A PLS regression model using NIR spectroscopy for on-line monitoring of the biodiesel production reaction

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ABSTRACT

In this work, a Partial Least Squares (PLS) regression model using Near-Infrared (NIR) spectroscopy was developed to monitor the progress of the catalyzed transesterification reactions of soybean oil that produce biodiesel. The NIR spectra were collected during the transesterification reaction with a lab made spectrophotometric flow cell. Proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy was employed for determining the conversion percentage of glycerides to methyl esters during the transesterification reaction and used as reference to build the PLS calibration model employing NIR spectroscopy data. The model, constructed with selected spectral range has not been tried before and allows the monitoring of the transesterification reaction in terms of conversion ratio for different temperatures. The model was validated and the values of Root Mean Square Error of Prediction (RMSEP) found for two different temperatures were 0.74% and 1.27% (of conversion) for reactions carried out at 20 ± 0.2 °C and 55 ± 0.2 °C, respectively.

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1. Introduction

Nowadays the need of reducing the environmental impacts caused by the use of fossil fuels, in addition to the increasing price and potential limits to petroleum sources shown in the last three decades, are the major factors responsible for the development of renewable and environmentally and economically sustainable energy sources [1–6].

In this context, biodiesel is a promising alternative fuel as substitute for mineral diesel, considering it is a renewable energy source that can be produced from vegetable oils and animal fat. Furthermore, biodiesel is economically viable, biodegradable, non-toxic and shows pollutant emission profiles lower than mineral diesel. Another advantage of biodiesel is its very similar physical characteristics to conventional diesel fuel, which enables it to be directly employed for diesel engines [2,7,8].

Chemically, vegetable oil and animal fat consist of triglyceride molecules having three long chain fatty acids that are bonded through an ester linkage to a single glycerol molecule. These fatty acids differ by the length of their carbon chains and by the number, orientation and position of double bonds in these chains [2]. Biodiesel is composed of alkyl esters derived from the long chain fatty acids and is produced by the transesterification of triglycerides with short chain alcohols. The most used alcohol is methanol due its lower cost [7]. In the transesterification reaction one alcohol is replaced by another alcohol. The reaction is similar to a hydrolysis except that alcohol is used instead of water.

The transesterification of a triglyceride produces fatty acid alkyl esters and glycerol. The reaction is reversible and, therefore, it depends on the reactant concentrations. Moreover, the reaction is slow, requiring a catalyst to accelerate triglyceride conversion to esters. Several catalysts have been employed, such as acids, bases and enzymes. However, the most used are sodium and potassium hydroxides, sodium and potassium methoxides and acids like sulfuric, hydrochloric and phosphoric. In general, the basic catalysts are preferred as they are less expensive, lead to faster reactions and demand lower temperatures (about 60 °C), when compared to acid catalysis, which usually requires reaction temperatures greater than 100 °C [2,9].

To obtain a high quality fuel and to achieve the requirements for commercialization, it is important to monitor the transesterification process to ensure low levels of mono- and diacylglycerols resulting from incomplete reactions, to follow the content of residual triacylglycerols that have not reacted, and other residuals such as glycerol, free fatty acids, alcohol and catalyst that have not been properly separated after the transesterification process.

Monitoring the transesterification in real time also allows for optimizing the experimental parameters of the reaction, in order to achieve better yields and minimize costs. Gas chromatography (GC) [10] and high performance liquid chromatography (HPLC) [9,11,12] are the most widely employed techniques to monitor the transesterification reaction. However, these techniques demand significant time and cannot be easily adapted for in/on-line

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monitoring of the progress of reversible reactions such as the transesterification of vegetable oils [13,14]. Thus, spectroscopic techniques appear to be more suitable, considering that they are fast and more easily adaptable for *in situ* applications [15–18].

The work by Gelbard et al. [19], published in 1995, and developed by using Proton Nuclear Magnetic Resonance (^{1}H NMR) shows the first application of a spectroscopic technique for monitoring the transesterification of vegetable oil, allowing the determination of reaction yields. However, the method requires a sample pretreatment. As a consequence, it cannot be directly applied in-line. On the other hand, some papers [13,20–24] describe monitoring the transesterification yield by using vibrational spectroscopic techniques, such as Near-Infrared (NIR), mid-infrared and Raman spectroscopies. These papers show the higher potential for *in situ* use because they do not require sample pretreatment, allow faster determinations and employ lower cost instrumentation.

Among the group of vibrational spectroscopic techniques for *in situ* application, NIR spectroscopy deserves special attention, due its lower instrumental costs, simplicity, and the fact that it is a well established technique used for a wide range of process controls in industry [25,26].

The present work is focused on the development of an analytical method based on NIR spectroscopy and multivariate regression that employs ^{1}H NMR in the calibration stage for on-line determination of the progress of the soybean oil transesterification reaction.

2. Experimental

2.1. Reagents and materials

Commercial soybean oil (Soya, lot 0809B, iodine number of 128.30, free fatty acid content of 0.06%, saponification value of 193.70 mg KOH/g and water content of 0.03%) was used in all transesterification reactions carried out in this work. Canola (Bünge, lot 27809), peanut (Sementes Esperança, lot 02) and sunflower (Bünge, lot 28009) oils were bought in a local market and used as received. Methanol (Fisher Scientific, HPLC grade), sodium hydroxide (Labsynth, analytical grade), acetic acid (Merck, analytical grade) and sodium sulfate (Acros, analytical grade) were also employed. Deuterated chloroform (Cambridge Isotope Laboratories) was used in ^{1}H NMR analyses.

A spectroscopic flow cell made of Teflon® was developed for monitoring the transesterification reaction of soybean oil by NIR spectroscopy. The cell has a 2.0 mm light path and an internal volume of 220 μL. Fig. 1 shows a transversal section of the cell.
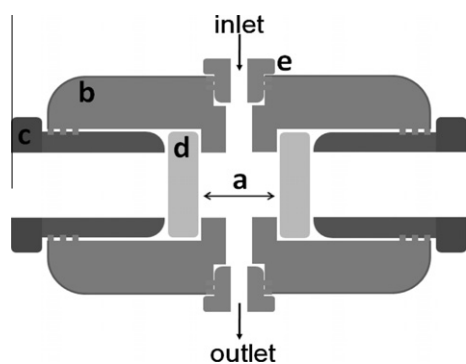

Fig. 1. Spectrophotometric flow cell: (a) Optical path; (b) Teflon® cell body; (c) Teflon® tapper cylinders, used to hold the circular glass cylinders against the optical path and to allow the electromagnetic radiation passing; (d) Circular glass cylinders; (e) Teflon® fittings for 1.0 mm Teflon® tubes for sample flow.

Transesterification reactions were carried out in a 1000 mL three-necked glass flask. The three inlets were properly sealed, by rubber stoppers, after insertion of a helix stirrer, a reflux condenser, a thermometer and three Teflon® sampling tubes. Two of three tubes were employed to allow the sample to flow through the spectrophotometric cell, and the third allows for sample collection from the glass reactor, for determination of ester content by ^{1}H NMR. Fig. 2 shows the experimental set up.

The reaction was processed at constant temperature by using a thermostatized water bath. A peristaltic pump was used to impel the reactor contents to the spectrophotometric flow cell. The NIR spectra were collected using a NIR spectrophotometer (ABB Bomem, model MB160D) in the range from 4000 to 14,000 cm^{-1} with a 4 cm^{-1} resolution. Each spectrum is an ensemble average of 80 scans, collected of the reaction mixture pumped at 3 mL min^{-1} through the flow cell. A spectrum of air, acquired with the same cell, was employed as reference for absorption calculations. The program *Unscrambler* (Camo, version 9.2) was employed to analyze the spectral sets and construct the regression models.

In order to obtain the ^{1}H NMR spectra of the reaction mixture, several samples were collected at different reaction times by using a vacuum pump connected through a centrifuge tube (Fig. 2j). 15 mL of the reaction mixture were collected in the tube containing 1.5 mL of glacial acetic acid to neutralize the NaOH employed as reaction catalyst [13]. After homogenization, the tube contents were washed three times with distilled water. After each washing operation the organic phase (supernatant) was removed to another tube. The remaining organic phase (after three washes) was rotaevaporated (70 °C and 260 torr) in the presence of anhydrous magnesium sulfate, to fully eliminate the residual water. 15 mg of the final material were dissolved in 700 μL of CDCl$_3$ for ^{1}H NMR spectrum acquisition using a Bruker-250 MHz spectrometer (model Avance-250 MHz). All the spectra are an average of 16 scans.

2.2. Transesterification reactions

All transesterification reactions were carried out by mixing 700 mL of soybean oil, 175 mL of methanol (6:1 M ratio) and 6.3 g of sodium hydroxide (1% m/m of base in relation to oil), previously dissolved in methanol. In this work the transesterification reactions were conducted at two different temperatures, 20.0 ± 0.2 °C and 55.0 ± 0.2 °C.
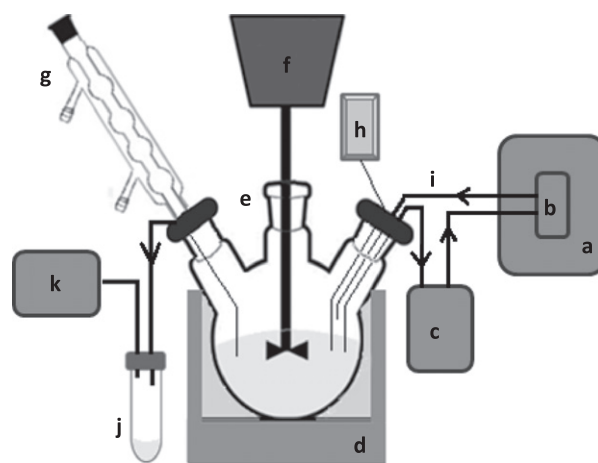

Fig. 2. Instrumentation set up: (a) NIR spectrophotometer; (b) Spectrophotometric flow cell; (c) Peristaltic pump; (d) Thermostatized bath; (e) Three-necked glass flask; (f) Mechanical helix stirrer; (g) Reflux condenser; (h) Digital thermometer; (i) Teflon® tubes, i.d. = 1.0 mm; (j) Centrifuge tube, for sample collection by vacuum suction; (k) Vacuum pump.

2.3. ^{1}H NMR and NIR transesterification reaction monitoring

The reactions were monitored by both ^{1}H NMR and NIR techniques, during 200 min and 80 min, when carried out at 20.0 ± 0.2 °C and 55.0 ± 0.2 °C, respectively. The time of reaction start to count with the addition of the NaOH:methanol solution into the thermostatized soybean oil. Spectra were obtained by both the ^{1}H NMR and NIR techniques at elapsed time intervals of 4, 8, 14, 20, 30, 40, 50, 60, 70, 80, 120, 140, 160, 180 and 200 min for reactions conducted at 20.0 ± 0.2 °C and at 4, 8, 14, 20, 30, 40, 50, 60, 70 and 80 min for reactions conducted at 55.0 ± 0.2 °C.

NIR data was start collected by turning on the peristaltic pump 45 s before spectral data acquisition, ensuring the representativeness of the composition in the flow cell. After each NIR spectral data acquisition, the flow passing the cell was switched to air. In this way the reaction mixture could not separate into two phases inside the cell and an effective cleanup of the spectroscopic flow cell was assured.

2.4. PLS calibration

PLS models for the conversion of triglycerides to their respectively methyl esters were constructed using data from three transesterification reactions carried out at 20.0 ± 0.2 °C. These three reactions were monitored by NIR and ^{1}H NMR spectroscopy as described above. For both techniques the spectra of the reaction mixtures were collected after the same elapsed intervals, as previously described. NIR spectroscopic data were preprocessed by first derivative, since it showed the best results, in terms of RMSEC and RMSECV, when compared to baseline correction, standard normal variate and second derivative. The triglyceride conversion ratios found by ^{1}H NMR were employed to produce the multivariate calibration model using the NIR spectra set.

In order to achieve conversion ratios close to 100%, the reaction carried out at 20.0 ± 0.2 °C was monitored for 200 min. In this case, 15 calibration samples, collected at the same time intervals, were analyzed by ^{1}H NMR and their spectra were also obtained by NIR.

2.5. Model validation

To validate the calibration model two other transesterification reactions were carried out, one at 20.0 ± 0.2 °C and one at 55.0 ± 0.2 °C. These two reactions were also monitored by both NIR and ^{1}H NMR spectroscopies. The spectra were collected at the same times as used for PLS calibration. Thus, validation samples were generated in duplicate for both reaction temperatures.

3. Results and discussion

3.1. Determination of the triglycerides conversion ratios by ^{1}H NMR

^{1}H NMR spectroscopy was employed as the reference technique for determination of the conversion percentage of the glycerides present in soybean oil to methyl esters during the transesterification reaction. These values were later used to build the PLS calibration model by NIR spectroscopy.

To determine the conversion ratio (C_{me}) by ^{1}H NMR the integral of the peak intensities for glyceryl protons and the integral of the peak intensities for methyl ester protons were used in the following equation[23]:

$$C_{me} = \frac{5 \times I_{me}}{(5 \times I_{me}) + (9 \times I_{tag})} \quad (1)$$

where I_{me} is the value found for integration of methyl ester protons (three protons with absorption at 3.67 ppm) and I_{tag} is value for

integration of glyceryl protons (five protons with absorption between 4.05 and 4.40 ppm), present in the tri-, di- and monoglycerides found in vegetable oils.

3.2. NIR spectroscopy results

Fig. 3 shows a NIR spectrum collected during the progress of a soybean oil transesterification reaction. The spectral regions located at the lower and higher extremes of the spectra were cut off due to excessively high absorption for wavenumbers lower than 4450 cm^{-1} and due to high instrumental noise found at wavenumbers greater than 9000 cm^{-1}.

Initially the NIR spectra were evaluated to find the best spectral region to develop the PLS calibration model. Therefore, a comparison was made between the spectra of soybean oil, soybean biodiesel and a NaOH:methanol mixture (at the same concentration as employed in the transesterification reaction). Fig. 4 shows these spectra where three promising highlighted regions (**a**, **b** and **c**, **d**) are shown, due to the major spectral differences observed between the pure soybean oil and its biodiesel.

3.3. PLS calibration model

For the development of the calibration model the reactions conducted at 20.0 ± 0.2 °C were used. At this temperature it is possible to access transesterification conversion ratios between 60% and 100%. For the usual temperature employed in commercial biodiesel production (between 50 and 60 °C) the transesterification ratios are higher than 90% for reaction times as short as 4 min. This fact restricts calibration range monitoring to higher conversion ratios, since the sampling of the reaction mixture for time intervals lower than 4 min is unreliable, due to sample preparation steps necessary for ^{1}H NMR analysis.

Conversion ratios established by ^{1}H NMR, for time intervals between 4 and 200 min were employed for the development of PLS calibration models.

Five different spectral regions were evaluated to be used in the model calibration. Four PLS models were developed using the regions **a**, **b**, **c** and **d** shown in Fig. 4. A fifth model refers to a combination of these regions. The use of entire spectral region resulted in calibration models whose error values for calibration and cross validation were always higher than those observed for the models obtained by using any of the regions shown in Fig. 4.
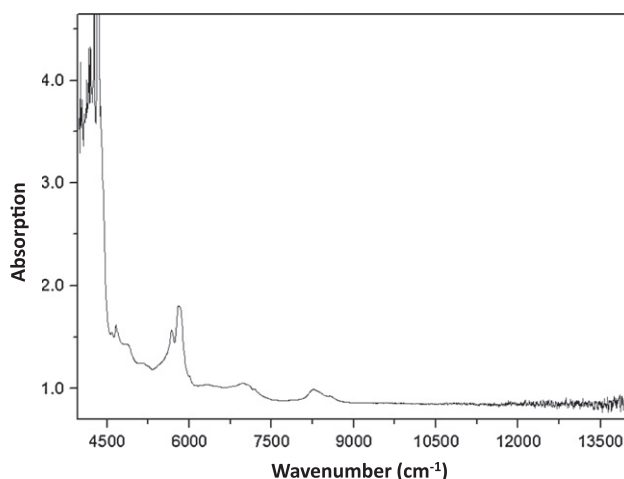

Fig. 3. Typical NIR spectrum obtained during a transesterification reaction of soybean oil. Spectral range of 4000–14,000 cm^{-1} (2500–714 nm).
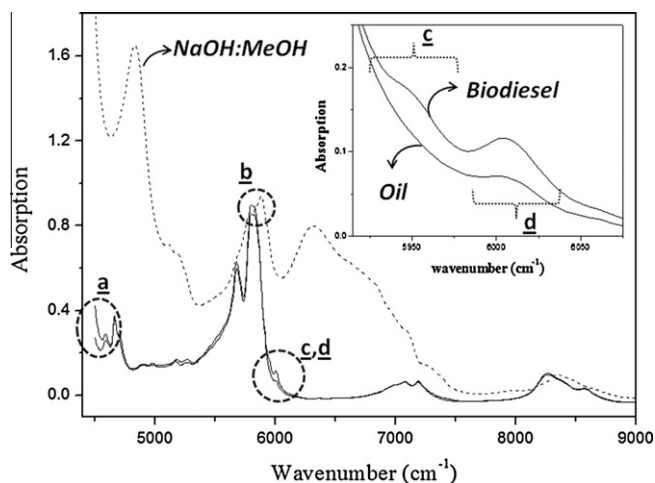
Fig. 4. Typical NIR spectra of a NaOH:methanol mixture, pure soybean oil and pure soybean biodiesel. The circles (**a**, **b** and **c**, **d**) mark the three regions where the major spectral differences between the oil and biodiesel occurs. The small insert shows the expanded **c**, **d** region.

Table 1
Results obtained with the PLS models evaluated.

Model	Emp. region (cm^{-1})	LVs	RMSECV (% Conv.)[a]	RMSEC (% Conv.)[a]
Reg. **a**	4451–4775	2	1.32	1.80
Reg. **b**	5770–5874	2	2.44	3.86
Reg. **c**	5928–5959	1	1.09	1.32
Reg. **d**	5978–6044	2	1.66	2.08
Reg. **a, b, c, d**	**a + b + c + d**	3	1.12	1.56

[a] Percent of glycerides conversion to methyl esters.

Table 1 shows the spectral range used for each calibration model. Furthermore, it shows the *Root Mean Square Error of Calibration* (RMSEC), *Root Mean Square Error of Cross Validation* (RMSECV) and the optimal number of *Latent Variables* (LVs) suggested for each model.

Region **c** (Fig. 4), which correspond to the first overtone of C–H stretching for CH$_2$ and CH$_3$ bonds [27], was shown to be the most attractive for this work, as the model built with this region shows the lowest RMSEC and RMSEP values. This result probably could be assigned to the spectral differences between oil and biodiesel found in this region, as can be seen in the inserted of Fig. 4. Moreover, in this region the NaOH:methanol mixture shows a lower absorption. It is important to consider that the NaOH:methanol absorption spectrum, shown in Fig. 4, was collected with the spectroscopic cell filled with the mixture. However, in the transesterification reaction mixture it represents 20% of the total volume and then the absorption intensities will be reduced five times, causing an even lower influence.

Region **d** (maximum at 6005 cm^{-1}), was used by Knothe [23,24] for quantitation of ester yield. However, region **c,** corresponding to the absorption band with maximum at 5940 cm^{-1}, shows a better performance than the one employed by Knothe, as can be demonstrated by the lower values of RMSEC and RMSECV. Furthermore, a smaller number of *Latent Variables* is required for the PLS model. This fact can be explained by assigning the 5940 cm^{-1} band to the first overtone of C–H stretching of CH$_3$ bonded to methoxyl carbons. This region shows an absorption band due to soybean biodiesel (esters of glycerides) and no band of the soybean oil (triglycerides). The region suggested by Knothe [23,24] also shows an oil absorption band. These features were also confirmed by analyzing the NIR spectra of other oils and their respective biodiesels,
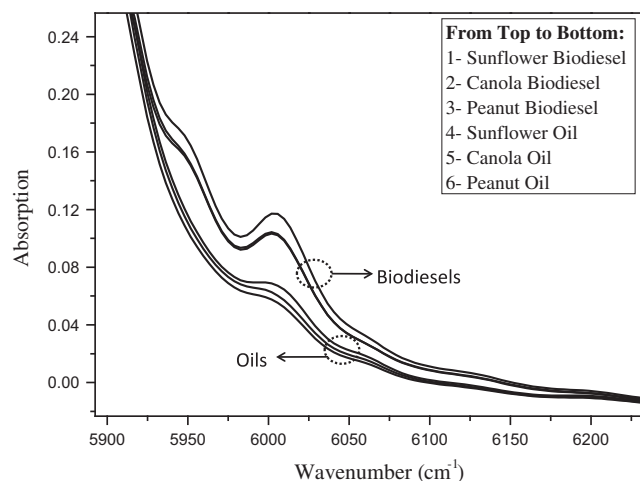

Fig. 5. NIR spectra of peanut, canola and sunflower oils and their respective esters.

such as peanut, canola and sunflower oils, as shown in Fig. 5. Therefore, it is reasonable that this region could also be employed to follow the progress of the transesterification reaction of these oils.

Thus, regions **a**, **b**, **d** (Fig. 4) or their combination were not used in this work as they produce models with higher RMSEC and RMSECV. In particular, for regions **a** and **b,** the lack of performance can be attributed to a great extent to the absorption of the NaOH:methanol mixture.

In summary, the best calibration model obtained in this work was built using the spectral range between 5928.7 and 5959.6 cm^{-1} (region **c**). The model shows $R^2 = 0.991$ and $R^2 = 0.983$ for calibration and cross validation, respectively, and a mean RMSEC = 1.09 and RMSECV = 1.32 (% of conversion) for the conversion ratio followed throughout the reaction.

3.4. Model validation

The validation of the elected calibration model was done by employing data from two new transesterification reactions carried out at 20 ± 0.2 °C and 55 ± 0.2 °C. The purpose of the second reaction was to verify the performance of the model, built from the data of a transesterification reaction carried out at 20 ± 0.2 °C, to predict the progress of reactions conducted at higher
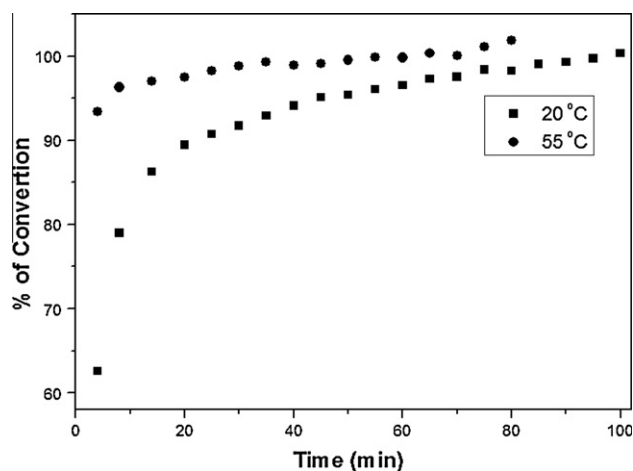

Fig. 6. Progress of soybean reactions monitored at 20 ± 0.2 °C and 55 ± 0.2 °C by using the model constructed with NIR spectral data of the reaction mixture.

Table 2
Prediction and reference values for the conversion ratio obtained for reactions carried out at 20 ± 0.2 °C, and 55 ± 0.2 °C. V_{ref} = Reference value; V_{pred} = Predicted value; E = Absolute error; Er = Relative error (%).

20 °C Time (min)	V_{ref} (^{1}H NMR) % Conv.	V_{pred} (NIR) % Conv.	E % Conv.	Er (%)	55 °C Time (min)	V_{ref} (^{1}H NMR) % Conv.	V_{pred} (NIR) % Conv.	E % Conv.	Er (%)
4	62.00	62.57	0.57	0.91	4	94.01	93.43	0.58	0.62
8	79.78	78.98	0.80	1.00	8	97.03	96.31	0.72	0.75
14	86.28	86.28	0.00	0.00	14	96.75	96.98	0.22	0.23
20	89.49	89.44	0.05	0.06	20	100.00	97.48	2.52	2.52
30	91.10	91.70	0.60	0.66	30	99.76	98.81	0.95	0.95
40	94.18	94.08	0.11	0.11	40	100.00	98.90	1.10	1.10
50	95.16	95.41	0.25	0.26	50	99.74	99.53	0.21	0.21
60	96.73	96.51	0.22	0.23	60	99.52	99.81	0.29	0.29
70	96.64	97.54	0.90	0.94	70	98.51	100.05	1.54	1.56
80	96.45	98.22	1.77	1.84	80	99.75	101.83	2.08	2.08
Mean	–	–	0.53	0.60	Mean	–	–	1.03	1.02

temperatures. It is important to consider that independent of the reaction temperature, the temperature of the reaction mixture sampled for acquisition of NIR spectrum is close to ambient, due to the Teflon® tubing used to transfer the mixture from the glass flask to the flow cell. The tubes (i.d. = 1 mm) are 50 cm long, allowing the reaction mixture sampled to equilibrate with ambient temperature, kept at 25 ± 1 °C. This fact was confirmed by monitoring the sample temperature at the output of the flow cell. Moreover, some data were obtained by using a glass coil (i.d. = 2 mm) 72 cm long immersed in a thermostatized bath (25 ± 1 °C), placed between the glass flask and the flow cell. There are no significant differences, with 95% of confidence, for results acquired with or without the glass coil.

Table 2 shows the predicted values of the conversion ratio of oil to ester employing the PLS model constructed by using the NIR spectra. ^{1}H NMR results were also taken for validation samples, and their respective prediction errors are shown. The *Root Mean Square Error of Prediction* (RMSEP) found during the progress of the transesterification reaction carried out at 20 ± 0.2 °C and 55 ± 0.2 °C were 0.74 and 1.27 (% of conversion), respectively.

3.5. Model employment

The developed NIR-based model allows for accurate monitoring of the progress of the transesterification reaction of soybean oil. Fig. 6 shows conversion percentages of soybean oil obtained by the proposed model carried out at 20 ± 0.2 °C, monitored for 100 min and for a reaction carried out at 55 ± 0.2 °C, monitored for 80 min. The NIR spectra were collected at 4, 8, 14, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 and 100 min in both cases. The difference in the kinetics of the two reactions is evident.

4. Conclusions

The proposed monitoring system can follow the progress of the transesterification reaction carried out at any temperature with reasonable accuracy.

For ambient acclimatized measurements, as in most instrumental analytical chemistry laboratories, it was not necessary to control the sample mixture temperature when acquiring the NIR spectra. However, for on-line monitoring of the transesterification reaction in an industrial environment, where temperature is not under control, a sample thermostatization system such as the one proposed in this work could be used.

The results shown in this work demonstrate that NIR spectroscopy can be an effective tool for on-line monitoring of the progress of transesterification reactions with mean error values close to 1% of oil to biodiesel conversion ratio. Therefore, a more effective control of reagent and energy consumption for biodiesel production

can be achieved. This, with time, will impact favorably on the cost of the final product.

The narrow spectral range (5928.7–5959.6 cm^{-1}), that has not been tried before, employed for construction of the regression model points towards the possibility of building a low cost NIR photometer, based on a lead sulfite detector and an interference filter to select the relevant spectral range.

Acknowledgements

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