



On-line monitoring of the transesterification reaction carried out in microreactors using near infrared spectroscopy

Romain Richard ^{a,b,c,d}, Brigitte Dubreuil ^{a,b}, Sophie Thiebaut-Roux ^{a,b,*}, Laurent Prat ^{c,d}

^a Université de Toulouse, INP-ENSIACET, LCA (Laboratoire de Chimie Agro-Industrielle), F-31030 Toulouse, France

^b INRA, UMR 1010 CAI, F-31030 Toulouse, France

^c Université de Toulouse, INP, UPS, Laboratoire de Génie Chimique, 4, allée Emile Monso, F-31030 Toulouse Cedex 4, France

^d CNRS, Laboratoire de Génie Chimique, F-31030 Toulouse, France

HIGHLIGHTS

- ▶ The biodiesel produced from sunflower oil and ethanol is of 100% renewable origin.
- ▶ EtONa is used as a homogeneous catalyst.
- ▶ The transesterification reaction was carried out in continuous systems: microreactors.
- ▶ On-line monitoring of the transesterification reaction was developed by using near infrared spectroscopy.
- ▶ A multivariate approach is used to establish calibration models.

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ABSTRACT

Biodiesel can be produced from vegetable oils, animal fats, and waste cooking oils by transesterification with ethanol (also called ethanolsis) in order to substitute fossil fuels. In this work, the batch ethanolsis of high oleic sunflower oil was transferred into a continuous microstructured device, which induces a better control of heat and mass transfers. Various parameters were studied, notably the initial ethanol to oil molar ratio. An innovative method using NIR spectroscopy was also developed to on-line monitor the transesterification reaction of high oleic sunflower oil with ethanol in microreactors (circular PFA tube 1/16" OD, 0.02" ID). The reactions were monitored directly in the microreactors through sequential scans of the reaction medium by the means of an adequate probe. The asset of the method is that no sample collection or preparation is necessary. Partial Least Squares regression was used to develop calibration and prediction models between NIR spectral data and analytical data obtained by a reference method (gas chromatography with flame ionization detection, GC–FID). This method is fast, safe, reliable, non-destructive and inexpensive contrary to conventional procedures, such as gas chromatography and high performance liquid chromatography generally used to determine the composition of crude transesterification medium.

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1. Introduction

Biodiesel can be produced from vegetable oils, animal fats, and waste cooking oils by transesterification [1,2] with an alcohol (alcoholysis) in order to substitute fossil fuels. Many works have used methanol [3–6] as alcohol reactant which is mainly produced by oxidation processes of methane, a natural gas component, hence a non-renewable energy. Ethanol and particularly bioethanol from sugar cane, sugar beet or corn is preferable to methanol due to its superior dissolving power for vegetable oils, low toxicity and its

renewable origin. However, using ethanol leads to additive problems which have to be overcome to obtain a profitable process. First of all, its reactivity is slightly less important as it is less acidic than methanol because of a longer carbon chain. Besides, fatty acid ethyl esters (FAEEs) production using ethanol is more costly than fatty acid methyl esters (FAMES) production with methanol, due to a process composed of more steps using, particularly, a refill with ethanol and catalyst, when the reaction equilibrium is reached, in order to shift it.

Various other factors such as free fatty acid (FFA) content, water content, type/amount of catalyst, vegetable oil to alcohol molar ratio, or temperature [3,7–9] can affect the process. This transesterification leads to high conversion of triglycerides (TGs) into ethyl esters [10] with diglycerides (DGs) and monoglycerides (MGs) as reaction intermediates and glycerol as by-product (reaction in

* Corresponding author. Address: INPT-ENSIACET, Laboratoire de Chimie Agro-Industrielle, 4, allée Emile Monso, BP 44362, 31030 Toulouse Cedex 4, France. Tel.: +33 5 34 32 35 04; fax: +33 5 34 32 35 97.

E-mail address: sophie.thiebautroux@ensiacet.fr (S. Thiebaut-Roux).

three consecutive steps). Ethanolysis is generally conducted in batch reactors. Depending on the reactional scheme and the thermokinetic properties of the system, continuous processes may withdraw existing obstacles of batch processes such as numerous steps, secondary reactions, stable equilibria and difficulties to separate the reaction products. Several works on biodiesel production using microreactors have recently been published [11–14]. The methanolysis system is complex due to changing phase equilibria [15]: two immiscible phases are present at the beginning (vegetable oil and methanol), then a single phase appears after a few minutes of reaction. Finally, two phases are obtained at the end of the reaction, majorly composed of methyl esters and glycerol. Moreover, this reaction involves simultaneous phenomena (mixing, heat and mass transfers) which have to be precisely controlled. Hence, to properly design a continuous process, numerous data are required. In this study, we transferred the batch ethanolysis of high oleic sunflower oil into a continuous microstructured device. Indeed, microreactors generally induce a better control of heat and mass transfers. Furthermore, process intensification using microreactors is less costly due to reduced equipment size and lower reactant consumption [16]. To extrapolate microstructured continuous processes, a numbering-up approach is chosen as it is faster and easier than a scale-up approach, generally used in batch processes.

Many analytical procedures have been developed to determine the composition of crude transesterification products. In previous studies, different analytical methods such as gas chromatography [17,18], high performance liquid chromatography [19], Fourier transform infrared spectroscopy [20,21] have been developed to off-line monitor the composition of reaction mixtures (FFA, ethyl esters, MG, DG, TG, glycerol) obtained during or after transesterification of vegetable oils with ethanol. Nevertheless, these techniques are long to handle and expensive. They generally require special training, samples collection and involve solvent for sampling preparation. Up to now, only a few works with different analytical techniques such as mid-infrared (MIR) spectroscopy [22,23], near infrared (NIR) spectroscopy [24–27], Raman spectroscopy [28], ultrasonication-assisted spray ionization mass spectroscopy [29], fluorescence [30] or UV spectroscopy [31] are able to on-line monitor organic reactions (mostly different from transesterification reaction). With these methods, process state can be obtained from whole sample finger-printing.

Faced to all these analytical techniques, we decided to on-line monitor the transesterification reaction of high oleic sunflower oil with ethanol in microreactors (circular polyfluoro alkoxy (PFA) tube 1/16" OD, 0.02" ID) using NIR spectroscopy, which is an innovative method for this type of reaction in such a process. NIR spectroscopy with multivariate analysis is a well-established, fast, reliable, inexpensive and non-destructive analytical technique, and does not require complex pre-treatment [32–34]. Among the various parameters which can be investigated, the initial ethanol to oil molar ratio was studied in this work. The reactions in the microreactors were monitored through sequential scans of the reaction medium with an adequate probe. Partial Least Squares (PLS) regression was used to develop calibration models between NIR spectral data and analytical data obtained by a reference method: gas chromatography with flame ionization detection (GC–FID). The developed models were validated by comparison with GC data.

2. Material and methods

2.1. Material and reagents

High oleic sunflower oil (97.9% TG, 1.6% DG and 0.5% FFA) was obtained from ITERG (Pessac, France). Its fatty acid composition

(% by weight) is as follows: 3.5% palmitic acid, 3.0% stearic acid, 87.6% oleic acid, 4.9% linoleic acid and 1.2% other acids. Hydrochloric acid (analytical quality, 37% solution in water) and sodium ethoxide EtONa (analytically pure, 21 wt.% in ethanol) were purchased from Acros Organics; absolute ethanol (99.95%) and cyclohexane (HPLC grade) were supplied by Scharlau. N-methyl-N-trimethylsilyl-heptafluorobutyramide (MSHFBA) and methylimidazole (MI) were purchased respectively from Macherey Nagel and Sigma-Aldrich.

2.2. Transesterification reaction

The transesterification reaction was performed in circular PFA tubes. These tubes were submerged in a temperature-controlled water bath to maintain the targeted microreactor temperature. As in batch processes, temperature was maintained at 65 °C, close to the boiling point of ethanol (78 °C) but lower than 70 °C in order to avoid the formation of ethanol boiling bubbles. Transesterification of high oleic sunflower oil was carried out by using the following procedure: liquids (oil and EtOH/EtONa mixture) were injected by syringe-pumps with perfect flow rate control. Several ethanol to oil molar ratios were tested (45.4, 22.7, 16.2, 9.0 and 6.0) with the same amount of catalyst (1 wt.% compared to oil mass) and the same water content in ethanol (0.08 wt.%, determined by Karl-Fisher titration). After mixing in a T-junction, the reaction medium flows into the tube. With constant flow rates, each tube length corresponds to a reaction time. A 2 m-length tube was used, which is equivalent to a reaction time of 16 min ($F_{\text{tot}} = 1.5 \text{ mL/h}$ and $U_{\text{tot}} = 2.12 \text{ mm/s}$). Maintaining the same flow rates, the tube was cut in order to obtain lower reaction times. Samples were collected during 15 min. The reaction was quenched by neutralizing the alkali catalyst with a concomitant addition of HCl (3.7% solution in water) at a constant flow rate. For each collected sample, the medium composition at different reaction times was determined by using GC–FID analysis. In the meanwhile, NIR spectroscopy was performed at the same reaction times as the sample collection in order to on-line monitor the transesterification reaction (see Fig. 1).

2.3. Gas chromatography analysis

The collected samples were analyzed by gas chromatography using a Perkin Elmer Instrument (Perkin Elmer, USA) coupled to a flame ionization detector (FID). Separation was carried out with a silica capillary column (CP-Sil 8 CB lowbleed/MS, 5% phenyl + 95% dimethylpolysiloxane, 15 m, 0.32 mm, 0.25 μm) from Varian (USA). The chromatograph was equipped with an automatic injector and the injections (1 μL) were performed with an "on-column" system.

The carrier gas was helium (Air Liquide, France) and the column head pressure was adjusted to 15 psi. Injector temperature was 55 °C during 0.5 min and ramped to 340 °C at 200 °C/min (held 43 min). Temperature in the oven was held 0.5 min at 55 °C, then ramped to 80 °C at 45 °C/min and finally increased to 360 °C at 10 °C/min (held 16 min). The total running time was 45 min. The temperature of the detector (FID) was 360 °C.

All the samples (180 μL) were previously silylated with 20 μL of a mixture of MSHFBA (1 mL) and MI (50 μL). This hydroxyl group silylation is intended to increase volatility and stability of the hydroxy compounds injected, and therefore to improve their detection. Cyclohexane was used as solvent to prepare standard solutions and heptadecane was used as an internal standard (1 mg/mL).

With this analytical procedure, molar concentrations of ethyl oleate, oleic acid, monoglycerides, diglycerides and triglycerides in the different phases resulting from the reaction were determined.

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