



# Biodiesel synthesis with alkaline catalysts: A new refractometric monitoring and kinetic study



Matthieu Tubino<sup>a,\*</sup>, José Geraldo Rocha Junior<sup>a,b</sup>, Glauco Favilla Bauerfeldt<sup>b</sup>

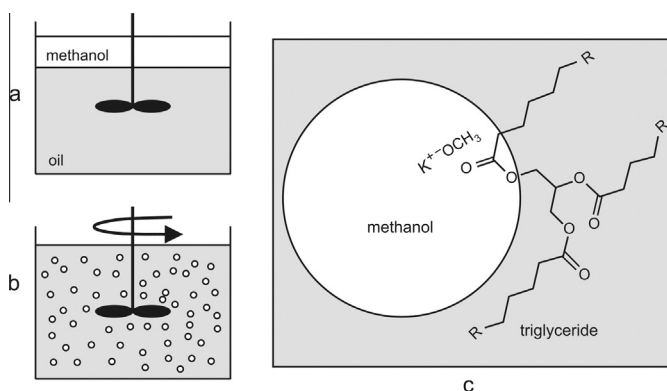
<sup>a</sup> University of Campinas, Institute of Chemistry, P.O. Box 6154, 13083-970 Campinas, SP, Brazil

<sup>b</sup> Universidade Federal Rural do Rio de Janeiro, Department of Chemistry, BR-465, Km 7, 23.897-000 Seropédica, RJ, Brazil

## HIGHLIGHTS

- The online monitoring method proposed is relatively simple and inexpensive.
- Two steps were identified in the alkaline methanolysis of triglycerides.
- The mixing step consumed most of the time of the overall reaction.
- The kinetics of methanolysis are best described by a zero-order model.
- The catalysis of methanolysis with KOCH<sub>3</sub> should be described as heterogeneous.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, an experimental system was designed to allow the online monitoring of a chemical reaction in continuous flow leading to biodiesel synthesis using a portable digital refractometer. The proposed method was applied to the monitoring of the methanolysis of soybean oil using KOCH<sub>3</sub> as the catalyst at temperatures from 30 to 60 °C, allowing data acquisition in a relatively simple, reliable and cheap fashion. It was also possible to identify, discriminate and monitor the mixing (emulsification) and the reaction steps, with the former being the rate determinant. The methanolysis reaction is better represented by a zero-order kinetic scheme than by a pseudo-first-order scheme; the activation energy was determined to be  $(31.3 \pm 1.8)$  kJ mol<sup>-1</sup>. This behavior suggests that methanolysis with alkaline catalysts, usually considered as a homogeneous process, should in fact be assumed to be heterogeneous. Therefore, the rate of mixing controls the reaction kinetics and is a key factor in decreasing the transesterification time.

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## 1. Introduction

The instability of the petroleum market, the limited availability of crude oil and particularly the environmental impact related to the use of fossil fuels have been encouraging the use of alternate

fuels. Biodiesel is an alternative fuel to petroleum diesel, and much attention has been given to the processes related to the synthesis and application of the biodiesel worldwide [1]. From a chemical composition point of view, biodiesel is a mixture of fatty acid alkyl esters obtained from renewable raw materials such as vegetable oils and animal fats. Transesterification is the most employed process for obtaining biodiesel, in which the triglycerides react with

\* Corresponding author. Tel.: +55 01935213133.

E-mail address: [tubino@iqm.unicamp.br](mailto:tubino@iqm.unicamp.br) (M. Tubino).

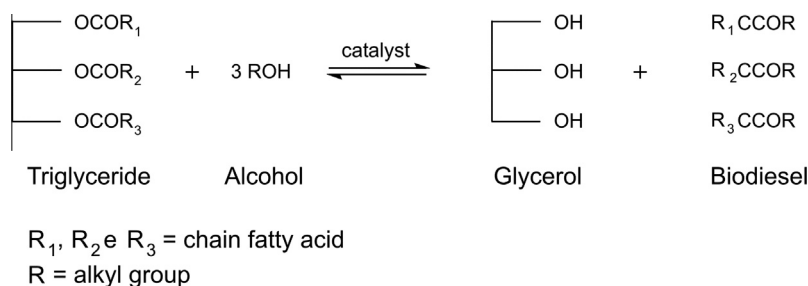


Fig. 1. General chemical equation of a triglyceride transesterification.

low molecular weight alcohols (the alcoholysis reaction), such as methanol and ethanol (Fig. 1).

Biodiesel is commonly produced by the transesterification of triglycerides with methanol (the methanolysis reaction) and alkaline compounds such as NaOH, NaOCH<sub>3</sub>, KOH and KOCH<sub>3</sub>, the most employed and studied catalysts. The global transesterification process can be described by consecutive and reversible steps in which diglycerides and monoglycerides are intermediates and glycerol is a byproduct (Fig. 2). Because each step is reversible, the alcohol is added in excess in relation to the initial amount of triglycerides to achieve the maximum generation of product (biodiesel and glycerol). Although the reaction proceeds via the simple mixing of the reactants, the use of catalysts is always necessary to rapidly achieve maximum conversion.

The kinetic equations are expressed as follows:

$$\frac{d[\text{TG}]}{dt'} = -k_1[\text{TG}]^j[\text{ROH}]^k + k_{-1}[\text{DG}]^l[\text{BD}]^m$$

$$\frac{d[\text{DG}]}{dt'} = k_1[\text{TG}]^j[\text{ROH}]^k + k_{-2}[\text{MG}]^n[\text{BD}]^o - k_{-1}[\text{DG}]^l[\text{BD}]^m - k_2[\text{DG}]^p[\text{ROH}]^q$$

$$\frac{d[\text{MG}]}{dt'} = k_2[\text{DG}]^p[\text{ROH}]^q + k_{-3}[\text{GL}]^r[\text{BD}]^s - k_{-2}[\text{MG}]^n[\text{BD}]^o - k_3[\text{MG}]^t[\text{ROH}]^u$$

$$\frac{d[\text{BD}]}{dt'} = k_1[\text{TG}]^j[\text{ROH}]^k + k_2[\text{DG}]^p[\text{ROH}]^q + k_3[\text{MG}]^t[\text{ROH}]^u - k_{-1}[\text{DG}]^l[\text{BD}]^m + k_{-2}[\text{MG}]^n[\text{BD}]^o - k_{-3}[\text{GL}]^r[\text{BD}]^s$$

$$\frac{d[\text{GL}]}{dt'} = k_3[\text{MG}]^t[\text{ROH}]^u + k_{-3}[\text{GL}]^r[\text{BD}]^s$$

where  $j, k, l, m, n, o, p, q, r$  and  $s$  are the orders with respect to each reactant.

Several authors have adopted this set of equations for the kinetic study of the alcoholysis of vegetable oils. The concentrations

are determined by any analytical method, and the set of differential equations is analytically (or numerically) solved, assuming values for the indexes  $j, k, l, m, n, o, p, q, r$  and  $s$  [2–6]. Richard and coworkers have also explicitly included the catalyst in the reaction rate equation, assuming a third-order reaction law [7].

In some reports, the kinetic scheme is simplified with respect to the reversible/consecutive reaction scheme shown in Fig. 2, assuming either irreversible/non-consecutive schemes [8], pseudo-first-order reaction schemes [9,10] or pseudo-second-order steps [10]. Models considering only the first (irreversible) step (triglyceride → diglyceride) [10] or the global reaction (triglyceride → biodiesel) [11–13] can also be found. A change in the reaction rate law along the course of the reaction (assuming pseudo-first-order kinetics at the initial stage and first- or zero-order kinetics at the final stage) has also been discussed [8]. A treatment of the global reaction as a zero-order kinetic process, to the best of our knowledge, has not been presented until now, although zero-order kinetics has been attributed to last reaction step while the initial steps have been treated with different orders, especially for the very beginning of the reaction [8,12]. This analysis suggests that the kinetics of biodiesel synthesis is an open question.

Despite the previous work available in the literature [5,11,13,14], a new study of the kinetic behavior of alkaline methanolysis can increase the understanding of the parameters that control the global process rate and identify the most relevant factors that should lead to the optimization of the biodiesel synthesis.

An apparent consensus related to the alkaline catalysts is that the maximum conversion is achieved after 1 h at 60 °C and a methanol:oil molar ratio of 6:1 [15]. However, some reports suggest that maximum conversion is observed at shorter times, such as 20 min at similar conditions [16,17] or 5 min for a 90% conversion of triglycerides to methyl esters [16–19].

The fast conversion observed for the methanolysis reaction makes most of the analytical methods usually adopted for monitoring the biodiesel synthesis, especially chromatographic methods, inadequate for a kinetic investigation. These analytical methods are not applicable for consecutive determinations in such small time intervals due to analytical limitations, such as the

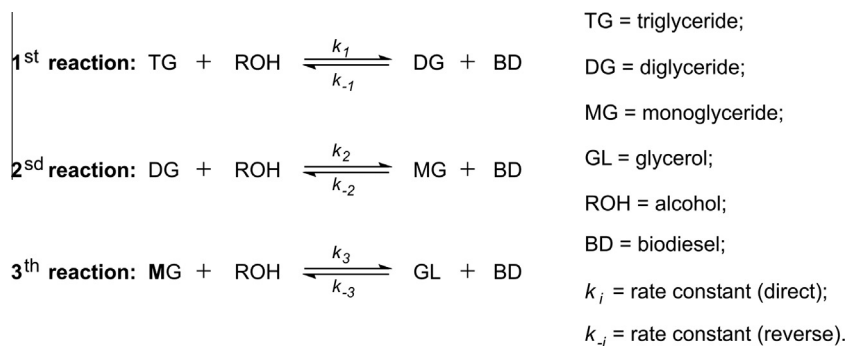


Fig. 2. Representative scheme for the sequential steps of the transesterification of a triglyceride.

necessity of sample preparation and derivatization, tedious calibrations and long analytical times. Other difficulties for the industrial implementation of such techniques are the generally high cost of the instruments and qualified personnel required for the acquisition of data and interpretation of the results. Moreover, despite the high sensitivity of these techniques, the time interval in which most of the reaction occurs cannot reliably monitored. Nevertheless, a considerable amount of work is reported in the literature regarding kinetic investigations based on such analytical methods [5,8,12,14,20,21].

For proper online monitoring and kinetic investigation of biodiesel synthesis, analytical methods based on physical properties such as viscosity, specific gravity and refractive index may be an alternative solution.

The monitoring of biodiesel synthesis based on measurements of the refractive index was first reported by Xie and Li [22]. The authors determined the conversion of soybean oil in samples obtained at different times, assuming a linear relation between the refractive index and the yield of methyl esters (0% conversion corresponded to the refractive index of unconverted soybean oil,  $n = 1.4704$  and 100% conversion to the refractive index of biodiesel,  $n = 1.4515$ ). The authors also reported that these results did not differ from those obtained by  $^1\text{H}$  NMR analysis by more than 4%. A linear correlation between the results based on the measurements of the refractive index (and other physical properties, such as specific gravity and flash point) and GC/FID results has also been observed, with the refractive index the most reliable physical property for the determination of the yield of biodiesel, showing the smallest relative errors in relation to the GC/FID results [19]. The measurement of the refractive index showed also good performance in the monitoring of the transesterification of soybean oil with ethanol [23]. However, none of these reports has employed refractometry as an online monitoring technique. For such a fast global reaction with reversible steps, taking a sample of the reaction mixture for further analysis can represent a significant delay between the actual and measured composition values.

For online monitoring of biodiesel synthesis based on measurements of the refractive index, digital refractometers are recommended because the measurement time is relatively small (ca. 5 s), and the data can be computationally acquired.

In this work, a digital refractometer was used for online monitoring of the transesterification of soybean oil with methanol in a continuous-flow system. Our main goals are to investigate the implementation of this technique for online monitoring (eliminating the problems caused by batch sampling and delayed analysis, with the further advantage of the possibility of a higher number

of measurements along a relatively small reaction time) and the re-evaluation of the kinetic scheme of this reaction.

## 2. Materials and methods

### 2.1. The monitoring device

The system employed to monitor the biodiesel synthesis consisted of a round-bottomed flask (300 mL), a refractometer (Mettler, model Refracto® 30GS, Fig. 3a), a thermostatic bath (Lauda RCS  $\pm 0.02$  °C), a peristaltic pump (Ismatec mp13 GJ4), a double helix (10 mm) mechanical mixer and two homemade phase separators. A Teflon® conical device with two holes (Fig. 3b) was also constructed in our laboratory to support the two capillary tubes that conducted the reaction mixture in and out of the refractometer sample cell, allowing the reaction to be monitored in a continuous flow regime. The first phase separator (Fig. 4a) is an acrylic cylindrical device (6 mm internal diameter and 10 mm height) with three holes at the top where three capillary tubes are inserted. The first tube leads the sample mixture to the phase separator, the second collects the denser (glycerol) phase and the third collects the lighter (biodiesel) phase. A second phase separator (Fig. 4b) consists of a quadrangular acrylic device with three faces perforated up to the center. The biodiesel enters horizontally through one of the faces and as it reaches the center of the device, air bubbles flow up vertically. The liquid biodiesel phase is finally conducted vertically down to the refractometer sample cell.

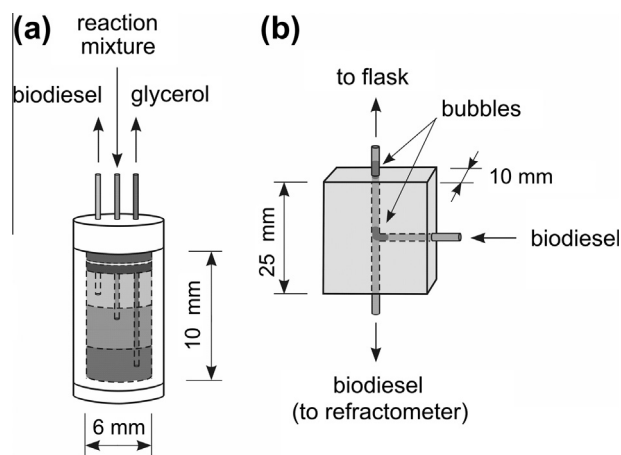


Fig. 4. Phase separators. (a) Liquid-liquid, S1, and (b) gas-liquid, S2.

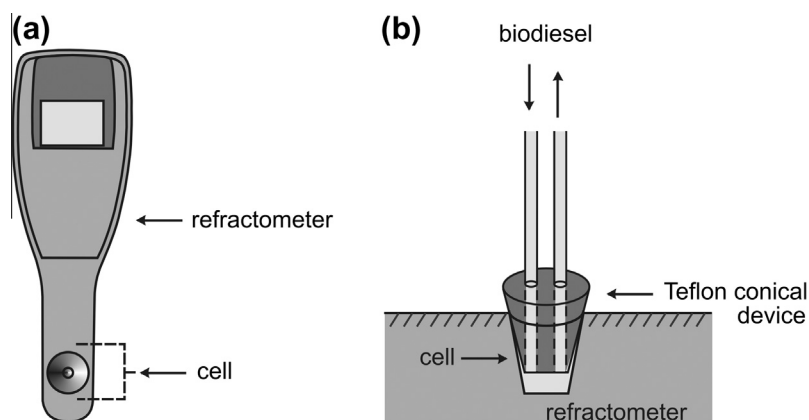


Fig. 3. (a) Refractometer; (b) conical device adapted to the refractometer sample cell.

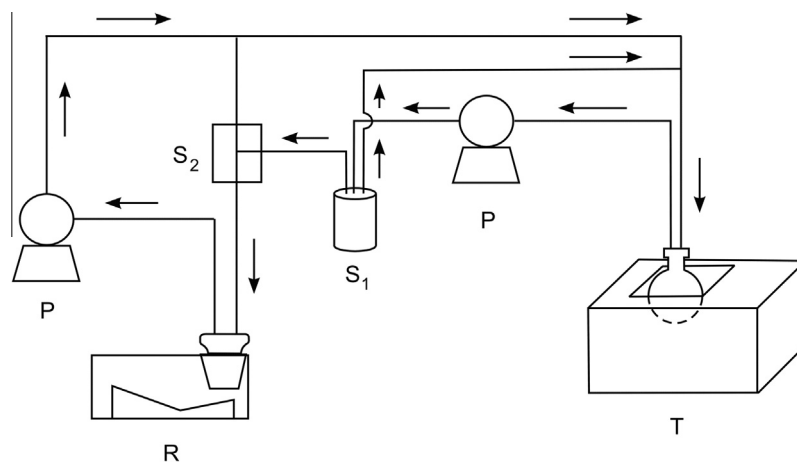


Fig. 5. The continuous flow system used in the reaction monitoring.

The importance of separating the glycerol from the reaction mixture is because the glycerol, being denser than biodiesel, should decant at the sample cell, impairing the refractometer index measurement. Gas bubbles could significantly reduce the volume of biodiesel at the sample cell, which might also prejudice the measurement.

The continuous flow system for monitoring the reaction (Fig. 5) was made in such a way that the reaction mixture is pumped from the round-bottomed flask to the phase separators, whereas the isolated biodiesel is transferred to the refractometer sample cell and then transferred back to the round-bottomed flask. The glycerol also returns from the first-phase separator to the reaction mixture.

## 2.2. The synthesis of biodiesel

The round-bottomed flask with 150.0 g of soybean oil was immersed in the thermostatic bath, and the oil was allowed to flow through the monitoring system at a volumetric flow rate of  $1 \text{ mL min}^{-1}$ . A flask containing 30.0 g of methanol (Synth, 99.8%) and 1.09 g  $\text{KOCH}_3$  (25% in methanol, *Sigma-Aldrich*) was also immersed in the thermostatic bath and, after thermal equilibrium was achieved, the mixture was rapidly added to the round-bottomed flask under mechanical agitation at 400 rpm. The chronometer was immediately started after addition. Experiments were performed in triplicate, at temperatures of 30.0, 40.0, 50.0

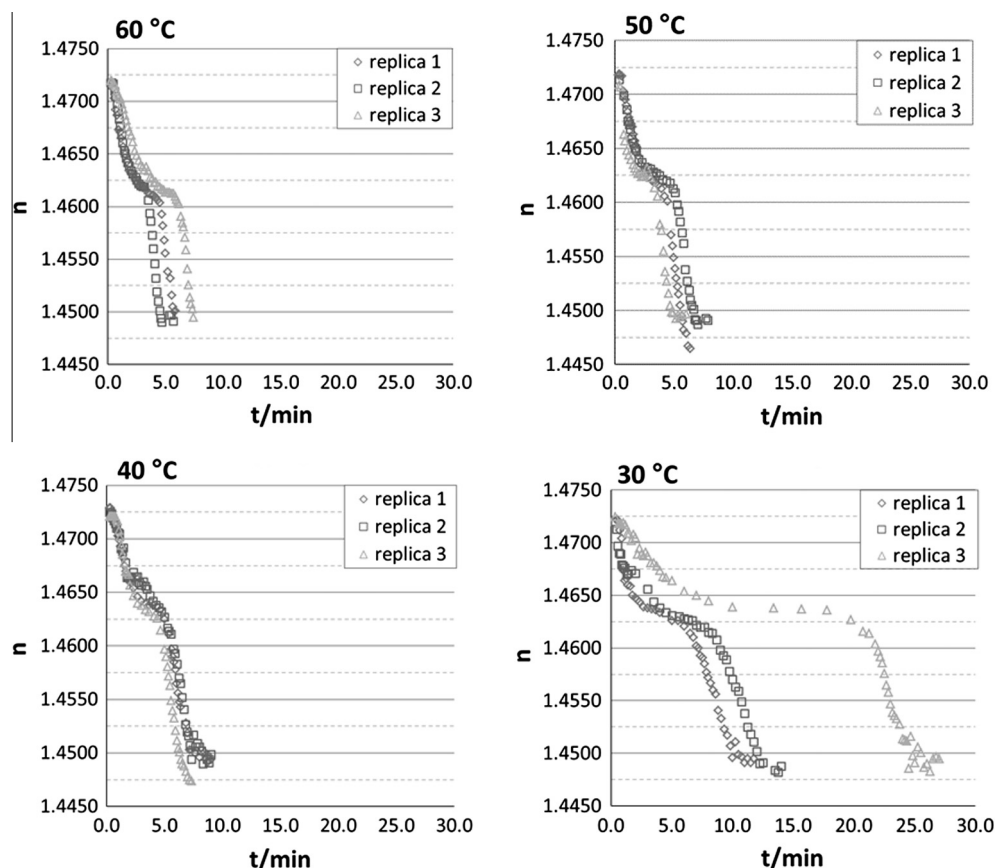


Fig. 6. Refractive index monitoring of the conversion of soybean oil into biodiesel at different temperatures (in triplicate).

and 60.0 °C. The determinations of the refractive index were performed at 5-s intervals, with a correction for the standard temperature (20 °C). The experiments were monitored up to equilibrium, when the refractive index reached a constant value.

An additional experiment was conducted in the absence of the catalyst to determine the mixing (emulsification) time and, therefore, identify the region of the global reaction profile that corresponds to the mixing and the region that is related to the transesterification reaction itself.

### 3. Results and discussion

#### 3.1. Online monitoring of biodiesel synthesis using refractometry

The monitoring system allowed the acquisition of the refractive index of the reaction mixture in real time. Although the reaction

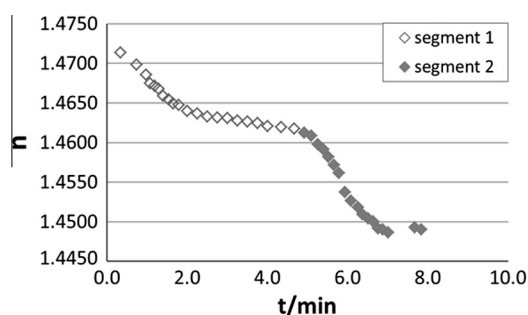


Fig. 7. Refractive index monitoring of the conversion of soybean oil into biodiesel at 50 °C.

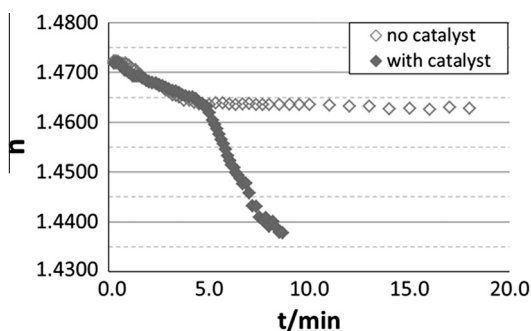


Fig. 8. Refractive index monitoring of the conversion of soybean oil into biodiesel at 50 °C with and without catalyst.

progress must also be considered during the course of the sample from the reaction flask to the refractometer sample cell (it took the sample 40 s to reach the refractometer sample cell), the cooling of the reaction mixture and phase separation both contributed to a decrease in the reaction rate. It is therefore expected that the measured refractive index values correspond to the amount of biodiesel in the reaction flask.

Fig. 6 shows the reaction profiles, expressed as the refractive index values versus time, for the several triplicate experiments conducted at different temperatures. The refractive indexes varied from values slightly above 1.4720 to approximately 1.4450, correlating well with the values found for the isolated soybean oil (1.4729) and the biodiesel [25]. In these reaction profiles, two regions are observed, both showing an initial sharp decrease of the refractive index followed by a slower decrease, as shown in Fig. 7. Because the oil is slightly soluble in methanol, and the measurements were started just after the addition of the KOCH<sub>3</sub>/methanol mixture to the reaction flask, the variation of the refractive index in the first instants of monitoring (the first decrease observed in Fig. 7) can be attributed to the dilution of the oil as a consequence of the formation of a methanol–oil mixture. This is corroborated by the experiments conducted in the absence of the catalyst, shown in Fig. 8, in which a coincidence of the refractive index values obtained in the experiment without a catalyst and the first segment of the reaction profile is observed. In the absence of the catalyst, no significant conversion is observed (the refractive index values of the oil ranged from 1.4740 to 1.4732), and it can be determined that the variation of the refractive index values is only due to dilution. The reaction itself is therefore observed in the second region of the registered curve, highlighted in Fig. 7. The values of the time spent for mixing the reactants ( $t_m$ ), methanolysis ( $\tau$ ) and the total conversion time ( $t_c$ ) of the triglycerides to biodiesel ( $t_c = t_m + \tau$ ) are shown in Table 1. A time  $t'$  was arbitrarily assumed for the separation of these regions, therefore setting the reaction initial time. The variation of the refractive index values,  $\Delta n$ , vs.  $t'$  is introduced in Fig. 9 (where  $t' < 0$  corresponds to the dilution and  $t' > 0$  to methanolysis).

The lack of coincidence of the curves in the region of  $t' < 0$  (Fig. 9) and the relatively high deviations found for the  $t_m$  values observed in Table 1 suggest low reproducibility in this step, which must be a consequence of the difficulties in controlling all the variables related to the mixing rate and dispersion of methanol in the oil phase. However, the superposition of the reaction segments ( $t' > 0$ ) obtained for all replicates (Fig. 9) and the relatively low deviations found for  $\tau$  (Table 1) are worth noting. This reproducibility is especially important for the investigation of the reaction kinetics.

Table 1

Mixing, methanolysis and total conversion times<sup>a</sup> ( $t_m$ ,  $\tau$  and  $t_c$ ) in minutes.

Temperature (°C)	Mixing time		Methanolysis time		Total conversion time	
	$t_m$	$\bar{t}_m \pm \sigma^b$	$\tau$	$\bar{\tau} \pm \sigma$	$t$	$\bar{t} \pm \sigma$
60	4.5		1.3		5.8	
	3.2	$4.5 \pm 1.4$	1.5	$1.4 \pm 0.1$	4.7	$6.0 \pm 1.4$
	5.9		1.5		7.4	
50	3.9	$4.0 \pm 1.0$	2.3	$2.1 \pm 0.3$	6.2	$6.1 \pm 0.8$
	5.0		1.8		6.8	
	3.0		2.2		5.2	
40	5.0	$4.8 \pm 0.3$	3.8	$3.5 \pm 0.6$	8.8	$8.3 \pm 0.9$
	5.0		3.8		8.8	
	4.4		2.8		7.2	
30	5.5	$11.4 \pm 8.2$	4.5	$5.3 \pm 0.7$	10.0	$16.7 \pm 8.7$
	8.0		5.5		13.5	
	20.7		5.8		26.5	

<sup>a</sup> Total conversion time ( $t_c$ ) = mixing time ( $t_m$ ) + methanolysis time ( $\tau$ ).

<sup>b</sup>  $\sigma$  = Standard deviation.



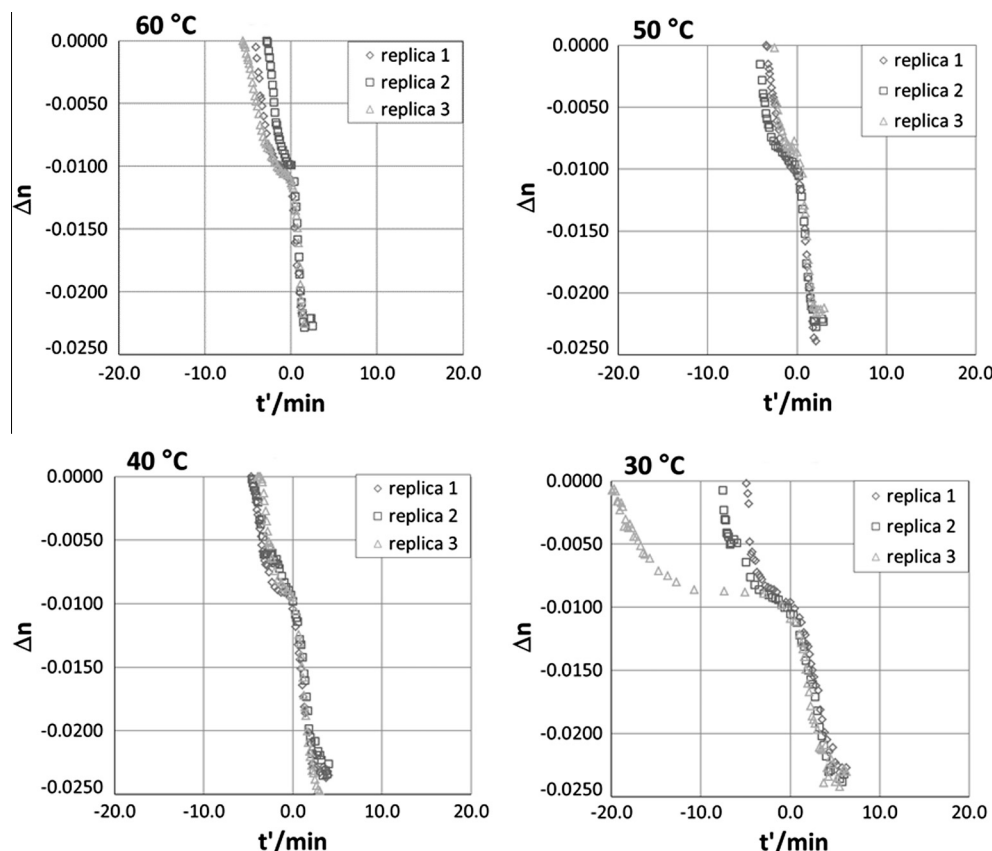


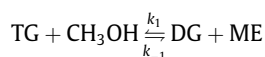
Fig. 9. Variation of the refractive index,  $\Delta n$ , as a function of time.

Table 1 also shows that the time  $t_m$ , spent for the reactant mixing was higher than the reaction time,  $\tau$ , for all cases, reaching 75% of the total conversion time,  $t_c$ , as, for example, in one of the methanolysis experiments conducted at 60 °C. The analysis of the transport phenomena is beyond the scope of this work, and more investigation is encouraged, aiming for the best control of the reaction mixing rate to optimize the global reaction time and conversion.

### 3.2. The kinetic investigation

The fundamental assumption for the investigation of the reaction kinetics in this work is that the global process is controlled by the first transesterification step, represented in Fig. 2, related to the attack of the methanol on the triglyceride, forming the diglyceride. This assumption is based on the fact that the long side chains must protect the ester bonds from nucleophilic attack due to steric effects. The reaction is more difficult in the case of the unreacted triglycerides, where the first attack is the slowest and the rate-determining step. After the removal of the first long side chain, the other ester bonds are less protected, the subsequent nucleophilic attacks are faster, and the relation  $k_1 < k_2 < k_3$  is therefore expected.

In this way, the global variation of the refractive index values must be due to the following reaction:



We consider two kinetic models for this reaction, both treating the direct step as irreversible ( $k_1 \gg k_{-1}$ ): a pseudo-first-order kinetics and a zero-order kinetics. The pseudo-first-order model is justified by the excess of methanol in relation to the triglycerides in the reaction mixture, reducing the kinetics from a bimolecular

law to a pseudo-first-order reaction in which  $k_{st} = k_1 \times C$ , where  $C$  is the concentration of methanol, which is assumed to be a constant value, and  $k_{st}$  is the pseudo-first-order rate constant. The reaction law is then expressed as follows:

$$-r_{TG} = -\frac{d[TG]}{dt'} = k_{st}[TG] \quad (1)$$

leading to the following integrated equation (where  $[TG]_0$  and  $[TG]_t$  are the triglyceride concentrations at time  $t' = 0$  and time  $t'$  of the reaction):

$$\ln \frac{[TG]_{t'}}{[TG]_0} = -k_{st}t' \quad (2a)$$

The linear correlation observed between the refractive index and the methyl ester concentration in vegetable oil/biodiesel mixtures [19,25] allows the use of this property to follow the reaction kinetics. Taking  $n_0$ ,  $n_t$  and  $n'_t$  as the refractive index values corresponding to the initial ( $t' = 0$ ), final ( $t' = \tau$ ) and  $t'$  times, Eq. (2) can also be expressed as follows:

$$\ln \frac{\Delta n_{t'}}{\Delta n_{total}} = -k_{st}t' \quad (2b)$$

where  $\Delta n'_t$  is the variation of the refractive index from the starting of methanolysis ( $t' = 0$ ) to the  $t'$  instant and  $\Delta n_{total}$  is the total variation of the refractive index (from  $t' = 0$  to the instant  $\tau$ ).

Catalysts can be assumed to be homogeneous or heterogeneous. The zero-order kinetic model would better describe the methanolysis in case of a heterogeneous process. By definition, a homogeneous catalysis is observed at processes in which all the substances, including the catalyst, are found in the same phase. For heterogeneous catalysis, the reactants and the catalyst are found in different phases (usually, the catalyst is a crystalline or amorphous solid), so the reaction proceeds in a limiting interface

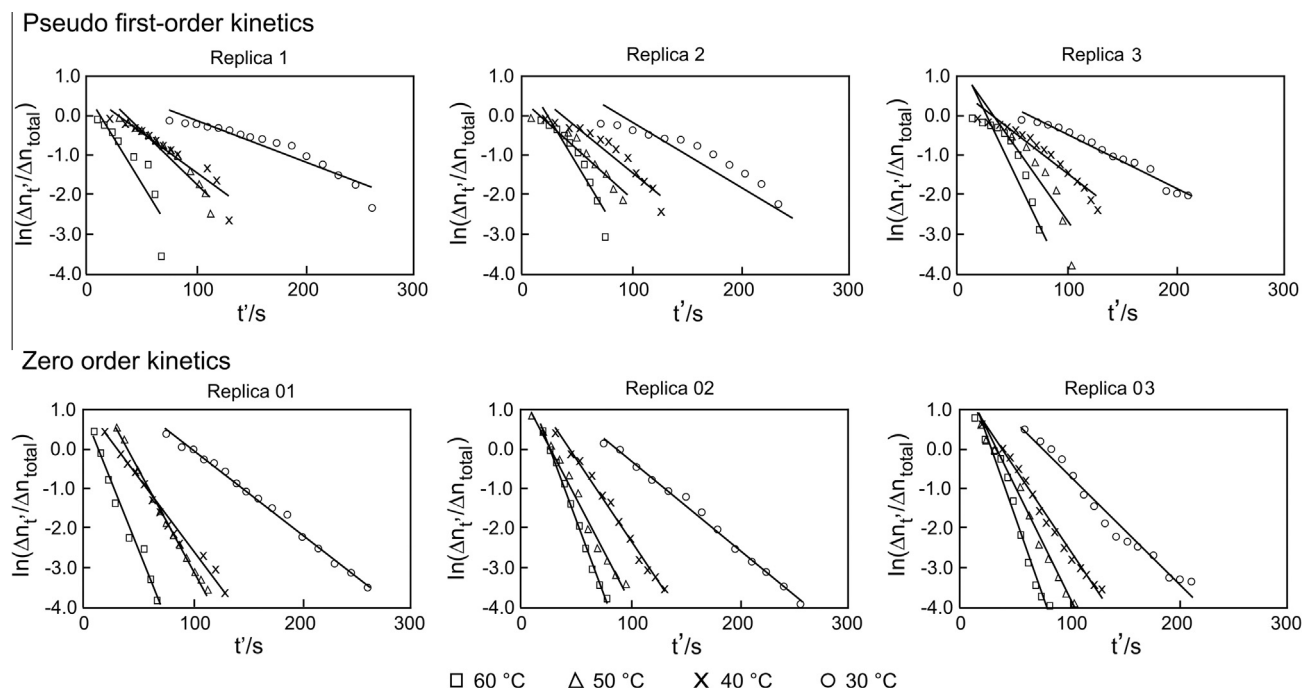


Fig. 10. Tests of the pseudo-first- and zero-order kinetic schemes.

[24]. Because the triglycerides and methanol are immiscible, two phases are observed in the reaction mixture, with the catalyst dissolved in the methanolic phase.

The rate equation is then expressed as follows:

$$-r_{TG} = -\frac{d[TG]_{t'}}{dt'} = k_0 \quad (3)$$

where  $k_0$  is the zero-order rate constant. The integrated equation is the following:

$$[TG]_{t'} - [TG]_0 = -k_0 t' \quad (4)$$

After dividing by  $[TG]_0$ , the following expression is obtained:

$$\frac{[TG]_{t'}}{[TG]_0} = -k_{obs} t' + 1 \quad (5a)$$

where  $k_{obs}$  is a new constant ( $k_0/[TG]_0$ ). Using the refractive index values, this equation is expressed as follows:

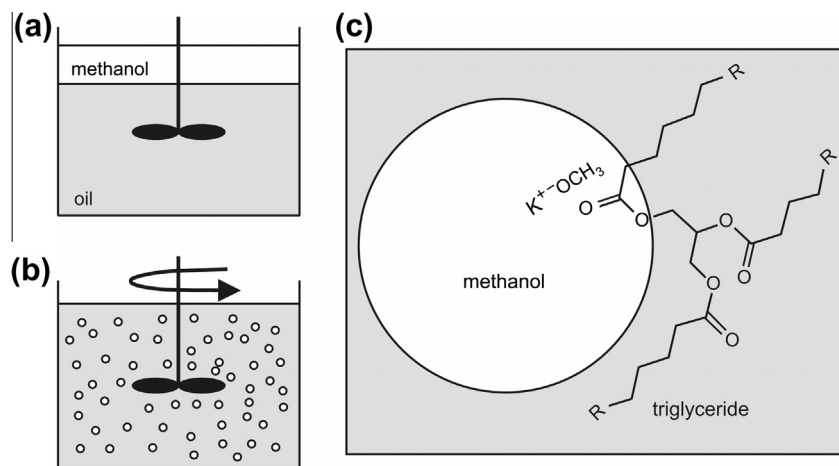
$$\frac{\Delta n_{t'}}{\Delta n_{total}} = -k_{obs} t' + 1 \quad (5b)$$

These models were tested on the basis of our experimental data in Fig. 10. Correlation coefficients are shown in Table 2. From Fig. 10 and the data in Table 2, it can be concluded that the reaction kinetics are better represented in the range of temperatures investigated in this work by the zero-order model, which is also consistent with the heterogeneous catalysis hypothesis assumed for this reaction catalyzed by  $KOCH_3$ .

The zero-order behavior may be justified because the reaction proceeds at the interface of the methanol/soybean oil mixture. In Fig. 11, the reaction in the interface is schematically represented. Agitation is responsible for the formation of droplets of one component (methanol or oil) in the bulk of the other phase. Methanolysis must proceed in the interfacial region, and the reaction rate must be augmented as the interfacial area increases. The process is not strictly related to the initial concentrations of the reactants. The emulsification process is governed by the mixing and physical chemical properties of the system and, once the

**Table 2**  
Rate constants (in  $\text{ms}^{-1}$ ) for the pseudo-first-order ( $k_{st}$ ) and zero-order ( $k_{obs}$ ) models at several temperatures ( $^{\circ}\text{C}$ ). The corresponding determination coefficient,  $R^2$ , is also shown.

Temperature ( $^{\circ}\text{C}$ )	Pseudo-first order rate constant			Zero order rate constant		
	$R^2$	$k_{st}$	$\bar{k}_{st} \pm \sigma$	$R^2$	$k_{obs}$	$\bar{k}_{obs} \pm \sigma$
60	0.800	46.2	$49.7 \pm 6.4$	0.976	13.8	$14.7 \pm 0.8$
	0.891	45.5		0.995	15.1	
	0.774	57.1		0.975	15.3	
50	0.934	26.4	$30.0 \pm 7.5$	0.995	10.0	$10.7 \pm 0.7$
	0.942	24.9		0.986	10.8	
	0.838	38.6		0.984	11.4	
40	0.888	20.0	$21.0 \pm 0.9$	0.984	7.31	$7.9 \pm 0.5$
	0.906	21.7		0.991	8.32	
	0.943	21.3		0.990	8.10	
30	0.901	10.5	$13.3 \pm 2.8$	0.994	4.30	$4.7 \pm 0.6$
	0.736	16.1		0.994	4.54	
	0.969	13.4		0.974	5.39	



**Fig. 11.** Schematic representation of the process of the formation of methanol droplets due to mechanical agitation (a); dispersion of the droplets in the oil phase (b) and the interfacial region (c).

maximum emulsification allowed for the system is achieved, it and the reaction rate must remain constant during the reaction.

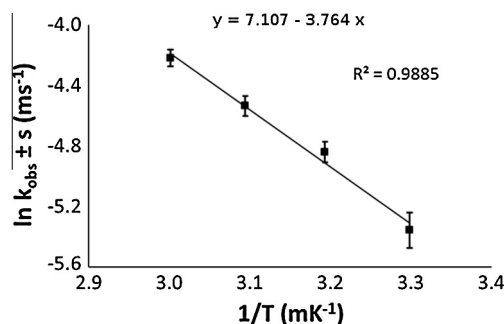
Although it is in molar excess in the reaction mixture, methanol contributes less than 20% of the volume of the methanol/oil mixture, suggesting that methanol is the dispersed component in the bulk of the oil phase. Moreover, the surface tension of the oil is greater than the value shown for the methanol ( $\gamma_{\text{methanol}} = 22.2 \text{ mN m}^{-1}$ ;  $\gamma_{\text{oil}} = 34.4 \text{ mN m}^{-1}$ ) [25,26], also suggesting that methanol is being dispersed in the oil.

The catalytic process should therefore be classified as heterogeneous and, considering all the discussions stated above, it is possible that the transesterification of a triglyceride follows the following general scheme: the catalyst, dissolved in methanol, is adsorbed in the methanol/oil interfacial region by attacking the carbonyl center of triglyceride and forming a glycerate ion, which further reacts with methanol, forming the diglyceride and the catalyst. With constant mechanical agitation, the size and number of methanol droplets are constant during reaction; therefore, the reaction rate is constant.

On the basis of a zero-order kinetic model and assuming the  $k_{\text{obs}}$  rate constants obtained at each temperature, the activation energy was determined assuming the following Arrhenius equation:

$$\ln k_{\text{obs}} = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad (6)$$

The Arrhenius plot is introduced in Fig. 12, and the curve is described by the equation  $y = 7.107 - 3.764x$  ( $R^2 = 0.9885$ ), where  $y$  is  $-\ln k_{\text{obs}}$  and  $x$  is the reciprocal of the temperature in Kelvin. The activation energy was determined as  $(31.1 \pm 1.8) \text{ kJ mol}^{-1}$ , which is in agreement with other previously determined activation



**Fig. 12.** Arrhenius plot for the alkaline methanolysis of soybean oil assuming a zero-order kinetic scheme.

energies for the methanolysis of vegetable oils using alkaline catalysts [14,20,4].

#### 4. Conclusions

In this work, the manufacture and evaluation of an experimental device allowing online monitoring of biodiesel synthesis by following the refractive index of the reactive mixture along the reaction time is introduced. The experimental system has been shown to be suitable and useful for the online monitoring of this reaction, promoting reliable data acquisition in a very simple and inexpensive fashion. The considerable volume of data acquired within a small time interval allowed the identification of the following two important reaction steps: mixing and methanolysis itself, the former being the rate-determining step. The methanolysis of soybean oil, using  $\text{KOCH}_3$  as the catalyst at temperatures from 30 to 60 °C, has been shown to proceed via a zero-order mechanism, also suggesting a heterogeneous model in which the reaction proceeds in the methanol/oil interfacial region.

The catalysis is heterogeneous, so the increase in methanolysis rate can only be achieved by increasing the surface area, which can be promoted by increasing the density of droplets of the methanol/catalyst solution in the reaction mixture. Attention to the mechanical agitation must be encouraged for the optimization of the methanolysis global process.

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