Near infrared spectroscopy can accurately estimate biodiesel cetane number

Good agreement between NIRS and proposed equations in literature

Near infrared spectroscopy can be used for real-time cetane number determination

Cetane number prediction of waste cooking oil-derived biodiesel prior to transesterification reaction using near infrared spectroscopy

Juan Francisco García-Martín*, Francisco Javier Alés-Álvarez, María del Carmen López-Barrera, Irene Martín-Domínguez, Paloma Álvarez-Mateos

Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, C/ Profesor García González, 1, 41012 Seville, Spain

*Corresponding author. E-mail address: jfgarmar@us.es

Abstract

Fifty waste cooking oils (WCOs) were transesterified with methanol (1:8 WCO:methanol molar ratio) at 60 ºC for 60 min using NaOH as catalyst (1 % wt.). Fatty acid methyl ester (FAME) composition of the resulting biodiesels was analysed by gas chromatography, and near infrared (NIR) spectra of these biodiesels and those of the starting WCOs were acquired. Biodiesel cetane number was then calculated from both FAME composition and from biodiesel NIR spectra, this last technique using the former one as reference data. Because of transesterification does not modify fatty acid distribution of the starting WCO, and the similarity between biodiesel and WCO NIR spectra, biodiesel cetane number was successfully predicted from WCO NIR spectra, achieving RPD (ratio of performance to deviation) of 3.83. Therefore, biodiesel cetane number (and, as consequence, any other biodiesel property related to FAME composition) can be predicted by NIR spectroscopy before performing the transesterification reaction, which allows beforehand selecting the most suitable substrates for biodiesel production.

Keywords: biodiesel; cetane number; NIRS; waste cooking oil.

1. Introduction

Because of fossil fuels are depleting and the hazardous effects of these fuels on the environment, current researches mainly focus on the search for economic raw materials that can reduce environmental pollution and can be used for the production of efficient substitutes for petroleum fuels. Concerning diesel, its combustion leads to air pollution by greenhouse gases emissions (NO_x, CO, CO_2), and to the destruction of the ozone layer by photochemical interactions of hydrocarbon, CO and NO_x emissions.

Due to these drawbacks, an alternative to diesel fuel is required. One of the most attractive and biodegradable alternatives is biodiesel, which is composed of fatty acid methyl esters (FAMEs). Biodiesel is obtained by transesterification of vegetable oils with methanol in the presence of a catalyst. Although other short-chain alcohols, such as ethanol, can be used, methanol is usually selected because it is the least expensive alcohol. This reaction normally does not alter fatty acid composition, so the biodiesel fatty acid profile matches with that of the starting oil [1–4]. The use of biodiesel can reduce the global emissions of CO_2 and greenhouse gas particles because the carbon contained in the biofuel is biogenic and renewable. That is, CO_2 enters a closed cycle generated by photosynthesis that helps to reduce the greenhouse effect. Besides, biodiesel can easily decompose under natural conditions (more than 90 % of pure biodiesel can be degraded in a few weeks), and its sulphur content is almost nil [4,5]. Furthermore, biodiesel has greater cetane number (an important diesel quality parameter) than petroleum diesel. This improves the combustion efficiency, shortens ignition delay, increases compression ratio of the engine and produces less noise and pollutants (NO_x, CO and hydrocarbons).

Cetane number depends on biodiesel fatty acid profile, so several equations that relate cetane number to FAME have been proposed [3,6–11]. Of note is that cetane number depends on both moieties of the fatty acid alkyl ester (the fatty acid and the alcohol), i.e. cetane number of biodiesel from the same oil will differ if the transesterification is carried out with methanol or ethanol. The application of these equations requires the previous determination of FAME composition by gas chromatography, which limits their application due to the cost of this technique.

Near-infrared spectroscopy (NIRS) is a low-cost, safe and non-destructive technique which requires minimal or no sample preparation and relatively small amounts of sample for analysis [12]. These features make NIRS suitable for online work. The potential of NIRS for biodiesel analysis, including biodiesel feedstock selecting, transesterification reaction monitoring, and determination of biodiesel blend level, properties and contaminants, has been comprehensively reviewed [13]. It has been verified that FAME composition of oils and biodiesel can be determined by NIRS with great accuracy [14,15]. As cetane number can be calculated from FAME composition, cetane number could be directly calculated from NIR spectra. What is more, since transesterification does not alter fatty acid composition, cetane number could be predicted from FAME composition of the starting oil.

The main problem in the production of biodiesel is the cost of the raw material (generally vegetable oils) resulting in biodiesel prices higher than those of petroleum diesel. One way to cut costs is the use of waste cooking oils (WCOs) as raw material. Used oils must be safely disposed in the EU in order to not to be harmful to humans or the environment (Council Directive 75/439/CEE of 16 June 1975). Therefore, the use of WCOs for biodiesel production can be the best economic alternative for the recycling and reutilization of these oils.

When an oil is used for frying, it undergoes numerous physical and chemical changes that modify its properties. The most common physical changes in WCOs are increase of viscosity [16,17], decrease of surface tension [18] and changes in sensory attributes [17,18], while the thermal (temperatures above 160 ºC), oxidative (through a mechanism of free radicals) and hydrolytic reactions result in the formation of alkanes, alkenes, symmetrical ketones of lower fatty acids, oxopropyl esters, aldehydes, semialdehydes, hydrocarbons, oxidized polymers, free fatty acids, glycerol, monoglycerides and diglycerides [17].

High acidity values are a significant hindrance for biodiesel production. If an oil has free fatty acids, the catalyst reacts with them to form soap and water (saponification reaction) with the consequent biodiesel yield decrease and reagent cost increase.
The main objective of this paper was to predict the cetane number of a future biodiesel from its starting WCO NIR-spectrum features, which will allow biodiesel manufacturers to select or discard a raw material for biodiesel production without the need to perform first the transesterification reaction. To do this, we first verified that cetane number can be obtained from biodiesel NIR spectrum and afterwards we assayed cetane number prediction from WCO NIR spectrum.

2. Material and Methods

2.1. Waste cooking oils (WCOs)

Fifty oils used for frying were supplied by the university canteen of the Reina Mercedes Campus (University of Seville) and private households. These WCOs were olive, sunflower and pomace oils, and mixtures of olive and sunflower oils (Table 1). This ensured a wide variety of oil types and frying habits in the WCO samples.

2.2. WCO conditioning

WCOs were firstly filtered to remove impurities such as leftover food, flour, etc. They may also contain a significant amount of water, however WCOs were not vacuum heated in order to obtain a wider range of biodiesel yields.

2.3. Biodiesel production

250 g WCO were mixed with 68.5 g methanol (1:8 molar ratio) and placed inside a 0.5-dm^3 stirred tank batch reactor together with 1 % (wt. WCO) sodium hydroxide. Transesterification reaction took place at 60 ºC for 60 min. Stirring was set to 750 rpm, diameter shovel being 6 cm. The reactor was equipped with a Dimroth condenser to prevent methanol losses.

Once the reaction was complete, the reaction mixture was let stand overnight. Two phases were separated, an upper phase of methyl esters in methanol and a lower phase containing about 10 % of the weight of the starting WCO, composed of glycerin and methanol excess. Subsequently, both phases were subjected to rotary evaporation to remove methanol. Finally, biodiesel was filtered using a Büchner funnel with a layer of Eco2Pure adsorbent (heat- treated hardwood shaving combined with crystalline aluminosilicate with binders) supplied by Filtertechnik Ltd. (United Kingdom), thus eliminating moisture and formed soaps from free fatty acids.

2.4. Analytical methods

2.4.1. Free acidity (FA) analysis

Once the WCOs were clean, FA was measured, that is, the percentage of free fatty acids WCOs contain. FA was expressed as oleic acid percentage and analysed according to the Official Methods of Analysis of the EC [19,20]. Briefly, 4–6 g WCO were placed into 250-cm^3 wide-mouth Erlenmeyer flask along with 50 cm^3 ethyl alcohol:ethyl ether solution (1:1 v/v) and a few drops of phenolphthalein, and then neutralized with 0.1 N NaOH until pink in colour. The FA contents ranged between 0.15 % and 9.73 % (Table

1). WCOs with FA higher than 2.5 % were pre-esterified with methanol using 1 % (wt.) sulphuric acid as catalyst in the same reactor and under the same conditions than for biodiesel production.

2.4.2. Fatty acid methyl esters (FAMEs) and cetane number determination.

Biodiesel FAME percentages were calculated following UNE-EN 14103:2011 standard. The percentage of each FAME in the sample was determined by gas chromatography using methyl heptadecanoate as internal standard. An HP 5890 series II gas chromatograph equipped with a SP2380 capillary column (60 m × 0.25 mm internal diameter × 0.25 μm film thickness) was used. The column temperature was set to 185 ºC and then the temperature program ramped from this temperature to 220 ºC at 3 ºC min^{-1}. The injection was operated in splitless mode, the injector and detector temperatures being 210 °C and 250 °C, respectively. FAMEs were identified by mass spectrometry, comparing the spectra with those in the database for this type of compounds (Wiley, NIST). Additionally, two WCO samples randomly chosen (samples 2 and 12) were analysed as well. To analyse these samples, 50 mg of each WCO were dissolved in 2 cm^3 heptane and then transesterified using 0.3 cm^3 2 N methanolic potassium hydroxide solution. After decanting, the supernatant was collected and FAME percentages were analysed in the GC system.

Cetane number (CN) of biodiesel was calculated from the FAME composition using the equation proposed by Bamgboye and Hansen [6]:

$$CN = 61.1 + 0.088x_2 + 0.133x_3 + 0.152x_4 – 0.101x_5 – 0.039x_6 – 0.243x_7 – 0.395x_8$$

where x_2, x_3, x_4, x_5, x_6, x_7 and x_8 stand for myristic, palmitic, stearic, palmitoleic, oleic, linoleic and linolenic acid methyl esters percentages (% wt.), respectively. The cetane number ranged between 46.8 and 59.8 (Table 1).

147 2.4.3. VIS/NIR spectra acquisition

148 Prior to spectra acquisition, WCO and biodiesel samples were placed in a thermostatic
149 water bath and maintained at 32 °C for 30 min, since temperature has an important
150 influence on the NIR radiation a sample reflects and absorbs.

151 A Vis/NIR Labspec Pro model LSP 350-2500P (Analytical Spectral Devices Inc.,
152 Boulder, CO, USA) spectrophotometer equipped with three detectors was used for
153 spectral acquisition, as described elsewhere [12]. The instrument is equipped with
154 internal shutters and automatic offset correction, the scanning speed time being 100 ms.
155 The spectrometer was equipped with a spectrophotometric cuvette accessory joined by
156 fibre optic connectors to the light source of the spectrometer on one side, and to the
157 detector of the spectrometer on the opposite side.

158 NIR spectra acquisition from 800 to 2200 nm was carried out in transmittance mode
159 using a 10-mm quartz cuvette with wavelength increment of 1 nm. This optical path
160 length was selected because it showed higher absorption intensity than 1 mm, 2 mm and
161 5 mm path-length quartz cuvettes when acquiring olive oil NIR spectra [12]. The
162 spectra of WCO and biodiesel samples were recorded using the Indico Pro software
163 (Analytical Spectral Devices Inc., Boulder). Two replicas of each sample were acquired.

164 2.4.4. Calibration procedure and model evaluation

165 Reflectance data was first transformed to absorbance. The resulting spectra were
166 divided into calibration and validation sets. Thirty randomly samples were used for
167 multivariable calibration and the 20 remaining samples were used as validation set.
168 Partial least squares (PLS) models using full-cross internal validation were built with
169 The Unscrambler software (CAMO Software AS, Norway).

The performance of the models was evaluated based on root mean square error of calibration (RMSEC), root mean square error of full-cross validation (RMSECV), multiple correlation coefficient of calibration (r^2_c) and multiple correlation coefficient of full-cross validation (r^2_{cv}) in the calibration sample set, and root mean square error of prediction (RMSEP), standard error of prediction (SEP) and ratio of performance to deviation (RPD) in the validation sample set. Among them, the most important parameters to assess the performance of the model are r^2_c (calibration) and RPD (validation): the higher these parameters are, the higher the accuracy of the model.

3. Results and Discussion

3.1. Features of the WCO and biodiesel NIR spectra

NIR absorption is assumed linear with the concentration of organic materials. The NIR spectrum of a sample is composed of the first and second overtones (800-1800 nm) and combinations bands (1800-2700 nm) of fundamental, largely hydrogenic, vibrations that occur in the MIR region. The acquired WCO and biodiesel absorbance spectra are shown in Fig. 1, showing various overlapping peaks. The obtained spectra for WCOs (Fig. 1a) are similar to those previously obtained for olive oils, so their main features are described elsewhere [12]. Briefly, from 800 to 2200 nm, firstly a broad absorbance band occurs at 1210 nm due to C–H second overtones and CH=CH– stretching vibrations. Then, a large, strong absorption band of the water first overtone is found in the range 1350-1450 nm. The absorption intensity near 1720 nm is related to the first overtone of the C–H vibration of several chemical groups (=CH–, $–CH_3$, $–CH_2–$). Another broad water combination band is observed at 1880-2100 nm. The two

described water bands consist of multiple overlapping bands. Finally, the absorption band of the C–H vibration of *cis*-unsaturation occurs in the area close to 2143 nm.

Interestingly, biodiesel NIR spectra were identical to WCO NIR spectra (Fig. 1b). Similarly to WCO spectra, the highest intensity peak in biodiesel spectra was found near 1725 nm, wavelength in which the maximum absorption band of the triolein spectrum has been reported [21]. Obviously, biodiesel does not contain triolein, so this absorption band and the one close to 2143 nm are probably due to the above-mentioned C–H vibrations of the fatty acids of the FAMEs (and therefore of the fatty acids of triglycerides in WCO spectra). Vegetable oils are mainly composed of triglycerides while biodiesel is composed of FAME. Since transesterification reaction (regardless the reactor type and operational conditions) does not alter the fatty acids of triglycerides [4], the fatty acid composition of the starting oil should be the same than the fatty acid composition of the resulting biodiesel [1–3]. Therefore, it can be logical that the NIR spectrum of an oil and that of its derived biodiesel are the same. The solely, slight difference between WCO and biodiesel spectra was found in the range 2150-2200 nm, the absorption intensity being higher in biodiesel spectra.

3.2. Free acidity

Three WCOs (samples 18, 35 and 42) had FA higher than 2.5 % (Table 1), so these samples were subjected to previous esterification to reduce their acidity. Neither the resulting FAs nor NIR spectra were measured after esterification because these WCOs were immediately subjected to transesterification in the same reactor. NIR spectra corresponding to these 3 samples were, therefore, those acquired for the starting WCOs.

3.3. Cetane number results from FAME composition

Biodiesel usually has cetane number higher than conventional diesel, providing thus better combustion efficiency. The FAME content is of major importance because the overall fuel properties of a biodiesel sample can be obtained from the properties of the individual fatty acid methyl esters that comprise it [1,3]. Cetane number is one of these properties depending on FAME composition and therefore was calculated from this composition applying the equation proposed by Bamgboye and Hansen [6]. There were noticeable differences in biodiesel FAME composition depending on the type of vegetable oil from which WCO came from (Table 1). On the contrary, there were not differences in FAME composition between starting WCO and resulting biodiesel of the two samples analysed (data not shown), which verifies that transesterification does not alter FAME profile. Thus, the palmitic, stearic, oleic and linoleic acids percentages in biodiesel sample 2 were 13.2, 3.1, 71.7 and 8.2, respectively, while they were 13.1, 3.2, 72.0 and 8.4, respectively, in the WCO sample 2.

Applying the Bamgboye and Hansen's equation, the cetane number of the 50 biodiesel samples ranged between 46.8 and 59.8 (Table 1), being the standard deviation 4.73. The standard deviation of the validation set (20 samples), required for the calculation of RPD in NIRS, was similar (4.74). Cetane numbers from olive oil-derived biodiesels were markedly higher than those of sunflower oil-derived biodiesels because of the higher content in linoleic acid of sunflower oil. The cetane numbers obtained are higher than those of petroleum diesel fuels (48-51) and are in the range indicated in the UNE-EN 14214:2013 standard for biodiesel derived from vegetable oils, which illustrates the potential of biodiesel fuel from WCO.

3.4. Cetane number calculation from biodiesel NIR spectra.

FAME determination by NIRS in vegetable oils [14] and biodiesel [15] has been previously reported. Since cetane number was calculated from FAME composition, it is logical to think that cetane number can be also obtained from biodiesel NIR spectrum.

The PLS calibration model built using NIR absorbance spectra of the 30 biodiesel samples of the calibration set, without any previous pretreatment or normalization, achieved r^2_c, r^2_{cv}, RMSEC and RMSECV of 0.990, 0.983, 0.470 and 0.621, respectively (Table 2). The number of optimal principal components to build this PLS model was four. According to Shenk *et al.* criteria [22], the PLS calibration model had excellent precision ($r^2_c \geq 0.90$), and the root mean square error was low. The full cross validation statistics confirmed the goodness of the PLS model. This calibration model was used in the prediction exercises. The predicted cetane numbers of the 20 samples of the validation set are listed in Table 1. As can be observed in Table 2, SEP was 1.108, providing RPD = 4.27, which accounts for the excellent precision of the obtained PLS model for cetane number determination from biodiesel NIR spectra. According to criteria mentioned earlier [22], RPD must be higher than 3 for a PLS model to be considered of excellent precision. Other author stated that predictive models with RPD values between 2 and 10 are suitable for routine analysis [23]. These results could be improved using normalized or derivative spectra, eliminating spectral variables without information related to the measured parameter, such as noise and background, or eliminating outliers in the calibration and validation sets [12]. However, these techniques were not assayed because it was not the aim of this work. Just as an example, by eliminating sample 37 from the validation set (sample marked by The Unscrambler software as outlier) SEP decreases up to 0.802 and therefore RPD increases to 5.90.

3.5. Cetane number prediction from WCO NIR spectra

As mentioned earlier, fatty acid composition was not modified by transesterification reaction and WCO and biodiesel spectra were similar. Therefore, biodiesel cetane number could be predicted from the NIR spectrum of the starting WCO. For further comparison with the results obtained with biodiesel spectra, the PLS model for cetane number prediction from WCO NIR spectra was also directly built without any spectrum pretreatment. The calibration statistics are shown in Table 2, showing the excellent performance of the PLS model (r^2_c = 0.971; RPD = 3.83), the number of principal components being again equal to four. The performance of cetane number prediction using WCO NIR spectra was somehow lower than when using biodiesel NIR spectra. This could be due to the fact that biodiesel samples are clean (distilled and filtered), being almost exclusively composed of FAME, while WCOs contained not only triglycerides, but also part of the other vegetable oil compounds and different degradation compounds due thermal, oxidative and hydrolytic reactions occurring during frying, as mentioned earlier [17], which can affect the PLS model. The removal of uninformative spectral variables from the PLS calibration model would enhance the prediction performance [12]. Nevertheless, the potential and accuracy of both cetane number calculation from NIR biodiesel spectra and cetane number prediction from starting WCO NIR spectra are demonstrated. SEP using biodiesel and WCOs spectra were 1.108 and 1.238, respectively. Other methods, such the ASTM D4737-10(2016) standard for the calculation of cetane number of distillate fuels from density and distillation recovery temperature measurements, have higher experimental errors. To be specific, this standard ASTM D4737-10(2016) estimates the ASTM cetane number (Test Method D613) of distillate fuels with cetane number within the range from 32.5 to 56.5 with an expected error of prediction lower than ±2 units for 65 % of the distillate fuels, indicating that errors may be even greater for fuels whose properties fall outside

the recommended range of application. The repeatability and the reproducibility of this ASTM D613 test method to calculate the cetane number of biodiesel samples from soybean oil have been reported to be ±0.9 units and ±4.3 units, respectively [11].

What is more, the r^2 of the equation used to calculate cetane number based on biodiesel FAME composition [6], used as reference data in this work, was 0.883, which indicates that this equation can predict cetane number with solely 88 % accuracy. Similar equations that correlate biodiesel cetane number with FAME weight composition can be found in literature [7–9]. A comparative study among these equations using biodiesels from many sources and feedstocks exhibited r^2 values of 0.82, 0.81, 0.80 and 0.83 for the equations of Bamgboye and Hansen [6], Gopinath *et al*. [7], Piloto Rodríguez *et al*. [8] and Giakoumis and Sarakatsanis [9], respectively. The absolute error when predicting cetane number of WCO-derived biodiesel using the Giakoumis and Sarakatsanis' equation was 8.9 % [9].

Biodiesel cetane number can be also calculated from the weight percentage of each FAME in the biodiesel sample and the cetane number of each FAME [3,10], percent errors between 1.6 % and 16.3 % being reported for different biodiesel fuels [10]. The cetane number of each FAME can be calculated through an equation based on its molecular weight and its number of double bonds with an average absolute deviation of 5.95 % [11]. Some authors have claimed that the biodiesel cetane number prediction errors using this last equation are minor than the previously reported by Bamgboye and Hansen [11].

It is worth noting that if FAME composition of a biodiesel and its starting oil are identical (transesterification reaction does not alter FAME profile), biodiesel cetane number could be also predicted by applying any of the aforementioned equations to oil fatty acid composition. However, NIRS is cheaper (not only in terms of equipment, but

313 also considering reagents and maintenance) and much quicker than gas
314 chromatography. Besides, NIRS would allow for real-time determination of cetane
315 number. Therefore, NIRS is more suitable for cetane number prediction than equations
316 based on FAME composition.

317

318 **4. Conclusions**

319 Near infrared spectroscopy showed great potential for the fast and accurate prediction of
320 biodiesel cetane number. NIRS allowed for the determination of cetane number not only
321 from biodiesel NIR spectra, but also from waste cooking oil NIR spectra, reaching high
322 RPD (4.27 and 3.83, respectively), thus demonstrating the accuracy of the PLS models
323 built from NIR spectra. The standard error of prediction of cetane number from waste
324 cooking oil NIR spectra was 1.2, which is in agreement with the errors provided by both
325 the ASTM standard method and the proposed equations based on FAME composition
326 available in literature. This implies that cetane number of a future biodiesel can be
327 predicted prior performing transesterification reaction by acquiring NIR spectrum of the
328 starting oil. The advantages for industrial implementation are, therefore, numerous,
329 because cetane number prediction from NIR oil spectra would allow discarding
330 substrates not suitable for biodiesel production, thus reducing costs. This NIRS
331 prediction is due to the fact that fatty acid distribution of the produced biodiesel and that
332 of its starting oil are the same, and biodiesel cetane number depends on the fatty acid
333 composition (mainly chain length and unsaturation number) of the substrate from which
334 it is produced. NIR spectra of biodiesels and waste cooking oils were alike, probably
335 because they show mostly C−H vibrations of fatty acids.

336

Acknowledgements

This work was supported by the European Union Funds under grant LIFE 13-Bioseville ENV/ES/1113.

References

[1] Knothe G. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process Technol 2005;86:1059–70. doi:10.1016/j.fuproc.2004.11.002.

[2] Giwa SO, Adama KO, Nwaokocha CN, Solana OI. Characterization and flow behaviour of sandbox (Hura crepitans Linn) seed oil and its methyl esters. Int Energy J 2016;16:65–72.

[3] Ramos MJ, Fernández CM, Casas A, Rodríguez L, Pérez Á. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresour Technol 2009;100:261–8. doi:10.1016/j.biortech.2008.06.039.

[4] García-Martín JF, Barrios CC, Alés-Álvarez FJ, Dominguez-Sáez A, Alvarez-Mateos P. Biodiesel production from waste cooking oil in an oscillatory flow reactor. Performance as a fuel on a TDI diesel engine. Renew Energy 2018;125:546–56. doi:10.1016/j.renene.2018.03.002.

[5] Xiao G, Gao L. First Generation Biodiesel. Biofuel Prod - Recent Dev Prospect 2010:45–64.

[6] Bamgboye AI, Hansen AC. Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition. Int Agrophysics 2008;22:21–9.

[7] Gopinath A, Puhan S, Nagarajan G. Relating the cetane number of biodiesel fuels to their fatty acid composition: A critical study. Proc Inst Mech Eng Part D J Automob Eng 2009;223:565–683. doi:10.1243/09544070JAUTO950.

[8] Piloto-Rodríguez R, Sánchez-Borroto Y, Lapuerta M, Goyos-Pérez L, Verhelst S. Prediction of the cetane number of biodiesel using artificial neural networks and multiple linear regression. Energy Convers Manag 2013;65:255–61. doi:10.1016/j.enconman.2012.07.023.

[9] Giakoumis EG, Sarakatsanis CK. Estimation of biodiesel cetane number, density, kinematic viscosity and heating values from its fatty acid weight composition. Fuel 2018;222:574–85. doi:10.1016/j.fuel.2018.02.187.

[10] Clements LD. Blending rules for formulating biodiesel fuel, in liquid fuels and industrial products from renewable resources. Proc. third Liq. fuel Conf. Nashville, TN, 1996, p. 44–53.

[11] Ramírez-Verduzco LF, Rodríguez-Rodríguez JE, Jaramillo-Jacob ADR. Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition. Fuel 2012;91:102–11. doi:10.1016/j.fuel.2011.06.070.

[12] García Martín JF. Optical path length and wavelength selection using Vis/NIR spectroscopy for olive oil's free acidity determination. Int J Food Sci Technol 2015;50:1461–7. doi:10.1111/ijfs.12790.

[13] Zhang WB. Review on analysis of biodiesel with infrared spectroscopy. Renew Sustain Energy Rev 2012;16:6048–58. doi:10.1016/j.rser.2012.07.003.

[14] Marquez AJ, Díaz AM, Reguera MIP. Using optical NIR sensor for on-line

virgin olive oils characterization. Sensors Actuators, B Chem., vol. 107, 2005, p. 64–8. doi:10.1016/j.snb.2004.11.103.

[15] Baptista P, Felizardo P, Menezes JC, Correia MJN. Multivariate near infrared spectroscopy models for predicting the methyl esters content in biodiesel. Anal Chim Acta 2008;607:153–9. doi:10.1016/j.aca.2007.11.044.

[16] Mittelbach M, Enzelsberger H. Transesterification of heated rapeseed oil for extending diesel fuel. J Am Oil Chem Soc 1999;76:545–50. doi:10.1007/s11746-999-0002-x.

[17] Nawar WW. Chemical Changes in Lipids Produced by Thermal Processing. J Chem Educ 1984;61:299–302. doi:10.1021/ed061p299.

[18] Cvengroš J, Cvengrošová Z. Used frying oils and fats and their utilization in the production of methyl esters of higher fatty acids. Biomass and Bioenergy 2004;27:173–81. doi:10.1016/j.biombioe.2003.11.006.

[19] EU standard methods. Commission Regulation (EEC) No 2568/91 on the characteristics of olive oil and olive-residue oil and on the relevant methods of analysis. Off J Eur Communities 1991:1–15. doi:2004R0726 - v.7 of 05.06.2013.

[20] European Union. COMMISSION IMPLEMENTING REGULATION (EU) No 1348/2013 amending Regulation (EEC) No 2568/91. Off J Eur Union 2013;2013:31–67.

[21] García-González DL, Baeten V, Fernández Pierna JA, Tena N. Infrared, raman, and fluorescence spectroscopies: Methodologies and applications. Handb. Olive Oil Anal. Prop., 2013, p. 335–93. doi:10.1007/978-1-4614-7777-8_10.

[22] Shenk JS, Workman JJ, Westerhans MO. Application of NIRS to agricultural

405 products. Handb Near-Infrared Anal 1992:383–431.
406 doi:doi:10.1201/9781420002577.pt4a.
407 [23] Fearn T. Assessing calibrations: SEP, RPD, RER and R2. NIR News
408 2002;13:12–3. doi:10.1255/nirn.689.
409

Table 1

Table 1. Free acidity (FA) of starting WCO, biodiesel FAME composition, cetane number of the produced biodiesels calculated by Bamgboye and Hansen equation (CN FAME) and biodiesel NIR spectra (CN Fuel-NIR), predicted cetane numbers using WCO NIR spectra (CN Oil-NIR) and type of vegetable oil used to produce WCO.

Sample	FA (%)	14:0 (%)	16:0 (%)	16:1 (%)	18:0 (%)	18:1 (%)	18:2 (%)	18:3 (%)	CN FAME	CN Fuel-NIR	CN Oil-NIR	Starting WCO
1	0.21	0.24	7.8	3.1	0.23	30.4	55.0	0.12	48.0			Sunflower
2	0.60	0.08	13.2	3.1	1.19	71.7	8.2	0.14	58.4			Olive
3	1.61	0.00	12.7	3.6	0.75	71.8	6.8	0.15	58.7			Olive
4	2.17	0.08	8.2	3.3	0.35	33.1	53.2	0.12	48.4			Sunflower
5	2.01	0.00	13.7	3.7	0.67	75.9	2.5	0.12	59.8			Olive
6	0.29	0.03	13.5	3.9	0.09	74.5	6.2	0.17	59.0			Olive
7	1.30	0.17	14.3	3.2	0.00	72.8	5.8	0.15	59.2			Mixture
8	0.67	0.03	14.4	3.2	0.00	74.1	5.7	0.19	59.2			Mixture
9	1.10	0.14	14.3	3.1	0.00	72.8	6.0	0.13	59.1			Mixture
10	1.16	0.13	13.9	2.8	0.00	74.0	5.3	0.16	59.1			Olive
11	0.62	0.09	14.6	3.1	0.00	73.5	5.6	0.15	59.2			Olive
12	1.22	0.17	14.5	3.0	0.00	73.5	5.8	0.39	59.1			Olive
13	0.50	0.03	14.5	2.5	0.00	70.3	7.3	0.13	58.9			Olive
14	0.24	0.06	7.6	2.9	0.13	36.8	49.2	0.09	49.1			Sunflower
15	0.66	0.08	9.9	3.5	0.14	73.2	10.6	0.19	57.4			Mixture
16	0.41	0.07	7.5	2.6	0.12	29.0	59.5	0.16	46.8			Sunflower
17	0.69	0.05	13.0	3.4	0.07	73.9	6.3	0.16	58.9			Olive
18	9.72	0.13	8.5	3.2	0.17	35.3	50.6	0.20	49.0			Mixture
19	0.94	0.20	14.2	3.2	0.00	44.0	34.6	0.15	53.3			Mixture
20	0.33	0.14	7.8	3.2	0.24	30.8	53.4	0.08	48.4			Sunflower

21	0.52	0.15	14.6	3.8	0.13	72.3	5.5	0.15	59.4			Olive
22	0.15	0.03	13.6	3.8	0.06	74.8	4.6	0.17	59.4			Olive
23	0.72	0.09	12.6	3.9	0.08	61.7	19.9	0.19	56.1			Mixture
24	0.24	0.13	8.1	3.4	0.00	31.3	52.8	0.09	48.6			Sunflower
25	0.21	0.17	7.6	3.1	0.00	29.5	57.0	0.08	47.6			Sunflower
26	0.88	0.06	13.2	3.3	0.93	71.7	4.6	0.34	59.2			Mixture
27	1.91	0.12	12.2	3.2	0.85	64.0	17.2	0.17	56.4			Mixture
28	1.21	0.08	13.0	3.0	0.96	66.4	13.7	0.17	57.2			Mixture
29	0.21	0.00	12.2	3.6	0.88	73.6	7.4	0.19	58.4			Olive
30	0.50	0.06	11.6	3.2	0.89	66.9	12.3	0.17	57.4			Olive
31	0.37	0.13	8.4	3.5	0.27	34.5	50.5	0.14	49.1	49.2	49.8	Sunflower
32	1.28	0.02	11.3	3.7	0.61	74.5	4.7	0.19	59.0	60.4	58.9	Olive
33	1.29	0.00	11.5	3.6	0.66	74.9	4.5	0.17	59.0	60.0	58.6	Olive
34	0.71	0.09	13.0	2.7	1.10	67.9	12.6	0.20	57.4	58.0	57.8	Olive
35	3.33	0.16	13.9	3.2	0.90	72.9	5.3	0.19	59.2	60.1	57.6	Olive
36	1.06	0.06	13.7	3.1	0.82	68.0	12.8	0.22	57.5	59.0	59.7	Pomace
37	1.05	0.06	13.9	2.6	0.68	69.1	10.7	0.19	57.9	62.5	59.1	Pomace
38	0.37	0.14	8.0	3.0	0.22	38.7	47.8	0.10	49.4	49.7	48.5	Sunflower
39	0.22	0.35	8.5	3.1	0.35	46.6	39.2	0.12	51.3	52.2	50.8	Sunflower
40	0.30	0.12	7.6	3.1	0.34	31.2	55.4	0.13	47.8	48.2	47.5	Mixture
41	2.22	0.04	13.3	3.5	0.91	74.9	5.0	0.21	59.1	60.4	58.4	Olive
42	3.37	0.13	13.8	3.9	0.97	74.2	4.7	0.13	59.4	62.3	58.1	Olive
43	0.98	0.10	7.7	3.8	0.12	31.5	55.6	0.10	47.9	50.8	48.7	Olive
44	0.65	0.05	10.6	3.4	0.61	62.7	21.6	0.15	55.2	56.1	57.2	Olive
45	0.21	0.08	7.2	3.1	0.13	31.4	55.9	0.09	47.7	48.5	46.5	Sunflower
46	0.28	0.15	8.3	3.0	0.31	34.5	51.3	0.09	48.8	49.6	50.5	Sunflower
47	0.61	0.05	9.4	2.9	0.56	74.3	10.5	0.19	57.2	57.8	58.8	Mixture
48	0.58	0.08	8.1	3.2	0.28	34.8	52.7	0.13	48.4	48.8	50.1	Sunflower

49	1.03	0.06	11.6	3.0	0.68	58.3	25.0	0.16	54.6	56.8	54.1	Mixture
50	2.30	0.17	13.2	4.3	1.26	69.2	9.2	0.15	58.4	58.7	58.8	Olive

14:0 = myristic acid; 16:0 = palmitic acid; 18:0 = stearic acid; 16:1 = palmitoleic acid; 18:1 = oleic acid; 18:2 = linoleic acid; 18:3 = linolenic acid.

Table 2

Table 2. Calibration and prediction statistics for cetane number calculation using biodiesel and WCO spectra.

	r^2_c	r^2_{cv}	RMSEC	RMSECV	RMSEP	SEP	RPD
CN Fuel-NIR	0.990	0.983	0.470	0.621	1.650	1.108	4.27
CN Oil-NIR	0.971	0.965	0.760	0.867	1.260	1.238	3.83

r^2_c: correlation coefficient of calibration; r^2_{cv}: correlation coefficient of full cross validation; RMSEC: root mean square error of calibration; RMSECV: root mean square error of full cross validation; RMSEP: root mean square error of prediction; SEP: standard error of prediction; RPD: ratio of performance to deviation.

Figure 1

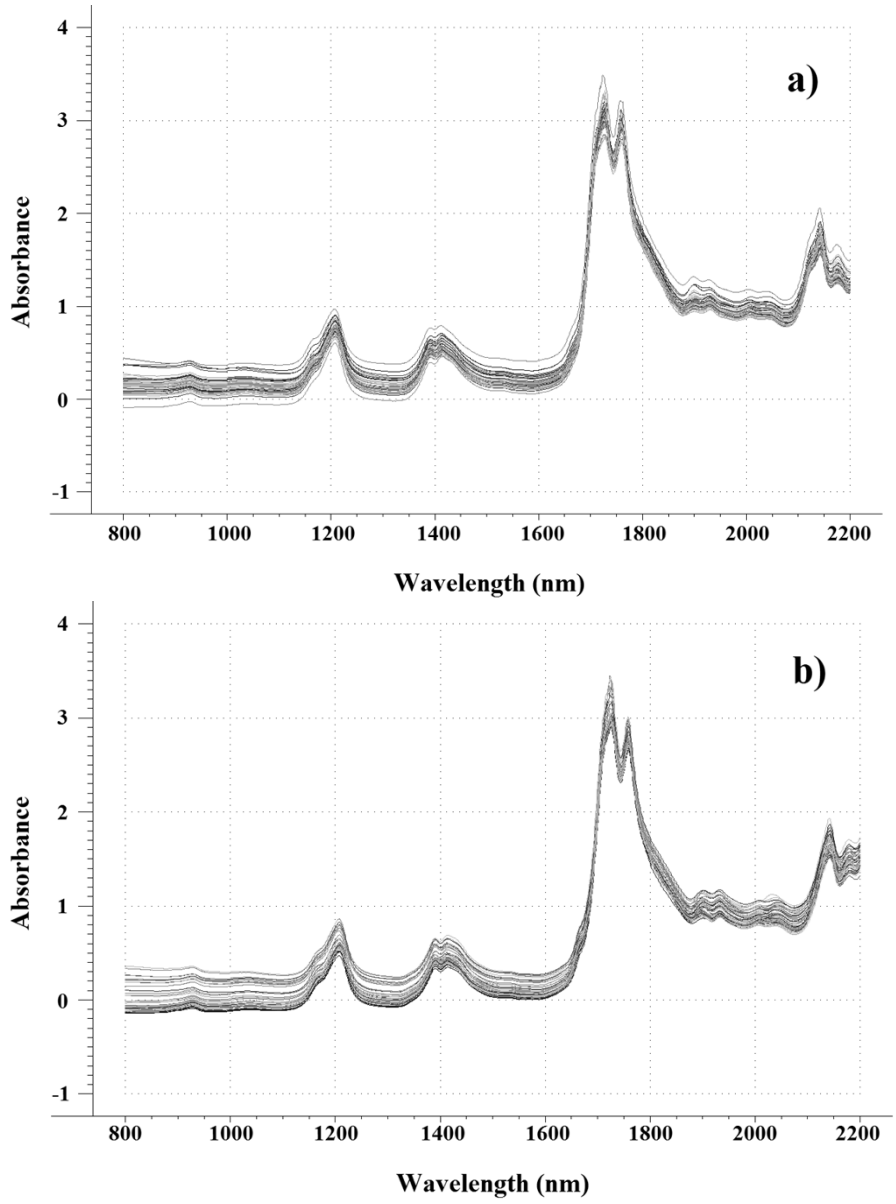

Fig. 1. WCO (a) and biodiesel (b) NIR spectra.