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ORIGINAL PAPER

Continuous Methanolysis of Palm Oil Using a Liquid–Liquid Film Reactor

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Abstract A system for the continuous methanolysis of palm oil using a liquid–liquid film reactor (LLFR) was developed and characterized. This reactor is a co-current, constant diameter (0.01 m), custom-made packed column where the mass transfer area between the partially miscible methanol-rich and vegetable oil-rich phases is created in a non-dispersive way, without the intervention of mechanical stirrers or ultrasound devices. An increase in contact area between phases enhances reaction rate while the absence of small, dispersed droplets of one phase into the other diminishes the settling time at the end of the reaction. In this study variations on the concentration of catalyst (sodium hydroxide), flow rate of palm oil and normalized length of the reactor (L/L_{max}) were explored, keeping constant both the methanol to oil molar ratio and the temperature of the reaction (6:1 and 60 °C). The best experimental results with a reactor of 1.26 m ($L/L_{max} = 1.0$) showed a conversion of palm oil of 97.5% and a yield of methyl esters of 92.2% of the theoretical yield, when the mass flow rate and the residence time of the palm oil were 9.0 g min^{-1} and 5.0 min, respectively. To determine the mean residence time and the degree of axial mixing in the reactor, a residence time distribution (RTD) study was performed using a step-function input. The dispersion model appears to fit well the RTD experimental data.

Keywords Biodiesel · Continuous process · Methyl esters · Palm oil · Methanolysis · Film reactor

Introduction

In recent years fatty acid methyl esters (FAME) have attracted widespread interest from governments, chemical engineering companies and researchers. FAME are products of methanolysis of fats and oils, which can be used as a partial or total substitute for diesel and as a raw material to produce oleochemical derivatives. The most common industrial method for producing FAME is a one-step or two-step batch transesterification process, using an alkaline homogeneous catalyst [1–3]. Compared to batch processes, continuous processes have several advantages: greater productivity, lower operating and labor costs, and a more consistent product quality. Batch processes for FAME production are slow, tedious and low in productivity [4]. However, continuous processes are an attractive choice only for large capacity, especially for production facilities larger than 4 million liters per year [5].

Continuous methanolysis of fats and oils has been studied by several researchers. Assmann [3], Cheah et al. [6], Noureddini et al. [2], Peterson et al. [7], Darnoko and Cheryan [1], He et al. [4], Shah and Suppes [8], Dubé et al. [9], Stavarache et al. [10] and Leevijit et al. [11], among others, have investigated continuous processes for the transesterification of triglycerides to methyl esters using different feedstock, reactors and schemes of production.

A factor of particular importance in the methanolysis is the degree of mixing between the alcohol and the oil.

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Several reports suggest methanolysis does not occur in one homogeneous phase [12, 13]. Initially, methanol and palm oil are only partially miscible, forming two liquid phases; the reaction is diffusion-controlled so mixing is needed to create enough contact area to start the reaction quickly [2]. Noureddini et al. [2] observed a lag phase at the beginning of the reaction, which decreased as the mixing intensity was increased and reached a constant value of 1–2 min for a Reynolds Number greater than 10,000. Similarly, Assmann [3] suggested very safe operation of a tubular reactor for transesterification when the Reynolds number was equal to or greater than 10,000.

During the reaction, two phases always coexist: one rich in FAME and the other rich in glycerol and methanol; mixing continues being necessary to keep both phases in contact so the reaction rate is not limited by mass transfer. Most reported studies on continuous processes for the methanolysis of fats and oils use either mechanical stirrers [1, 6, 11], turbulent flow induced by pumps and static mixers [2, 3, 7] or ultrasound [10] to mix the reacting phases. Stirring or turbulent flow causes the dispersion of small drops of one phase into the other; ultrasound induces asymmetric cavitational bubbles to collapse at the oil–alcohol interface, creating tiny drops of each liquid in the other [10]. As the reaction proceeds, mono and diglycerides are formed that help to stabilize the dispersion; Zhou and Boocock [12] suggested that for methanolysis, an emulsion is formed by the synergistic action of a minimum mixing time of approximately 3 min at the beginning of the reaction and the surfactant nature of monoglycerides and diglycerides. However, although stabilizing the emulsion helps to speed up the reaction rates, it also increases separation time, especially when oils with high contents of water and free fatty acids are used as feedstock. Several authors [14–17] have pointed out that the acidity and water content of oils have a rather strong negative impact on the reaction, glycerol separation and methyl ester conversion, because the free fatty acids react with the alkaline catalyst generating soaps; a similar effect is caused by the hydrolysis of triacylglycerol in the presence of water [16]. The resulting soaps cause an increase in viscosity or gel formation, interfering with the reaction as well as with the separation of the glycerol-rich phase [16]. Regarding the separation time, Assmann [3] reported times from 15 min to 2 h downstream of a tubular reactor operating in a turbulent regime. Similarly, the authors know of at least one commercially available technology, requiring several hours between batches, where each reaction stage takes only about 1 h, inferring that a significant part of the remaining period is spent in the two-phase separators.

Since the dispersion of the two phases created by stirring devices generates separation problems, in this study the mass transfer area is created in a different, non-dispersive way through the use of a liquid–liquid film reactor (LLFR); as a consequence, the time required for the separation of the effluent phases from the LLFR decreases. Another advantage of the LLFR over stirred reactors involves the prevention of back-mixing of the glycerol formed as a result of the co-current flow pattern, helping to drive the reaction to the products; the same effect is expected to be obtained through glycerol extraction by the methanol not dissolved in the ester phase.

In this study, a LLFR was evaluated for the continuous methanolysis of palm oil. This reactor is a co-current flow system that allows transferring at least one component between two immiscible or partially miscible phases; one of the phases wets preferentially a semi-structured packing that fills the reactor's cross-sectional area, and the other phase flows over the first. The frictional force between the phases increases the interfacial area creating a thin film over the packing [18]. A close approach to plug flow is achieved in this reactor, as in any co-current apparatus, which means that for a single equilibrium-limited contact the size of the reactor can be much smaller than that of a single continuous flow stirred reactor [18].

This research explores the applicability of a LLFR for the continuous methanolysis of palm oil. The effect of the flow rate of palm oil, concentration of catalyst (sodium hydroxide), and length of the reactor on the concentration of products, conversion and yield were studied, while temperature and the molar ratio of methanol to palm oil were kept constant. Likewise, the residence time distributions (RTD) for palm oil and methanol were measured in order to establish the distribution function, the residence time and to characterize the state of axial mixing, and thus, better understand the reactor behavior. Additionally, a mathematical model of the LLFR was used to predict the concentration of feedstock and products, as well as conversion and yield, in reactors of greater length than the experimentally evaluated ones.

Experimental Procedure

Materials

Refined, bleached and deodorized edible grade palm oil was obtained from INTERGRASAS S.A. (Bogotá, D.C. Colombia). The acid value of the palm oil, which was determined according to ASTM D-664, was 0.22 mg KOH g^{-1}, and the water content, determined according to ASTM D-1744, was less than 0.01 wt.%. Methanol with >99.5% purity and 0.12 wt.% of water was obtained from INTERQUIM S.A. (Medellín, Colombia). Sodium hydroxide and zinc chloride were of analytical grade and obtained from MERCK (Darmstadt, Germany).

Reference standards such as methyl palmitate, methyl oleate, DL-α palmitin, dipalmitin (mixture of isomers), tripalmitin and glyceryl trioleate, and the silylation agent *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with $>99\%$ purity, as well as sudan red technical grade were purchased from Sigma Aldrich Chemical Company (St. Louis, MO, USA). The internal standards, tricaprin and 1,2,4 butanetriol, were obtained from Fluka (Buchs, Switzerland) and Accustandar (New Haven, CT, USA) respectively. Pyridine, isopropanol and toluene of Baker ACS grade were obtained from Mallinckrodt Baker Inc. (Phillipsburg, NJ, USA).

Reaction Conditions

The temperature and methanol to oil molar ratio were kept constant for every experiment, at 60 °C and 6:1, respectively. These values were selected according to the results of a previous experiment developed in a LLFR of normalized length, $L/L_{\max}$, 0.24, where the effects of temperature, methanol to oil molar ratio, concentration of catalyst (NaOH), and palm oil flow rate on palm oil methanolysis were studied and optimized [19]. The normalized length, $L/L_{\max}$, is the ratio between the experimental length of the reactor in a particular run, L, and the length of the longest experimental reactor, $L_{\max}$, which was 1.26 m.

Experimental Design and Statistical Analysis

The evaluation of the continuous methanolysis of palm oil in a LLFR explored the influence of the flow rate of the oil, of the concentration of catalyst (sodium hydroxide) and of the reactor length. A multilevel factorial experiment was designed for three variables for a total of 16 tests, which were each conducted two times. Two levels were studied for the flow rate of the oil (9.0 g min^{-1} and 27.0 g min^{-1}) and for the concentration of catalyst (0.6 wt.% and 1.0 wt.% based on the weight of the oil). With reference to the normalized reaction length and taking into consideration that it was very difficult to obtain samples along the reactor without changing the flow pattern and thus, the reactor performance, four reactors of $L/L_{\max}$ 0.24, 0.56, 0.78 and 1.0 were tested. The flow rates of methanol were calculated from the flow rate of palm oil and the molar ratio and set at 2.0 g min^{-1} and 6.1 g min^{-1}.

Analysis of variance (ANOVA) was carried out using the Analysis Design Procedure of STATGRAPHICS Centurion (StatPoint, Inc., Warrenton, VA, USA) statistical software to test the effect of the normalized reactor length, flow rate of palm oil and concentration of catalyst on the concentration of feedstock and products, conversion and yield.

Equipment

A diagram of the experimental setup is presented in Fig. 1. The liquid–liquid film reactor consisted of a borosilicate glass column packed with a semi-structured stainless steel packing with surface area of about 7.94×10^{-2} m^2 m^{-1}; the packing was custom made by placing 500 stainless steel threads axially aligned and homogeneously distributed following a triangular pitch; every thread had a diameter of 0.15 mm, and was fixed to the distribution plate at the top and to a central core at the bottom of the reactor. To maintain the reaction temperature, the reactor had a heating jacket, which was connected to a Julabo F34 Heating Circulator (JULABO Labortechnik GmbH, Seelbach, Germany) equipped with an external Pt-100 sensor. The palm oil and the solution of NaOH in methanol were stored in two tanks installed on two balances Metler Toledo 4000 (Mettler Toledo GmbH, Schwerzenbach, Switzerland), that allowed measurement of the mass flow. Two metering pumps HMS EXT 2001 (EMEC Srl, Vazia, Italy) were used to feed the palm oil and the solution of NaOH in methanol at controlled flow rates. Before entering the reactor, the palm oil and the solution were independently heated up to the reaction temperature using heating systems equipped with silicon-shielded resistances and SHIMADEN SR 91 temperature controllers (Shimaden Co. Ltd., Tokyo, Japan), capable of maintaining the temperature within ±0.1 °C.

Procedure

The system was preheated to 60 °C to avoid palm oil solidification. Initially the palm oil was fed to the reactor using the respective metering pump. When the oil flow rate reached the desired value, the solution of sodium hydroxide in methanol, which was prepared no more than 1 hour prior to the start of the reaction, was fed to the reactor using the respective metering pump. The initial time ($t = 0$) was set as soon as the pump began feeding the methanol solution.

Analysis

Samples of 10 mL were taken every 20 min at the outlet of each reactor tested, until the reactor operation time was 200 min. The analysis method is an adaptation of ASTM D-6584. Briefly, after 30 s of separation, 20 mg of the upper phase of every sample were derivatized at room temperature for 60 min by adding BSTFA as the silylating agent and pyridine as the catalyst, in the presence of 5 mg of tricaprin as an internal standard. After derivatization, samples were stored at −2 °C for posterior GC analysis. The derivatized samples were analyzed for methyl esters,

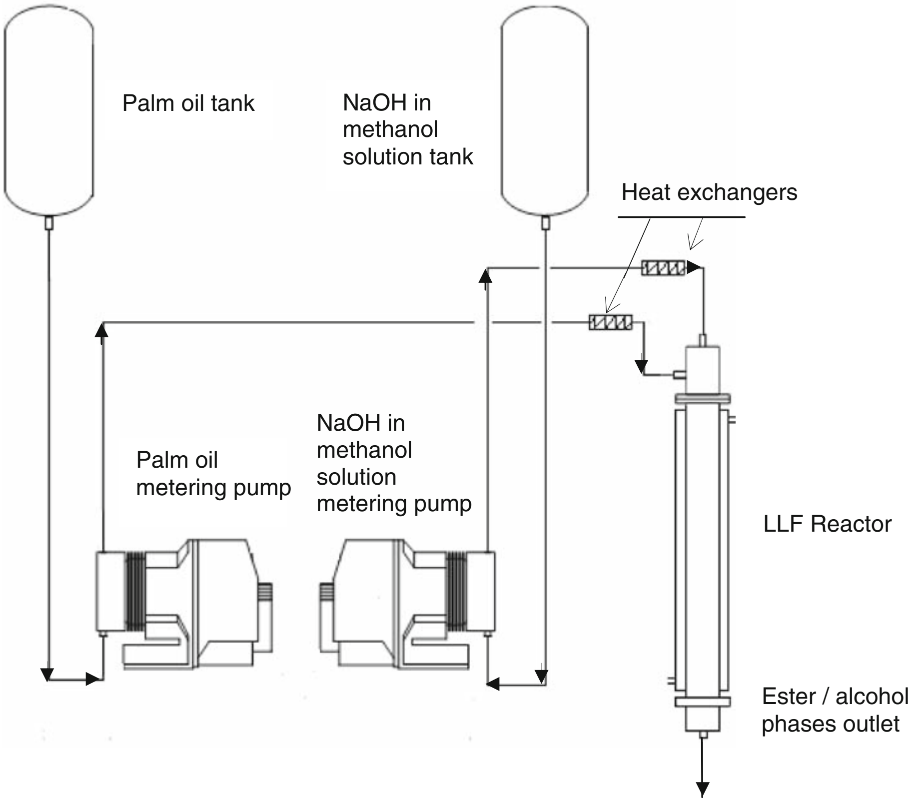

Fig. 1 Flow diagram of the system used in the continuous methanolysis of palm oil using a Liquid–Liquid film reactor

monoglycerides, diglycerides, and palm oil by gas chromatography in a GC Agillent 6820 (Agilent Technologies Co. Ltd., Shangai, China), equipped with a flame ionization detector, a fused silica (0.3 m × 0.53 mm) pre-column and a fused silica capillary column SUPELCO SGE HT-5, 12 m × 0.53 mm × 0.15 μm (SGE International Pty. Ltd., Victoria, Australia). The samples of 0.4 μL were manually injected. After 1 min of stabilization at 140 °C, the oven temperature was programmed from 140 °C to 380 °C at 20 °C/min and then was held at 380 °C for 10 min. The injector temperature was 350 °C and that of the detector was 390 °C. Each run was 23 min long. The carrier gas was nitrogen with a flow of 8 mL/min, and 50:1 split ratio. The acquisition and processing of data were achieved with the program Cerity (Agilent Technologies Co. Ltd., Shangai, China). Samples from the lower phase were also analyzed for methyl esters, monoglycerides, diglycerides, and palm oil using the same methodology, but no detectable amounts of these compounds were found; small amounts of FAME were detected in several samples but the concentration was always less than 1% w/w so they were considered negligible.

Concentrations of glycerol and methanol were calculated through material balance; however, direct measurement was performed for the tests developed in the reactor of $L/L_{\max}$ 1.0 in order to confirm the calculated values. For glycerol, GC was performed following a procedure similar to the described above but using 1,2,4 butanetriol as a second internal standard and starting the analysis at 50 °C; determination of methanol was accomplished by evaporation of samples of about 10 g, at 55 °C, using a moisture balance AMB 50 (Adam Equipments Co., Danbury, CT, USA). In order to explore the separation of the effluent phases from the reactor of $L/L_{\max}$ 1.0, ten samples of about 50 mL were taken during the test at palm oil flow rate 9.0 g min^{-1} and 1.0% of NaOH as catalyst. The samples were placed in a graduated funnel, and with the aim of measuring the separation time and to detect problems in the separation, the lower phase volume was recorded as a function of time.

Residence Time Distribution (RTD)

The RTD study was developed in the LLFR of $L/L_{\max}$ 1.0 applying a step function perturbation. A solution of Sudan red in palm oil and a solution of $ZnCl_2$ in methanol were used as tracers. Palm oil mass flow rates were 9.0 g min^{-1} and 27.0 g min^{-1}, and methanol mass flow rates were 2.0 g min^{-1} and 6.1 g min^{-1}, respectively. The values of the normalized concentration of the tracer presented are the average of duplicate tests.

To establish the RTD of the palm oil, pure oil was fed to the reactor and as soon as the flow rate of the test was reached, the solution of Sudan red was fed to the reactor.

Samples of 1 mL (about 1/100th of the total volume of the reactor) were taken at the reactor outlet at intervals that depended on the palm oil flow rate; i.e., at a palm oil flow rate of 9.0 g min^{-1}, samples were taken every minute during the first 5 min of the test, and every 2 min during the following 10 min. Samples were diluted 1:10 with *n*-hexane and their absorbance was determined at 510 nm. Absorbance was measured in a SPECTRONIC GENESYS 5 spectrophotometer (Spectronic Instruments Inc., Rochester, NY, USA). In order to evaluate the influence of methanol on the RTD of the palm oil, similar tests to the one described before were made, but in the presence of methanol.

To determine the RTD of methanol, pure alcohol was fed to the reactor, and as soon as the flow rate of the test was established, the solution of $ZnCl_2$ was fed in. Samples of 0.5 mL were taken at the reactor outlet at intervals that depended on the methanol oil flow rate; i.e., for the methanol oil flow rate of 2.0 g min^{-1}, samples were taken every minute during the first 10 min of the test, and every 2 min during the following 10 min. Samples were diluted with methanol and their absorbance was measured at 410 nm.

Results and Discussion

Residence Time Distribution (RTD)

Figure 2 shows the RTD of palm oil and methanol in the LLFR. Values in Fig. 2 are the average of two tests; error bars correspond to the standard deviation. Experimental data appear to be a good fit in the dispersion model shown in Eq. 1 [20]:

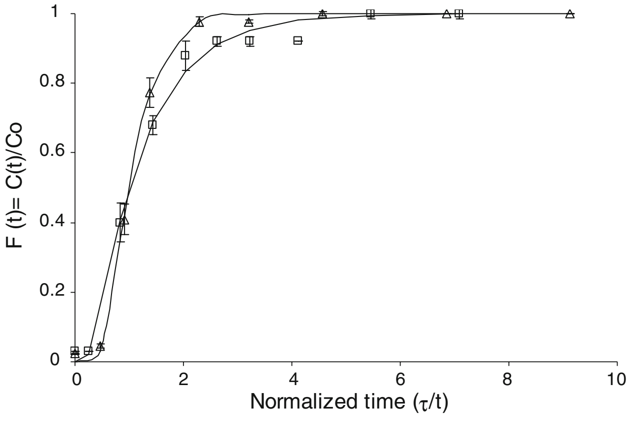

Fig. 2 Residence time distribution in a LLFR. Palm oil flow rate 27.0 g min^{-1}, methanol flow rate 6.1 g min^{-1}, 60 °C, $L/L_{\max}$ 1.0. The *solid lines* represent the fitted dispersion model for a tubular reactor (Eq. 1). (Triangle) palm oil; (Square) methanol

$$F(t) = \frac{C(t)}{C_0} = \frac{1}{2}\left[1 - erf\left[\frac{1}{2}\sqrt{\frac{vL}{D_L}}\left(\frac{1-\frac{t}{\tau}}{\sqrt{\frac{t}{\tau}}}\right)\right]\right] \qquad (1)$$

where $F(t)$ is the normalized concentration of the tracer, $C(t)$ is the measured tracer concentration at the exit, C_0 is the step tracer concentration, v is the axial velocity, L is the reactor length, D_L is the effective diffusivity, t is time, τ is the mean residence time and *erf* is the error function. In this model, axial dispersion takes place according to D_L and the mixing state can be represented by a particular value of $D_L\ v^{-1}\ L^{-1}$ (the reciprocal of the Péclet number, *Pe*). Table 1 shows the values of τ and *Pe* obtained after a minimizing process of the summed squared error between the average experimental and predicted data. For every flow rate of palm oil and methanol studied, the coefficients of determination were satisfactory ($R^2 > 0.998$).

Regarding *Pe*, the axial dispersion for methanol seems to be greater than the axial dispersion for palm oil. However, for both phases, the reactor behavior is closer to a plug flow tubular reactor ($Pe > 50$) than a stirred tank reactor ($Pe < 0.05$), such as is expected in co-current systems. Based on mean residence time, the ratio of effective diffusivities, the ratio of axial velocities and the empty volume fraction of the reactor were calculated. For the flow rates studied the ratio of effective diffusivities ranged from 1.3 to 1.8, the palm oil axial velocity was higher than that of the methanol, and when the palm oil flow rate increased, the empty volume fraction of the reactor decreased. The empty volume fraction at a palm oil flow rate of 9.0 g min^{-1} was 33% as compared to 20% at 27.0 g min^{-1}.

Statistical Analysis

The analysis of variance (ANOVA) of the experiment showed that the effect of flow rate, normalized reactor length and percentage of catalyst are significantly different from zero at the 95.0% confidence level ($p \leq 0.05$), for the concentration of methyl esters, palm oil, glycerol and methanol, conversion and yield.

Table 1 Calculated mean residence time (τ) and Péclet number ($Pe = LvD_L^{-1}$) for palm oil and methanol in a LLFR of $L/L_{\max}$ 1.0 according to a dispersion model (Eq. 1)

Palm oil/methanol mass flow rate (g min^{-1})	Palm oil		Methanol	
	τ (min)	*Pe*	τ (min)	*Pe*
9.0/2.0	5.0	18.6	10.1	5.5
27.0/6.1	2.2	10.6	3.4	3.6

Reactor Performance

Figure 3 shows the overall concentration of palm oil, FAME, monoglycerides (MG) and diglycerides (DG), at the outlet of the LLFR, when the mean residence time of the oil was 2.2 min. Values in Fig. 3 are the average of two tests; error bars correspond to the standard deviation. The reactor appears to reach the steady state after 20 min of operation, approximately ten and six times the mean residence time of the palm oil and the methanol, respectively. The methyl ester concentration in the ester-rich phase at the outlet was 80.4 wt.%, while palm oil conversion and yield of methyl esters were 92.9% and 87.3%, respectively. Yield of methyl esters is defined in Eq. 2, where C_{TGo} and C_{TG} are the triglycerides (TG) concentrations at the reactor inlet and outlet, respectively, and C_{FAME} is the concentration of methyl esters at the reactor outlet. However, when the flow rate of palm oil diminished to 9.0 g min^{-1}, and the mean residence time of the palm oil increased to 5.0 min, the methyl ester concentration in the ester-rich phase at the outlet was 89.3 wt.%, while palm oil conversion was 97.5% and yield to methyl esters was 92.2% of theoretical yield. The reactor appears to reach the steady state after 40 min, nine and four times the mean residence time of the palm oil and the methanol, respectively.

$$\mathrm{Yield}_{\mathrm{FAME}} = \frac{100C_{\mathrm{FAME}}}{3(C_{\mathrm{TGo}} - C_{\mathrm{TG}})} \tag{2}$$

Figure 4 shows the typical performance of the LLFR, including the overall concentrations at the outlet of the four experimentally tested reactors, $L/L_{\max}$ 0.24, 0.56, 0.78 and 1.0. Values in Fig. 4 are the average of the steady state data for two tests; error bars correspond to the standard deviation. Concentration of methyl ester increases with the reactor length, while concentrations of DG and MG have a maximum and then diminish. The largest increase in the methyl ester concentration was observed between the inlet of the reactor and $L/L_{\max}$ 0.24, which corresponds to the maximum reduction of the concentration of palm oil. This behavior is a consequence of the kinetics of the palm oil methanolysis, which shows the highest rate within the first minutes of reaction [21, 22]. The maximum concentration of DG was observed at a lower reactor length than the maximum concentration of MG, which confirms that there are three stepwise reactions in the transesterification of a triglyceride (TG) [22]. In the reactors of $L/L_{\max}$ 0.56, 0.78 and 1.0, the experimental concentration of MG is higher than the concentration of DG, which indicates that MG seems to accumulate during the reaction. This behavior suggests that the rate-limiting step is the glycerol (G) formation from MG, as it was proposed by Stavarache et al. [23], who reported that under ultrasonic activation the rate-determining reaction switches from DG ↔ MG to MG ↔ G.

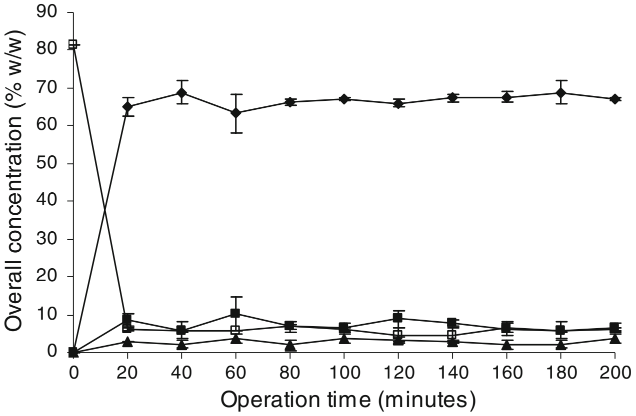

Fig. 3 Overall concentration of palm oil, methyl esters, monoglycerides and diglycerides at the outlet of the LLFR of $L/L_{\max}$ 1.0, during the palm oil methanolysis. Palm oil flow rate 27.0 g min^{-1}, methanol to oil molar ratio 6:1, temperature 60 °C, 1 wt.% NaOH based on palm oil. (Filled diamond) methyl esters; (filled square) monoglycerides; (filled triangle) diglycerides; (square) palm oil

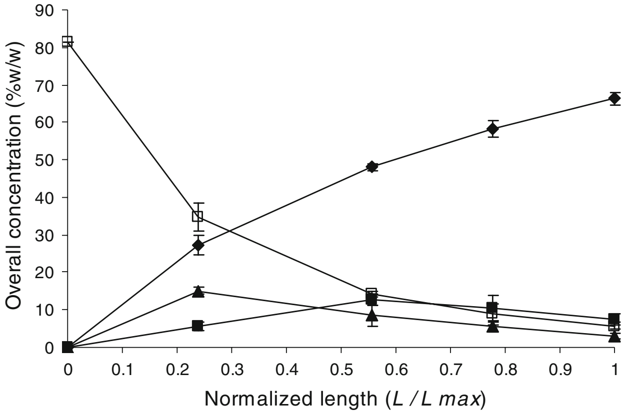

Fig. 4 The effect of the LLFR length on the overall concentration of some feedstock and products during palm oil methanolysis. Palm oil flow rate 27.0 g min^{-1}, methanol to oil molar ratio 6:1, temperature 60 °C, 1 wt.% NaOH based on palm oil. (Filled diamond) methyl esters; (filled square) monoglycerides; (filled square) diglycerides; (square) palm oil. Experimental data correspond to the steady state behavior of the reactor

To estimate the behavior at greater lengths, a mathematical model of the LLFR was used to predict the conversion and yield. Since the co-current flow system's behavior is closer to plug flow, as confirmed by the RTD study, the model is based on the ideal tubular-flow reactor equations presented by Smith [20]. In the LLFR model, the reactor volume was calculated from an equivalent diameter obtained from the empty volume fraction determined in the RTD study (8.92×10^{-3} m at 9.0 g min^{-1} and 9.83×10^{-3} m at 27.0 g min^{-1}). Reaction kinetics coupled to the reactor model was presented by Narváez et al. [21].

Table 2 Effect of the LLFR length on experimental (Exp.) and predicted (Pred.) palm oil conversion and yield of methyl esters during palm oil methanolysis

Normalized reactor length L/L_{max}	Palm oil mass flow rate (g min^{-1})							
	9.0				27.0			
	Palm oil conversion (%)		Yield of methyl esters (%)		Palm oil conversion (%)		Yield of methyl esters (%)	
	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
0.24	77.4 ± 2.1	75.4	71.2 ± 2.0	74.9	57.4 ± 1.6	54.1	58.1 ± 1.8	56.9
0.56	95.2 ± 1.4	94.3	83.6 ± 2.0	90.8	82.6 ± 2.7	76.1	71.0 ± 2.8	74.4
0.78	96.6 ± 1.8	97.3	91.2 ± 2.7	93.8	89.1 ± 2.7	83.8	79.6 ± 2.0	80.7
1.0	97.5 ± 2.5	98.9	92.2 ± 2.5	95.4	92.9 ± 1.0	89.6	87.3 ± 2.0	86.0
1.3*	–	99.8	–	96.1	–	96.2	–	89.4
1.6*	–	99.9	–	96.5	–	98.8	–	92.6

Methanol to oil molar ratio 6:1, temperature 60 °C, 1 wt.% NaOH based on palm oil

* Conversion and yield for these normalized reactor lengths were extrapolated from the adjusted model

Table 2 shows the experimental palm oil conversion and yield of methyl esters at the outlet of each reactor evaluated as well as the predicted values for modeled reactors of L/L_{max} 1.3 and 1.6. Experimental values correspond to the average of the steady state data for two tests; standard deviation is included. Experimental data in Table 2 are monotonically growing with increasing reactor length; a similar behavior is shown by the model, which represents the conversion of palm oil and the yield of methyl esters in a LLFR, with satisfactory coefficients of determination ($R^2 > 0.994$ for conversion and >0.996 for yield). Predictions suggest conversion and yield could be close to the required in the biodiesel industry.

Figure 5a and b shows the effect of the palm oil flow rate on conversion of palm oil and yield of methyl esters at different normalized reactor lengths including the conversion and yield predicted by the model. Differences in conversion and yield between the two studied flow rates are a consequence of the increase in the mean retention time when the flow rate of palm oil diminishes; however, these differences are reduced at higher reactor lengths because kinetics and chemical and physical equilibrium seem to govern the reactor performance. At any flow rate, the increase in conversion and yield per unit length was higher between normalized reactor lengths, L/L_{max}, from 0 to 0.56, and lower from L/L_{max} 0.78 to 1.0. This behavior was more noticeable at a flow rate of 9.0 g min^{-1}, where conversion and yield increased by less than 2% when the reactor length changed from L/L_{max} 0.78 to 1.0.

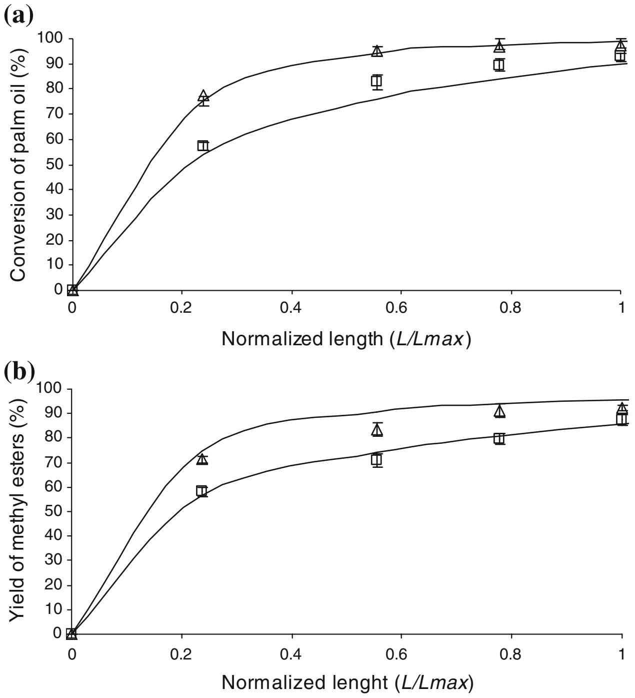

Fig. 5 Effect of the palm oil flow rate on (**a**) conversion of palm oil, (**b**) yield of methyl esters during palm oil methanolysis in a LLFR. Methanol to oil molar ratio 6:1, temperature 60 °C, 1 wt.% NaOH based on palm oil. (Triangle) flow rate 9.0 g min^{-1}; (square) 27.0 g min^{-1}. The *solid lines* represent conversion and yield predicted by the mathematical model of the LLFR. Experimental data correspond to the steady state behavior of the reactor

Yields of methyl esters obtained in the LLFR and presented in Table 2 and Fig. 5b are lower than those obtained by Noureddini et al. for the continuous methanolysis of soybean oil in a tubular reactor with static and high shear mixers [2], in excess of 98% in a total reaction time of 6–8 min, but they are in the range achieved in a continuously stirred tank reactor (CSTR) and in a reactive distillation system (RD). Darnoko and Cheryan [1] reported an average yield of methyl esters of 89.5% for the methanolysis of palm oil in a CSTR at 60 °C, methanol to oil molar ratio 6:1, 1 wt.% of KOH based on oil as catalyst and a residence time of 60 min, while Cheah et al. [6]

reported conversions of palm oil to methyl ester of 85% and 97% at the exits of the first and the second CSTR, respectively, at 70 °C and a molar ratio of 6:1, but using 0.35 wt.% of NaOH as catalyst. He et al. [4] reported a conversion of 95.6% and a yield of 91.3% for the canola oil methanolysis in a RD system when temperature was 65 °C, concentration of KOH was 1 wt.%, palm oil flow rate was 4.95 mL min^{-1}, methanol to oil molar ratio was 4.0:1, and total retention time was 3 min.

Figure 6 shows the effect of the concentration of catalyst on concentration of methyl esters. At the two flow rates evaluated and especially when the concentration of NaOH was 0.60 wt.%, the concentration of methyl esters as a function of the normalized reactor length, Fig. 6a, suggests a sigmoidal shape since it changes from completely concave (27 g min^{-1}, 0.60 wt.%) to completely convex (9 g min^{-1}, 1 wt.%). As the reaction kinetics at 60 °C for 0.6 wt.% and 1 wt.% of NaOH are practically identical [21], the observed differences between curves at the same flow rate and different percentage of catalyst in Fig. 6a are probably caused by mass transfer limitations in the reactor, associated with both hydrodynamic phenomena and/or differences in the concentration gradient of the catalyst.

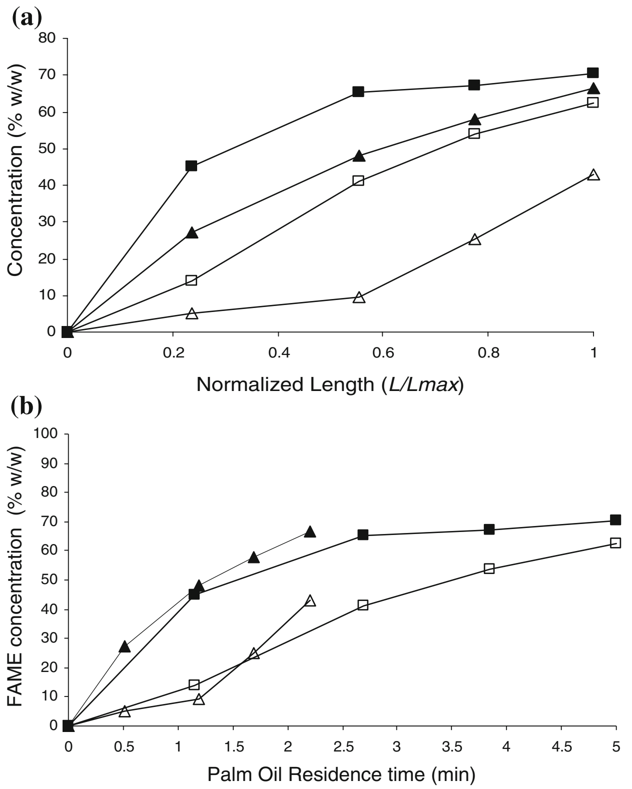

Fig. 6 Effect of the concentration of catalysts on the overall concentration of methyl esters during the palm oil methanolysis in a LLFR as a function of (**a**) Normalized length and (**b**) Palm oil residence time. A methanol to oil molar ratio 6:1, temperature 60 °C. (Square) palm oil flow rate 9.0 g min^{-1} and 0.60 wt.% NaOH; (filled square) palm oil flow rate 9.0 g min^{-1} and 1 wt.% NaOH; (triangle) palm oil flow rate 27.0 g min^{-1} and 0.60 wt.% NaOH; (filled triangle) palm oil flow rate 27.0 g min^{-1} and 1 wt.% NaOH. Experimental data correspond to the steady state behavior of the reactor

For tests at the same flow rate and different concentration of catalyst, hydrodynamic behavior is the same because the only difference was the change on concentration of catalyst (NaOH) in the methanol from 2.5×10^{-2} g g solution^{-1} to 4.2×10^{-2} g g solution^{-1}. As Fig. 6b shows and the ANOVA confirmed, the difference in concentration of catalyst seems to have a greater influence on the concentration of methyl esters than the flow rate does.

There has been wide discussion concerning the reaction mechanism and where the reaction actually takes place; Zhou et al. [13] and Boocock et al. [24] suggested that the reaction occurs in the bulk of the alcohol-rich phase; on the other hand, Dasari et al. [25] presented evidence that reaction rates are limited by methanol solubility in the ester-rich phase, suggestive that the reaction actually takes place in the bulk of the ester-rich phase. Ma et al. [15] and Ataya et al. [26] postulated that the reaction occurred at the interface, where reactants are actually in contact.

The results from Fig 6b show the concentration of the catalyst in the methanol-rich phase strongly affects the extent of the reaction from the *beginning* of the reaction although the intrinsic kinetics at both catalyst concentrations are practically identical [21]. This behavior is incompatible with the reaction taking place in the bulk of the methanol-rich phase because in such phase there is no initial gradient of the methoxy ion as the methanol is in a large excess, the methoxy ion is not consumed and its initial concentration is homogeneous in the fed methanol; the only reason to generate a gradient in the methanol-rich bulk phase is as a result of mass transfer from the reaction zone towards the methanol-rich bulk phase that would dilute the methoxy ion, but the formation of G from MG is small in the initial length of the reactor, as it can be deducted from Fig. 4 (1.6 wt.% for the reactor of L/L_{max} 0.24), and the solubility of methyl esters and palm oil (the other two compounds present in relatively large concentration) in methanol at 60 °C are <1 wt.% [27] and <0.3 wt.% (measured in this work), respectively.

Therefore, the results obtained in the present work are compatible with the reaction actually taking place in a thin film forming at the interface between alcohol-rich and methyl ester-rich phases but within the ester-rich phase. In this case, the methoxy ion would need to migrate from the bulk of the methanol-rich phase to this film; that would explain why a bigger concentration of NaOH has such an important effect on the extent of the reaction. To further support this hypothesis, the presence of NaOH was experimentally found in the bulk of the ester-rich phase (as measured by titration), as Chiu et al. reported too [28].

Moreover, although solubility of methanol in palm oil at 60 °C is about 10 wt.%, when the reaction advances at the very early stages forming methyl esters, the solubility of methanol in the ester-rich phase at 60 °C increases, reaching values as high as 61 wt.% [27]; this increment in solubility reduces the limitation in reaction rate by methanol transfer, highlighting the effects of the transfer of the methoxy ion.

Leevijit et al. [11] reported the effect of the residence time and the percentage of catalyst (NaOH) in the purity of methyl esters, for the palm oil methanolysis at 60 °C and a methanol to oil ratio of 6:1 in a 6-stage continuously stirred tank reactor; such multi-stage perfectly well mixed reactor approaches the behavior of a plug-flow reactor when the number of stages goes to infinity [20]. Under the mentioned conditions, an augment in residence time increases the purity of methyl esters but saturation is observed after 6–9 min depending on the catalyst concentration. The reported methyl ester purity for a palm oil methanolysis at 1 wt.% catalyst was 97.5% and 99.2% when the residence time was 6 and 12 min, respectively; those results follow the same trend of the curve for flow rate of 9 g min^{-1} and 1 wt.% catalyst in Fig. 6, but are slightly larger than those for the LLFR at similar residence times.

Two phases were observed at the reactor outlet in every test, even in the reactor of L/L_{max} 0.24, where the concentration of methyl esters was as low as 27.3 wt.% and the concentrations of MG and DG were as high as 5.7 wt.% and 15.1 wt.%, respectively. The time to separate the effluent phases of the LLFR at the highest experimental values of conversion and yield, reactor of L/L_{max} 1.0, palm oil flow rate 9.0 g min^{-1} and 1.0% of NaOH as catalyst, was less than 5 min, while usually the residence time in separators down stream of the tubular reactor ranges between 15 min and 2 h [3]. The presence of emulsions or gels was not observed. This difference could be an effect of the generation of interfacial area without dispersing the alcoholic phase in small droplets inside the oily phase. During the residence time of 5 min in the funnel, conversion of palm oil and yield of methyl esters increased from 97.5% and 92.2% to 98.9% and 96.9%, respectively; in this case, there was no temperature control, so the temperature of the mixture was at some point between 60 °C and ambient temperature (20 °C).

Finally, for a modeled reactor of L/L_{max} 1.6 at a flow rate of palm oil of 27 g min^{-1}, the model predicts productivity of about 7.9 m^3 FAME per m^3 reactor volume per hour, which is higher than the productivity of 6.6 m^3 FAME per m^3 reactor volume per hour of a reactive distillation system [4]. The predicted productivity is also about 7–11.5 times higher than that of a batch process [4], 2.6 times the productivity of an ultrasonically driven continuous reactor [10] and very similar to the reported by Leevijit et al. [11] for a 6-stage continuously stirred tank reactor, which remarkably resembles closely the behavior of the studied LLFR, according to the RTD analysis.

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