

SPECTROMETRIC DETERMINATION OF CONTENT OF METHYL PALMITATE IN METHYL ESTERS OF WASTE COOKING OILS

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ABSTRACT

The second-generation liquid biofuels are fuels derived from non-food raw materials, i.e. waste cooking oils and animal fats. They are waste raw materials from the agri-food industry, hence their quantity is limited, and their quality depends, *inter alia*, on the place of their acquisition. Considering the fact that rheological properties of liquid biofuels are closely correlated with the quality of raw materials from which they are obtained, the industrial production of biofuels from waste fats requires development of new analytical methods, allowing for a quick assessment of the quality of the obtained products. The aim of the study was to confirm the possibility of using near infrared spectrometry to assess the content of methyl palmitate in biofuels produced from waste cooking oil. The calibration models were based on 41 absorbance spectra recorded in the range of 400-2170 nm for samples containing from 0 to 5 % of methyl palmitate. The obtained results confirmed that there is a possibility of effective detection of the concentration of this ester in biofuel using the spectrum in the range of 1644-1778 nm. The developed PLS calibration models are characterized by a determination coefficient (R^2) exceeding the value of 0.99.

Introduction

In recent years an increase in the society's demand for energy with a simultaneous decrease in fossil fuel resources has resulted in the dynamic development of renewable energy sources, including biodiesel (Nigam, 2011; Nejad, 2018). Biodiesel is methyl ester of higher fatty acids that can be easily obtained from oils and fats of various origins, i.e. vegetable oils (Lang, 2001; Çelikten, 2010), waste cooking oils (Gao, 2019) and animal fats (Sander, 2018). Biodiesel is a result of transesterification of triacylglycerols with low molecular weight monohydroxy alcohols (methanol or ethanol), most frequently catalysed by NaOH or KOH (Semwal, 2011). The purchase of fat may be up to 80% of the total cost of biodiesel production (Sajjadi, 2016). The research conducted by Xu (Xu, 2016) compared and showed the total cost of biodiesel production in China from waste fats (USD 979 per tonne) and palm oil (USD 1145 per tonne), which proves the economic benefits of using waste fats as a raw material for the production of liquid biofuels. The European quality standard EN 14214

provides for thresholds of 25 biofuel quality parameters that comply with the requirements of motor-vehicles users (Silva, 2019). According to this standard biodiesel should not contain free fatty acids and its acid number should not exceed 0.5 mg KOH/g. The physico-chemical properties of biodiesel strictly depend on the type and quality of the applied raw material (Liu, 2008). At present, the commonly applied diagnostic methods apply high-performance liquid chromatography (HPLC) or gas chromatography (GC) (Freedman, 1984; Schale, 2012). Spectroscopic methods such as near infrared transmittance (NIT) are an interesting alternative to chromatographic methods in the study of physical and chemical properties of biodiesel (Paul, 2016; da Silva, 2017; García-Martín, 2019).

This study discusses the method of determining methyl palmitate in methyl esters of waste cooking oil, using calibration models based on spectroscopic spectra. It constitutes a development of previous research conducted by the authors (Golimowski, 2017; Czechłowski, 2019).

Experimental

Materials

The waste cooking oil (WCO) was provided by a local confectionery. Before being used to produce biodiesel, it was filtered to separate solid impurities. Methanol, methyl palmitate and potassium hydroxide were purchased from the Aldrich company. Physico-chemical properties of waste cooking oil and profile of fatty acids of fats used to produce biodiesel were described before (Czechłowski, 2019).

Table 1.

Physico-chemical properties of waste cooking oil used for production of biodiesel

Parameter	Unit	WCO	Standard
Acid value	(mgKOH·g ⁻¹)	2.6	PN-EN 14104
Density (15°C)	(kg·m ⁻³)	912	ISO 12185
Kinematic viscosity (40°C)	(mm ² ·s ⁻¹)	53.99	ISO 3104
Ignition point	(°C)	242	ASTM D 92
Heating value	(kJ·kg ⁻¹)	38868	PN C 04062

Table 2.

Profile of fatty acids of fats used for production of biodiesel

Fatty acids (%)		WCO
Saturated fatty acids	14:0	-
	15:0	-
	16:0	5.45
	17:0	-
	18:0	2.19
	20:0	0.65
	22:0	0.33

Spectrometric determination...

Fatty acids (%)		WCO
Monounsaturated fatty acids	14:1	-
	16:1	0.27
	17:1	-
	18:1	64.91
	20:1	1.61
Multiple unsaturated fatty acid	22:1	0.68
	18:2	16.46
	18:3	5.15

Obtainment of biodiesel from waste cooking oil

A reaction mixture comprising methanol and waste cooking oil at a molar ratio of 6:1 was placed in a laboratory biodiesel processor. The solution was heated up to 35°C. The catalyst, potassium hydroxide (1.7% w/w), was dissolved in a minimum amount of methanol and added to the reaction mixture. The reaction was carried out for 1 hour at 35°C and then left for 24 hours to separate the glycerine phase from biodiesel. The excess amount of methanol was evaporated by heating the biofuel to 70°C. The obtained methyl esters of waste cooking oil were washed with a 3% phosphoric acid solution (V) and brine (saturated with a sodium chloride solution) until a clear solution was obtained.

Preparation of mixtures of biodiesel with methyl palmitate

Each analysed sample resulted from adding a specific amount of methyl palmitate to 400 cm³ of the prepared biodiesel at 50°C. At 21°C methyl palmitate has a crystalline form; hence it was heated up to 50 °C to obtain a liquid phase. Initially, methyl palmitate was added to biofuel in 0.2 cm³ portions until its concentration equalled to 1% and then its dosage was increased to 0.8 cm³ until its concentration amounted to 5%. Each time a dose of methyl palmitate was added to biodiesel, the solution was mixed for 5 minutes, then 5 cm³ were put into a measuring cell and the absorbance spectrum was recorded using the transmission method. After recording the spectrum, the sample was poured back into the stock solution and another dose of methyl palmitate was added. In this way, 41 samples of biodiesel mixtures with concentrations of methyl palmitate in the range of 0-5% were obtained.

Recording of absorption spectra

The absorption spectra were recorded with the AgroSpec spectrometer from tec5, which was equipped with two detectors: MMS1 (VIS) and PGS 2.2 (NIR) manufactured by Carl Zeiss. The combined and effective spectral range of the device was 400-2170 nm. During the measurements, absorbance spectra were recorded with a resolution of 2 nm. The spectrometer was equipped with two probes: the RP-7 probe that was used as light and was placed 25 mm above the sample in the optical axis of the receiving probe. This probe generated a light beam that penetrated the biofuel sample put into the measuring cell. The A40 probe was put 50 mm below the sample and collected light passing through the sample. The spectra were recorded by using tec5 MultiSpec Pro 3.6

Development of calibration models

The obtained absorption spectra of biodiesel and methyl palmitate mixtures were the basis for developing calibration models using the method of partial least squares regression (PLS). The independent variable was the concentration of methyl palmitate put into the analysed sample. The calibration models were developed using the NIPALS algorithm, whereas any necessary calculations were carried out using the Camo Unscrambler X software version 10.1. Subsequently, the models were cross validated to evaluate their suitability for determining the content of methyl palmitate in biodiesel produced from waste cooking oil. The following parameters of cross validation (CV) were evaluated (CAMO, 2015):

- root-mean-square error (RMSECV):

$$RMSECV = \sqrt{\frac{1}{I_{tot}} \sum_{s=1}^{N_{seg}} \frac{1}{yWeights^2} \sum_{i=1}^{I_s} Fiys(i, j)^2}$$

where:

- I_{tot} – number of samples used to build the calibration model,
- N_{seg} – number of data segments used for cross-validation,
- $yWeights$ – weights of variable y ,
- I_s – number of data in the segment,

- determination coefficient (R^2CV):

$$R^2CV = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y}_i)^2}$$

- directional coefficient of the regression equation (Slope):

$$Slope = \frac{N \sum y \cdot x - \sum y \sum x}{N \sum x^2 - (\sum x)^2}$$

- free expression of regression equation (Offset)

Results of research and discussion

Figure 1 shows the absorption spectrum recorded for pure methyl palmitate, from which it may be concluded that the substance strongly absorbs radiation for the following wavelengths: 1200, 1420, 1460, 1690, 1721 and 2070 nm.

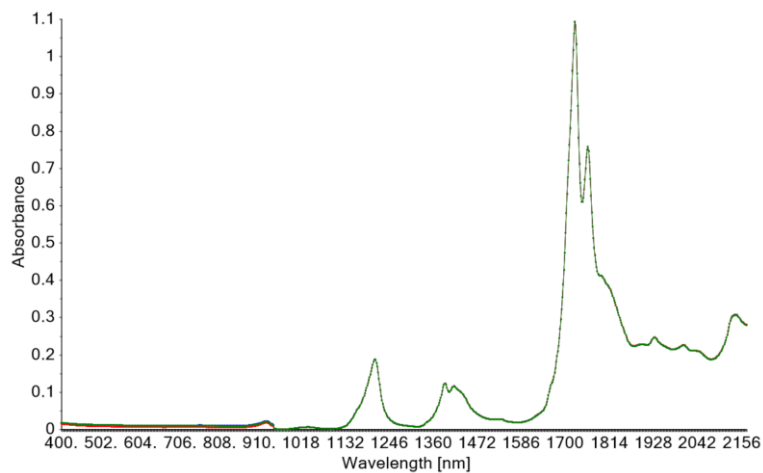


Figure 1. Absorption spectrum of methyl palmitate

Figure 2 shows the absorption spectra of mixtures of biodiesel and methyl palmitate in the concentration range of 0-5% (v/v). 41 absorption spectra were applied to develop calibration models in the concentration range of 0-5% of methyl palmitate. Absorptions in the NIR region (780–2500 nm) are generated from fundamental vibrations by two processes - overtones and combinations. In the spectrum shown in Figure 2, the following bands can be observed: 816 nm – third overtone C-H bond; 1193 nm – second overtone of C-H bond; 1410 nm – combination band of C-H bond; 1743 nm – first overtone of C-H bond.

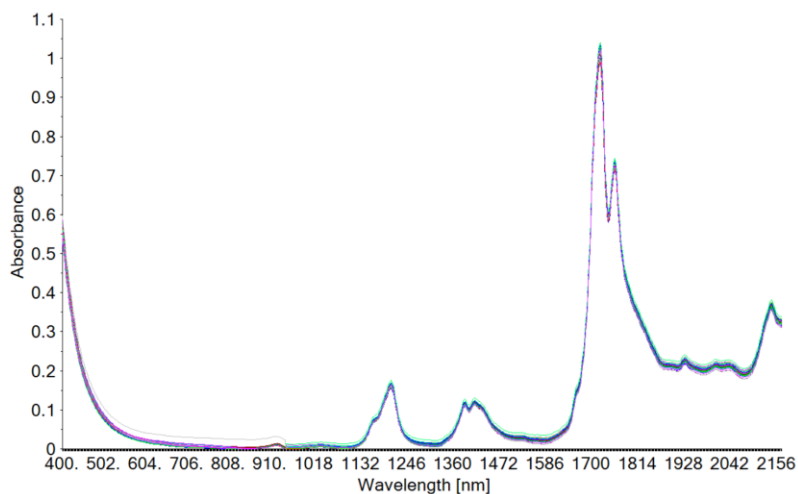


Figure 2. Absorption spectra of mixtures of methyl esters of waste cooking oil and methyl palmitate (concentration range of 0-5%)

The calibration model developed based on the absorption spectra shown in Fig. 2 was applied to determine the relationship between regression coefficients and the wavelength of the absorbed radiation (Fig. 3).

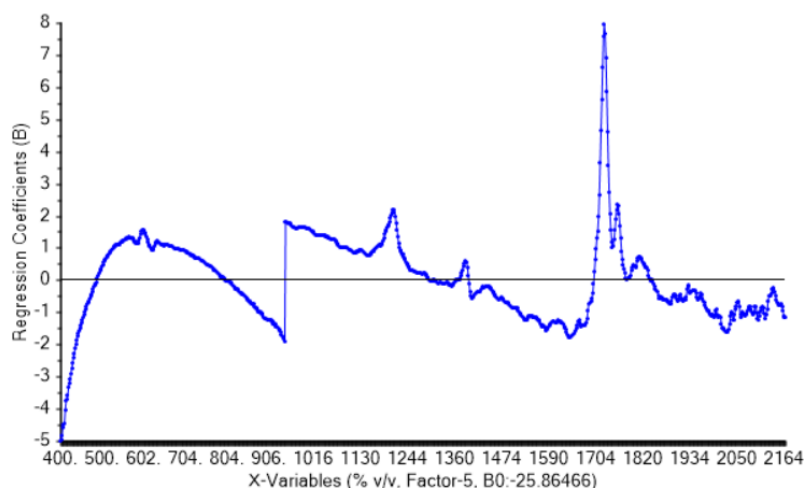


Figure 3. Relationship between regression coefficients and wavelength for the whole range of recorded spectrum 400-2170 nm

Based on the graph shown in fig. 3, the following wavelength ranges were selected for which calibration models were developed: 492-792 nm; 950-1254 nm; 1134-1178 nm; 1198-1220 nm; 1134-1178 nm and 1780-1840 nm.

Figure 4 shows the results of prediction (blue) and cross-validation (red) for the calibration model made based on the whole registered range of the absorbance spectrum. The determination coefficient of cross-validation for the wavelength range 400-2170 nm equalled to 0.957 and the mean square error amounted to 0.325%. The graph shows a similar linear relationship between prediction results and data acquired in a laboratory where the methyl palmitate content of the sample is known. The directional coefficient of the regression equation (slope) is close to units and the regression line runs at an angle close to 45°.

The next step was to collect all parameters to assess the accuracy of the calibration model for each of the previously selected ranges. These parameters are summarised in Table 3. In the course of developing calibration models, attempts were made to randomly combine ranges to improve the quality of the calibration model.

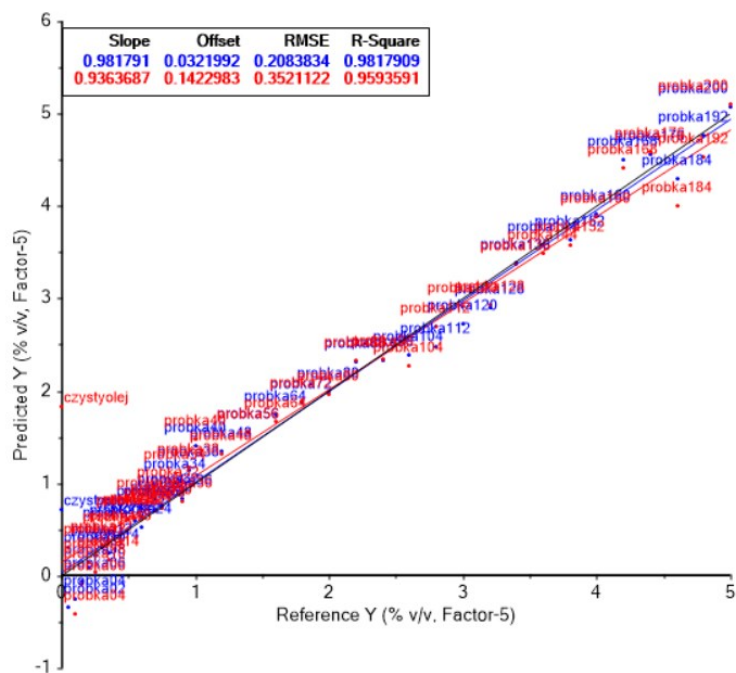


Figure 4. Graph showing a comparison of prediction results for the entire tested wavelength range 400-2170 nm. Red – cross-validation results, blue – data for making the calibration model, slope – directional coefficient of the regression equation

Table 3.

Cross-validation parameters of calibration models based on the spectral data recorded for methyl esters of waste cooking oil, with methyl palmitate content ranging from 0 to 5%

Spectral (nm)	range	Slope	Offset	RMSECV (%)	R ² CV
400-2170		0.956	0.104	0.325	0.957
492-792		0.941	0.085	0.478	0.908
950-1254		0.972	0.040	0.217	0.983
1134-1178		0.984	0.022	0.331	0.955
1198-1220		0.913	0.133	0.584	0.861
1644-1676		0.599	0.785	1.132	0.486
1704-1778		0.998	0.002	0.116	0.995
1780-1840		0.943	0.100	0.352	0.949
1850-2170		0.883	0.144	0.511	0.894
1134-1178 + 1198-1220		0.969	0.048	0.255	0.977
1644-1676 + 1704-1778		0.998	0.005	0.132	0.994
1644-1676 + 1780-1840		1.006	0.017	0.201	0.985

The results of the development of calibration models for the spectra shown in Table 3 prove that the wavelength range 1704-1778 nm and its combination with the range 1644-1676 nm are the best model matching results. In the range 1704-1778 nm the determination coefficient R^2CV equals to 0.995. The same range has a 0.116% mean square error for RMSECV cross-validation. At the same time, the model developed based on data from the range 1704-1778 nm reaches the best values for both the directional coefficient and the independent part, respectively 0.998 and 0.002. Results for R^2CV and the directional coefficient (0.994 and 0.998) comparable in terms of a quality to the aforesaid range are characteristic of the model developed for the combined ranges 1704-1778 nm and 1644-1676 nm, however, such a combination is qualitatively worse in terms of the mean square error and independent part, amounting to 0.132% and 0.005, respectively.

The results of the development of the calibration model for the range of 1644-1676 nm are characterised by the highest mean square error and the value of the determination coefficient R^2CV of 1.132% and 0.486, respectively. For this range, the directional coefficient equals to 0.599 and the independent term of the regression equation amounts to 0.785. These are the worst results achieved for this attempt to develop a calibration model. They unequivocally indicate the unsuitability of the spectrum range 1644-1676 nm for prediction of methyl palmitate content in methyl esters of waste cooking oil.

Parameters determining the quality of matching the obtained calibration models to model sets were compared with the results presented in an earlier paper (Golimowski, 2017) focused on calibrations to determine the concentration of methyl palmitate in methyl esters of pork fat. In the previous study, the calibration model developed for the analyzed wavelength range 1750-1900 nm was characterized by values of R^2 and RMSECV parameters of 0.990 and 0.160%, respectively. Based on these values we can conclude that the parameters of calibration models presented in this publication (for the ranges 1704-1778 nm and 1644-1676 + 1704-1778 nm) are similar. To sum up, the wavelength range 1650-1900 nm of the absorption spectrum can be successfully used to build calibration models for the determination of methyl palmitate in biodiesel obtained from waste fats.

Summary

As a result of the research, absorption spectra were conducted for 41 solutions of biodiesel made from waste cooking oil with methyl palmitate at concentrations in the range of 0-5%. They formed the basis for developing calibration models for prediction of methyl palmitate in biodiesels synthesised from waste cooking oils. To summarise the results included in Table 3, the best parameters are the calibration models developed for the analysed wavelength range 1704-1778 nm and for the combined range 1644-1676 nm and 1704-1778 nm. In both cases the determination coefficient for the cross validation of this model equalled to > 0.99 .

The results obtained in this study allow us to conclude that the use of the selected ranges of near infrared spectrum allows to effectively determine the content of methyl palmitate in biofuel produced from waste cooking oil.

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SPEKTROMETRYCZNE OZNACZANIE ZAWARTOŚCI PALMITYNIANU METYLU W ESTRACH METYLOWYCH ODPADOWYCH OLEJÓW KUCHENNYCH

Streszczenie. Biopaliwa ciekłe II generacji są paliwami otrzymywanymi z surowców niespożywczych tj. olejów posmażalniczych oraz tłuszczów zwierzęcych. Są to surowce odpadowe, pochodzące z przemysłu rolno-spożywczego, w związku z czym ich ilość jest ograniczona, a jakość uzależniona m. in. od miejsca pozyskania. Biorąc pod uwagę fakt, że właściwości reologiczne otrzymywanych biopaliw ciekłych ściśle korespondują z jakością surowców z jakich są otrzymywane, przemysłowa produkcja biopaliw z tłuszczów odpadowych wymaga opracowania nowych metod analitycznych, pozwalających na szybką ocenę jakości uzyskiwanych produktów. Celem badań było potwierdzenie możliwości zastosowania spektrometrii bliskiej podczerwieni do oceny zawartości palmitynianu metylu w biopaliwach produkowanych z tłuszczy posmażalniczych. Bazę do budowy modeli kalibracyjnych stanowiło 41 widm absorbancji zarejestrowanych w zakresie 400 -2170 nm dla próbek zawierających od 0 do 5 % palmitynianu metylu. Uzyskane wyniki potwierdziły, że istnieją możliwości skutecznej detekcji stężeń tego estru w biopaliwie za pomocą widma z przedziału 1644-1778 nm, a opracowane modele kalibracyjne PLS charakteryzują się współczynnikiem determinacji przekraczającym 0,99.

Słowa kluczowe: biodiesel, biopaliwa, oleje posmażalnicze, spektroskopia, modele kalibracyjne

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