{l,CH_3OH}\times a\times\left([CH_3OH]_p-H_{CH_3OH}\times[CH_3OH]_{a,*}\right) \tag{13}$$

$$J^p_G=-k_{l,G}\times a\times\left([G]_p-H_G\times[G]_{a,*}\right) \tag{14}$$

$$J^p_{G^-}=-k_{l,G^-}\times a\times\left([G^-]_p-H_G\times[G^-]_{a.*}\right) \tag{15}$$

Apolar phase:

$$J^a_{CH_3OH}=k_{l,CH_3OH}\times a\times\left([CH_3OH]_{a,*}-[CH_3OH]_a\right) \tag{16}$$

$$J^a_G=-k_{l,G}\times a\times\left([G]_{a,*}-[G]_a\right) \tag{17}$$

$$J^a_{G^-}=-k_{l,G^-}\times a\times\left([G^-]_{a,*}-[G^-]_a\right) \tag{18}$$

The interfacial concentrations (*) can be calculated by solving the following balance that, in steady-state condition, is valid for each C component.

$$J^p_C\times V^p=J^a_C\times V^a \tag{19}$$

By solving the previous equation it is possible to obtain:

$$[J]^{a,*}=\frac{V^p\times\beta_C\times[C]^p+\beta_C\times V^a\times[C]^a}{\beta_C\times V^a+V^p\times\beta_C\times H_C} \tag{20}$$

$$[J]^{p,*}=H_C\times[C]^{a,*} \tag{21}$$

where $\beta_C=k_{l,C}\times a$. For solving the mass transfer equations it is necessary to also define the solubility parameters $H_C=[C]^a/[C]^p$ for both methanol and glycerol. By using ChemCAD V. 6.3 and the UNIFAC LLE model, we can determine the evolution of the solubility parameters with the triglycerides conversion (x). The following optimized polynomial equations have been obtained [10]:

$$\frac{1}{H_{CH_3OH}}=25.85-23.00\times x-11.21\times x^2+36.41\times x^3 \tag{22}$$

$$\frac{1}{H_G}=6304.75-15430.10\times x-1643.71\times x^2+64912.73\times x^3 -92127.03\times x^4+43103.45\times x^5 \tag{23}$$

4. Results and discussion

The described mechanism suggests that the formation of a high interface area in the initial step of the reaction to consume the methoxide anions as soon as possible is very important. Then, the reaction acts against the oil phase in the chemical regime until the catalytic species, soluble in oil, are present. In this paper, we have demonstrated this qualitative view by performing the transesterification reaction in a micro-mixer coupled with a void tubular reactor (MM+TR). The same void tube fed with oil, methanol and 1% of catalyst, in the absence of the micro-mixer, has given a 3% of conversion, whereas, by using a very efficient micro-mixer, conversions of 82–84% were obtained in the same operative conditions. The obtained results are reported in detail in Table 1 together with the operative conditions. As can be seen, by using 1% of catalyst, the highest conversions (87–88%) have been obtained at the lower residence times of 12–19 s. By increasing the residence times the conversion slightly decreases to 82–84%. It is interesting to note that the highest values of conversion have been obtained with the shorter tube of 10 cm length. By using 2% b.w. of catalyst the conversions strongly increase, at the same residence times, giving values of 95–97%. A certain invariance of the conversion with the residence time confirms the hypothesis that the reaction occurs in a very short time when the interface area is very high. By contrast, by considering the high conversions obtained in a so small volume, a rigorous approach to the evolution of the interfacial area along the length of the reactor is not possible because the properties of the liquid-liquid mixture change very much starting as a mixture of methanol+triglycerides and finishing as a mixture of methanol-glycerol+methylesters. There are changes of densities, viscosities, solubilities and tenside properties. We have considered the changes of the relevant properties for the model as the partition and the densities of any single component for evaluating the volume and composition change, but not the influence of the physical properties on the interfacial area.

However, a long tube with a longer residence time can favor the agglomeration of the dispersed drops with a detrimental effect on the reaction rate. Probably, for this reason, the performances of MM+TR related to the shorter tube seem slightly better. However, it must be pointed out that the increase of the catalyst concentration. From 1 to 2%, leads to dramatic increase of the conversion, in agreement with the previous results obtained in the same tubular reactor packed with different types of static mixers [9, 10]. Then, considering the observed invariance in the conversion with the residence time in the explored flow rates range we have also made a run at very low residence time using a short capillary Teflon tube after the micro-mixer. The obtained results are reported in both Table 1 and Figure 2. As can be seen, the conversion is significantly reduced. This means that the transesterification reaction does not occur completely in the micro-mixer but needs a discrete volume for the completion.

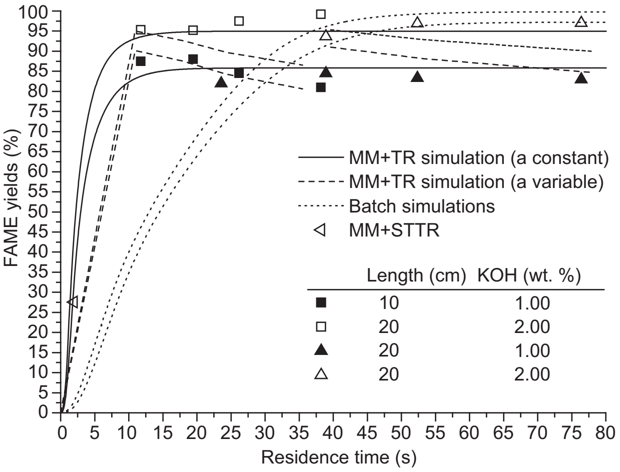

Figure 2 Obtained agreements for the experimental runs reported in Table 1. Symbols represent the experimental points, whereas lines represent the simulations. In the same plot, the simulation obtained by assuming the kinetic parameters valid for the stirred batch reactor is also reported. MM+STTR stays for Micro mixer+Small Teflon Tubular Reactor (10 cm length, 1/16″ of external diameter).

4.1. Estimation of the interface area

All the obtained results in the MM+TR reactor suggest that very small droplets of one phase (methanol) are dispersed in the other one (oil phase). In similar fluid dynamic conditions [Slit Interdigital Micro Mixer (SIMM-V2) of standard type with a 45 μm height of slit], the dispersion of water in n-hexane yields droplets with an experimentally measured average diameter from 5 to 55 μm [16]. For this purpose, in Figure 3 the evolution of the interface area with the volumetric flow rate is reported, as derived from Löb et al. [16]. In our opinion, the curve reasonably goes to a plateau representing a limiting value of dispersion connected with the efficiency of the device and the characteristics of the two liquid phases. We have arbitrarily assumed the limiting value at 5 μm of the drop diameter. The equation used for interpolating the experimental results reported in the literature [16] is as follows:

$$a=12015.87\times(1+(10.55-1)\times\exp(-0.96\times(Q-26.84)))^{1/(1-10.55)}\times(\mathrm{cm}^2/\mathrm{cm}^3) \tag{24}$$

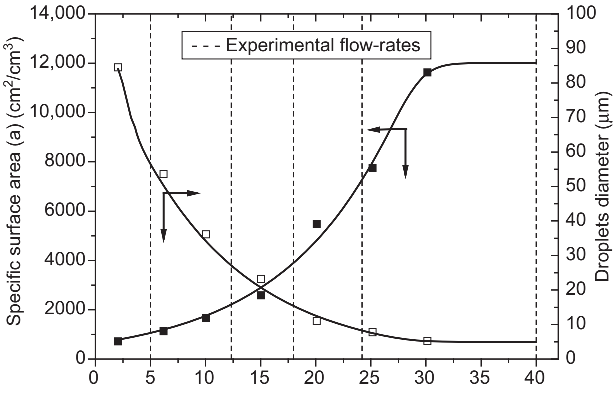

Figure 3 Evolution of the droplets diameters and of the interfacial area as a function of the overall volumetric flow rate (data taken from the work of Löb et al. [16] related to the system water n-hexane).

The range of flow rates, covered by our experiments, is 5.6–40 cm³/min. Although the fluid dynamic conditions of these experiments are similar to the ones reported in Figure 3 the liquid-liquid system studied by us is very different, because it starts as a mixture of methanol and soybean oil and transforms, as a consequence of the reaction, to a mixture of a glycerol solution in methanol and biodiesel, with a strong change in both the apolar/polar volume ratio [9] and the amount of methanol that is reduced is approximately 50%. Therefore, a rigorous evaluation of the evolution of the interface area with both the overall flow rate and conversion is somewhat impossible on an experimental basis. Nevertheless, the plot of Figure 3 is a satisfactory draft starting point for our calculations. As will be seen, the agreement obtained by roughly assuming a constant interfacial area, i.e., independent of the flow rate in the examined range, leads to a best fitting of the experimental results. However, we reported the results of both the approaches and related parameters.

4.2. Application of the biphasic kinetic model to the description of the kinetic runs performed in the MM+TR

The described biphasic kinetic approach is based on the following main hypotheses:

i. Only glycerol and methanol are considered partitioned between the two phases. Although all the components are partitioned and we can evaluate the composition of the two phases as a function of the conversion [17] by using ChemCAD 6.3 software setting the UNIFAC LLE model.
ii. All the reactions have been considered irreversible with the exclusion of reaction (8).
iii. There are only two species acting as catalyst in the oil phase that are M^- and D^-.
iv. Methanol and glycerol mass transfer have been evaluated by adopting the Withman's two films theory [18].

It is now possible to write the mass balances for both the polar and apolar phase:

Polar phase

$$\frac{d[A]^p}{dV}=\frac{-J_A^p-r_7}{Q} \tag{25}$$

$$\frac{d[G]^p}{dV}=\frac{+J_A^p+r_7}{Q} \tag{26}$$

$$\frac{d[Acat]^p}{dV}=\frac{-\left(r_1+r_1'+r_1''\right)\cdot\frac{Q_a}{Q_p}+r_7}{Q} \tag{27}$$

$$\frac{d[G^-]^p}{dV}=\frac{+J_{G^-}^p-r_7}{Q} \tag{28}$$

$$[Acat]^{p,0}=[KOH]^p \tag{29}$$

Apolar phase

$$\frac{d[T]^a}{dV}=\frac{-r_1-r_4}{Q} \tag{30}$$

$$\frac{d[D]^a}{dV}=\frac{+r_4-r_5-r_1'}{Q} \tag{31}$$

$$\frac{d[M]^a}{dV}=\frac{+r_5-r_6-r_1''}{Q} \tag{32}$$

$$\frac{d[G]^a}{dV}=\frac{+r_6-J_G^a}{Q} \tag{33}$$

$$\frac{d[E]^a}{dV}=\frac{+r_1+r_1'+r_1''+r_2+r_3+r_4+r_5+r_6}{Q} \tag{34}$$

$$\frac{d[A]^a}{dV}=\frac{-r_2-r_3-r_4-r_5-r_6+-J_A^a}{Q} \tag{35}$$

$$\frac{d[D^-]^a}{dV}=\frac{+r_1-r_2}{Q} \tag{36}$$

$$\frac{d[M^-]^a}{dV}=\frac{+r_2-r_3+r_1'}{Q} \tag{37}$$

$$\frac{d[G^-]^a}{dV}=\frac{+r_3-J_{G^-}^a+r_1''}{Q} \tag{38}$$

The equation system has been solved by using a fourth order Runge-Kutta algorithm. The kinetic parameters of the model are the same determined by mathematical regression analysis performed on many kinetic runs, made in batch conditions, reported in the literature [10, 12, 13]. These parameters, determined in a previous work [10], are summarized in Table 2. The same parameters have also been used for describing the runs performed in the continuous MM+TR with the exception of the parameters correlated with the interface area that are: the kinetic constant of the reactions occurring at the interface (3, 7, 8) and the overall methanol mass transfer coefficient. Two different approaches have been followed in the calculations, one assuming a constant interfacial area, independent of the flow rate, assuming that a maximum possible interfacial area is obtained at the exit of the micro-mixer, the other assuming a variable interfacial area as reported in

Table 2 List of the parameters obtained by mathematical regression analysis on several runs, performed in a stirred batch reactor, reported in the literature [12, 13].

Parameters	Values	Units
k_2	0.225	$l^a/(mol \cdot min)$
k_3	0.225	$l^a/(mol \cdot min)$
k_4	18.16	$l^{2,a}/(mol^2 \cdot min)$
k_5	4.61	$l^{2,a}/(mol^2 \cdot min)$
k_6	1.92	$l^{2,a}/(mol^2 \cdot min)$
$K_{eq,7}$	1.69 e-3	–
Ea_1	≈ 0	kcal/mol
Ea_2	17.61	kcal/mol
Ea_3	26.62	kcal/mol

Figure 3. All the obtained parameters are reported in Table 3, where are compared with the same parameters obtained for a stirred batch reactor [10]. It is interesting to observe that, by assuming the interfacial area constant, $\gamma_l = k_l \times a$ for the MM+TR is 2.6 times greater than the value obtained in the batch reactor. The same difference has not been observed for the $\beta_C = k_l \times a$, because in the continuous reactor a chemical regime is operative. As the comparison has been made at the same temperature, this difference can be ascribed only to the interfacial area difference in the two different reaction conditions. In the stirred batch reactors, the liquid-liquid interfacial area increases with the stirring rate as a consequence of the new generated smaller droplets, but stirring also favors the droplets agglomeration and the interface area increases until a maximum is reached when the two mentioned effects are balanced. In the MM+TR device, a relatively stable emulsion is probably formed as a consequence of the liquid in liquid atomization and agglomeration can intervene only after a relatively long residence time. In Figure 2, it is possible to appreciate the agreement between experimental and calculated data for both the approaches made (interface area constant and variable). It is possible to appreciate in this figure that assuming constant the interfacial area in the adopted range of flow rates leads to a much better agreement. The reasons have already been explained in a previous section. From the approach with variable interfacial area it is possible to estimate a value for $k_l=7.6\times10^{-2}$ (cm^4 mol^{-1}min^{-1}). Applying this value to the constant interface area approach, an interfacial area of approximately 14,500 cm^2/cm^3 and an average value of the dispersed drop size of 4.13 μm can be calculated from the value of γ_l reported in Table 3. These values confirm the obtainment of a limiting value for the studied system (methanol/oil) also at the lowest flow rates, probably owing to the tenside properties of mono- and di-glycerides favoring the formation of a stable emulsion.

However, it is possible to conclude that a complete conversion can be obtained in a residence time of approximately 10 s. By contrast, this limit has already been reached in some cases reported in the literature [4, 10]. In Figure 2, a simulation made by assuming the same parameters related to the stirred batch reactor is also reported. As can be seen more than 60 s are necessary for reaching the plateau in agreement with the trend reported for this run in batch conditions. In this case, mass transfer contribution cannot be neglected.

In conclusion, the developed biphasic model, although the introduced approximations, has demonstrated a general validity being able to describe: (i) experimental runs performed in different reactors, characterized by very different reaction rates such as: stirred batch reactors, also dominated by mass transfer, continuous tubular reactors containing static mixer elements and microreactors; and (ii) the difference in the final conversion obtained by using different KOH concentrations. Moreover, the use of a very efficient micro-mixer that gives place to a very high liquid-liquid interface area has given a dramatic increase of the reaction rate confirming the validity of the mechanism on which the biphasic model has been developed. The general validity of the proposed biphasic kinetic model can be better appreciated by observing the parity plot reported in Figure 4, in which all results of the simulations made by using different types of reactors [9, 10, 19] (well stirred batch, continuous with different types of static mixer elements and runs with the micro-mixer device) are compared with the experimental results. As can be seen, almost all the points are inside a range of 10% of error, which is fairly satisfactory considering the span of residence times adopted between seconds and hours.

Finally, the possibility of obtaining very high biodiesel yields in a few seconds, simply by increasing the interface area, is a very important starting point for biodiesel process intensification.

Table 3 List of the adjustable parameters obtained by simulating the continuous runs with two different approaches: one considering [MM+TR (1)] interfacial area constant, the other variable according to Figure 3 [MM+TR (2)].

Reactor	k_l [cm^4/(mol·min)]	$\gamma_l=k_l\times a$ [l^p/(mol·min)]	$\beta_C= k_l\times a$ [min^{-1}]
MM+TR (1)	–	1.1±0.1	–
MM+TR (2)	7.6×10^{-2}	–	–
Stirred batch	–	0.43±0.02	1.52±0.05

For comparison the same parameters obtained in the stirred batch reactor used for determining the parameters of Table 2 are also reported.

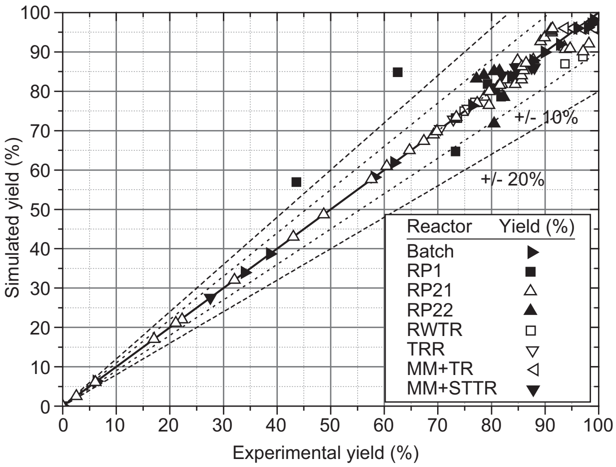

Figure 4 Parity plot in which all results of the simulation made by using different types of reactors are compared with the experimental results. Well stirred batch reactor (▶), continuous reactor filled with: (■) stainless steel spheres of 2.5 mm diameter, (△) double distribution of stainless steel spheres of 2.5/1 mm diameter, (▲) double distribution of stainless steel spheres of 2.5/0.39 mm diameter, (□) stainless steel wool, (▽) threaded roads, (◁) micro-mixer in series with a void tube of 1.27 cm external diameter and 10 or 20 cm length, (▼) micro-mixer in series with a Teflon capillary tube of 0.159 cm external diameter and 10 cm length. Runs taken from [9, 10, 19].

5. Conclusion

In this work, it has been shown, first of all, that by increasing very much the interface area between oil and methanol, this last containing KOH as catalyst, the rate in biodiesel formation strongly increases and the reaction can be completed in a few seconds. The final conversion is affected by the initial catalyst concentration. This means that the reaction slows down not because near to the equilibrium but because the catalyst deactivates. A mechanism congruent with these experimental observations, proposed in a previous work [10], has been confirmed in the present paper. According to this mechanism, methoxide anions, formed for the reaction of methanol with KOH, react at the interface with triglycerides molecules yielding di-acylglycerolate anions, and then, from these anions mono-acylglycerolates anions are obtained and finally glycerolate anions. These last anions are not soluble in oil and migrate in the methanolic polar phase, subtracting catalyst to the reaction and consequently the rate dramatically slows down. On the basis of this mechanism, a biphasic kinetic model, previously developed [10], has been successfully applied to the interpretation of the kinetic runs performed in a continuous reactor constituted by a micro-mixer device followed by a void tube. The same model is able to describe any type of reactor, starting from the kinetic parameters derived from the interpretation of runs performed in a stirred batch reactor [12, 13], simply by adjusting the liquid-liquid interface area. Finally, the use of an efficient micro-mixer for performing the reaction has shown a very simple and efficient way for realizing biodiesel process intensification.

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Nomenclature

Symbols

MM+TR	Micro-mixer put in series with a void tubular reactor
A1	Methoxylic groups single signal at δ =3.7 ppm
A2	Methylenic groups triplet signal δ =2.3 ppm
SIMM-V2	Slit Interdigital Micro Mixer
T	Triglycerides
D	Diglycerides
M	Monoglycerides
G	Glycerol
E	Methylesters
CH_3O^-	Methoxide anion
D^-	Di-acylglycerolate anion
M^-	Mono-acylglycerolate anion
G^-	Glycerolate anion
r_i	Reaction rate (mol/l/min)
k_i	Kinetic constant (units depend on the reaction)
a	Interfacial area (cm^2/cm^3)
γ_1	Kinetic parameter of reaction defined as $k_1 \cdot a$
Ea_i	Activation energy (kcal/mol)
$K_{eq,i}$	Equilibrium constant
J_C^i	Mass transfer rate for the C component in the phase i (mol/l/min)
$k_{l,C}$	mass transfer coefficient of the C component (cm/min)
β_C	Mass transfer parameter of the C component defined as $k_{l,C} \times a$ (min^{-1})
H_C	Partition coefficient of the C component ($[C]^a/[C]^p$)
x	Conversion degree (-)
Q	Overall volumetric flow rate (cm^3/min)
τ	Residence time (min)
V	Reactor’s volume (cm^3)

Subscripts and Superscripts

oil	Oil phase
p	Polar phase
a	Apolar phase

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