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CALIBRATION MODEL FOR SPECTRAL ANALYSIS OF DRY MATTER CONTENT IN FERMENTING HYBRIDS SUBSTRATE

Summary

Anaerobic digestion is a complex, multi-step biological process. Control of this process can be carried out by analyzing the parameters of dry matter, organic matter and the dry matter concentration of volatile fatty acids (VFA). The aim of the study is to assess the possibility of using near-infrared spectroscopy in the construction of calibration models of dry matter content in the fermenting mixture of substrates. The starting material included the test obtained from the pulp digestion process. The fermentation process uses mixed pulp rumble (22% dry matter content), ground corn (34.5% dry matter content) and bovine manure (3.21% dry matter content). For the obtained samples an acquisition of spectral absorbance spectra by the transmission in the wavelength range of 400 - 2170 nm was effected. These data were used to build the PLS calibration model spectrophotometer intended for the prediction of dry matter content of the substrate. The model with the best fit to the spectral data was obtained for the spectral range of 900 - 1300 nm. He is characterized by a coefficient of determination R2 of 0.95 and an error determination RMSECV ratio of 0.56 g.
***Key words**: spectrophotometry, PLS calibration models, dry matter, biogas, fermentation*

MODEL KALIBRACYJNY DLA ANALIZY WIDMOWEJ ZAWARTOŚCI MATERII SUCHEJ W FERMENTUJĄCEJ MIESZANCE SUBSTRATÓW

Streszczenie

Fermentacja beztlenowa jest złożonym, wieloetapowym procesem biologicznym. Kontrola tego procesu może odbywać się poprzez analizowanie parametrów zawartości materii suchej, suchej materii organicznej oraz stężenia lotnych kwasów tłuszczowych (LKT). Celem pracy jest dokonanie oceny możliwości zastosowania spektroskopii bliskiej podczerwieni w zakresie budowy modeli kalibracyjnych zawartości materii suchej w fermentującej mieszance substratów. Materiał wyjściowy do badań stanowiła pozyskana z procesu fermentacji pulpa. W procesie fermentacji wykorzystano zmieszane wysłodki burczane (22% zawartości materii suchej), rozdrobnione ziarno kukurydzy (34,5% zawartości materii suchej) i gnojowicę bydlęcą (3,21% zawartości materii suchej). Dla pozyskanych próbek dokonano akwizycji widm spektralnych absorbancji metodą transmisyjną w zakresie długości fali 400-2170 nm. Dane te wykorzystano do budowy modeli kalibracyjnych PLS spektrofotometru przeznaczonego do predykcji zawartości materii suchej w substracie. Model o najlepszym dopasowaniu do danych spektralnych uzyskano dla zakresu spektralnego 900-1300 nm. Charakteryzował się on współczynnikiem determinacji R^2 na poziomie 0,95 oraz błędem oznaczenia RMSECV wynoszącym 0,56 g.
***Słowa kluczowe**: spektrofotometria, modele kalibracyjne PLS, materia sucha, biogaz, fermentacja*

1. Introduction

In March 2008, EU member states have signed the document, which declared reducing energy consumption by 20% till 2020, the share of biofuels in transport will increase by 10% and 20% of energy consumption will come from renewable sources [7, 10]. It is also anticipated that the production of renewable energy in Poland will be associated with the use of biomass from waste and deliberately produced for the purpose of conversion processes [3, 8, 23]. Therefore, the increased interest in biomass for energy purposes [1, 4, 6, 17]. Biomass Organic, which can be used as a source of renewable energy capacity is obtained intentionally as a result of agricultural or forestry production, or as waste plant or animal production, it can also be a fraction of municipal waste [6, 16, 24, 29]. This biomass can be used for energy purposes, including the production of biogas, which can be prepared in biogas-works agricultural digesters of sewage sludge, municipal sewage treatment plants and municipal landfills degasification systems [1, 2].

The process of biological decomposition of biomass takes place with adequate performance only at well defined physico-chemical conditions. The most important of these are: lack of oxygen and sunlight, the type of input materials and their pH, organic matter content and the degree of decomposition, the content of inhibitors or a dry matter content. The degree of fragmentation and conversion of the substrate significantly affect this process using mechanical biological and chemical methods. The process temperature is the result of the biogassing technology and used substrates.

Process control of biogas production is related to the acceleration and deceleration of organic matter decomposition by bacteria [14]. These phenomena may be associated with inhibitors of the process. The inhibitory nature may result from the properties of the substrate tract or a wrong dose. Also, excessive dosage variability caused by deterioration of the nutritional properties of the substrate can act inhibitory [19]. Acetic acid, a monocarboxylic volatile acid (VFA) is one of the products of organic matter digestion generated by bacterial beds. Acetic acid is an important indicator for quick assessment of the intensity of nutrient uptake by the bacteria [14]. The levels of volatile fatty acids (VFA) based on the acetic acid concentration suggesting a balance of the process are specific to a particular fermentation step, the substrates used, the mode and the intensity of pumping feedstock and nutrients between the inoculum and main fermentation chamber [15, 25]. The large variation in the course of fermentation generates the need for frequent measurements of concentrations LKT. This process can be costly and time consuming when traditional methods of detection such as chromatographic are applied. Therefore levels in the fermenting substrate dry matter and organic matter are important considerations for clarifying the conditions of the process in collaboration with a known content of acetic acid. To change the content of dry matter in the process of quasi-continuous fermentation allows an assessment of the burden on the digester and the level of use of food matter. Normally dry matter content changes affect strongly the instantaneous production of biogas. This important new methods for monitoring and evaluation of the dry matter content of the fermenting pulp as opposed to the previously used methods of the dryer-weight.

The rapid development of applications in the analysis of organic matter is attributed to spectral analysis, using the band of visible and infrared light. Spectral analysis uses the fact variable absorption of radiation by organic matter. Wherein the intensity of the absorption is often dependent on the length of the electromagnetic wave reflected from the surface or passing through an object [18, 20].

Spectral methods have many advantages over traditional methods, for example. Non-invasive way to obtain information about the tested materials and the short duration of the measurement while maintaining the accuracy and repeatability of test results. Further advantage of the near infrared spectroscopy NIRS (ang. Near infrared spectroscopy), as compared to the standard methods of analysis consists in the ability to measure multiple parameters for a plurality of calibration models [9, 12, 22, 28]. Near infrared spectroscopy is a widely used method for measuring the concentrations of constituent gases of biogas [11, 12, 13, 14]. Real-time monitoring process of biogassing dynamics may allow its optimization, but the introduction of the use of new construction spectrometric probes must always be preceded by the development of high-quality calibration models. The quality of the models in turn depends on the used spectral range. The method of sample preparation and normalization of obtained spectra also is an important factor influencing the quality of calibration [27, 30].

Based on the analysis of the state of knowledge, actions were taken to produce a research tool that allows you to monitor the dry matter content in the fermentation process, leading to the production of biogas.

They set the goal of work. The aim of the study is to assess the possibility of use of near-infrared spectroscopy in the construction of calibration models of dry matter content in the fermenting mixture of substrates.

An intermediate goal was to show how the measuring range from 400 to 2170 nm in spectral analysis affects the observation of changes in the content of dry matter.

2. Material and methods

The starting material included the test obtained from the pulp digestion process. The fermentation process uses mixed pulp rumble (22% dry matter content), ground corn (34.5% dry matter content) and bovine manure (3.21% dry matter content). Prepared mix of dry matter content of 6.7% m / m contained 1292.0 g of bovine manure, 104 g of crushed grains of maize (CCM), 104 g of beet-dried draff. The fermentation process was maintained at 360C. In the prepared conditions kept the process quasi-continuous production of biogas through cyclic feeding of the deposit samples with a total weight of 23 g.

Obtained sample of fermenting pulp with 1200 g weight was dried at 105°C and mechanically minced. With so prepared material sample was selected to create learning sets with different dry matter content: between 1% m / m and 12% m / m. Different contents of dry matter are obtained by adding to the dried digestate appropriate dose of distilled water in the range of 39.59 - 34.39 g. Hydrated samples with a known amount of dry matter were placed in a Petri dish. Stirring was applied to reduce the effect of delamination. In addition, the test stand of the acquisition of spectra is equipped with a rotating system that forces swirl of the liquid fraction at the time of analysis. They made the acquisition of absorption spectra using a spectrophotometric probe Niron, used to scan mixtures of liquid and pasty.

Spectra acquisitions with spectral range of 400-2170 nm were carried out using AgroSpec spectrometer (Fig. 1). The device is equipped with two optical sensors MMS 1 and PGS 2.2, allowing to conduct measurements in ranges from 370 to 1050 nm and 900-2200 nm. The acquisition trials have spectra with a spectral range of 400 to 2170 nm, the interpolated resolution of 2 nm.

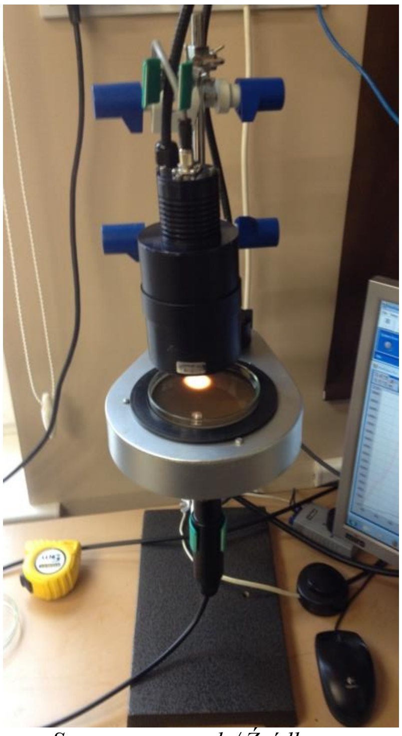

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Fig. 1. Spectrometer AgroSpec
Rys. 1. SpektrometrAgroSpec

The measuring head of NIRON contact probe is active with the internal light source in the form of a halogen lamp with a power of 10 W. The test sample is illuminated with a beam angle of incidence equal to 90°. Acquisition of light scattered by the sample is carried out by optical system disposed at an angle of 45° relative to the observed surface of the sample. The optical system of the NIRON probe head is adapted for acquisition of optical signal of inhomogeneous and liquid sample.

For the construction of calibration models we used regression method of partial least squares (PLS called partial least squares regression) implemented in software Unscrambler X 10.1. To assess the quality of developed models used for cross-validation method in which as indicators of correctness obtained model uses parameters such as the coefficient of determination R^2 and the mean square error of validation RMSECV. The following rating scale models were adopted, depending on the value of R^2:

- <0.81, low quality models
- 0,82 - 0,9 for models with sufficient prediction,
- > 0.9 models fit well [5, 26, 27, 30].

3. Results

A total of 14 spectra were recorded, which were used to develop a model calibration models. After a series of laboratory tests on the samples and spectrophotometric study, it was possible to create a learning sets needed to build calibration models.

The impact of the dry matter content on the absorption spectrum change of analyzed samples is shown in figure 2. In all considered wavelengths it is visible an increase in reflection of the optical wave with increasing dry matter content. The resulting relatively high absorbance values confirm the good quality of the obtained optical signal used for laboratory and field measuring head NIRON. It may be noted, however, significant noise signal within the range of action of the spectrometer, ie. below 450 nm and above 2000 nm, which can be a direct source of photoelectric sensors spectrometer.

Obtained in the process of parameterization of spectra models were characterized by varying degrees of fit and quality designations depending on the spectral range. Detailed statistics for created regression equations are summarized in Table.

Table. Statistics of obtained calibration models for determination of the dry matter content in the range from 1% w / w to 12% w / w in liquid samples
Tab. Statystyki uzyskanych modeli kalibracyjnych dla oznaczenia zawartości materii suchej w przedziale od 1 do 12%m/m w próbkach ciekłych

Wavelength [nm] / Zakres fali		Models calibration / Modele kalibracyjne	
		R^2	RMSECV
400-2170	Z1	0,92	0,47
400-800	Z2	0,90	0,78
400-1300	Z3	0,90	0,57
900-1300	Z4	0,95*	0,56
952-2170	Z5	0,92	0,43
952-1700	Z6	0,93	0,54
952-1370	Z7	0,86	0,67

Source: own work / Źródło: opracowanie własne

Match factor R^2 ranged from 0.86 to 0.95, which shows the different potential models obtained for qualitative analysis and screening. Least fitting model was obtained for a range of 952-1370 nm, while best suited for waveband 900-1300 nm. Magnitudes of error indication RMSECV of dry matter content in distilled water in the range of 0,43-0,78 $mg \cdot dm^{-3}$ appear in a similar manner. Comparing the values shown in the table for analyzed bands it can be concluded that the most powerful models on the whole are obtained for the spectral range of 400-2170 nm. Not obtained model here is worse than R^2 below 0.92.

The results can indicate the usefulness of the procedure used to prepare the samples and the selected methods of construction of calibration models for quantitative determination of dry matter content in the samples of distilled water. If we need to analyze a large number of samples, this method is cheaper and less time-consuming than standard methods.

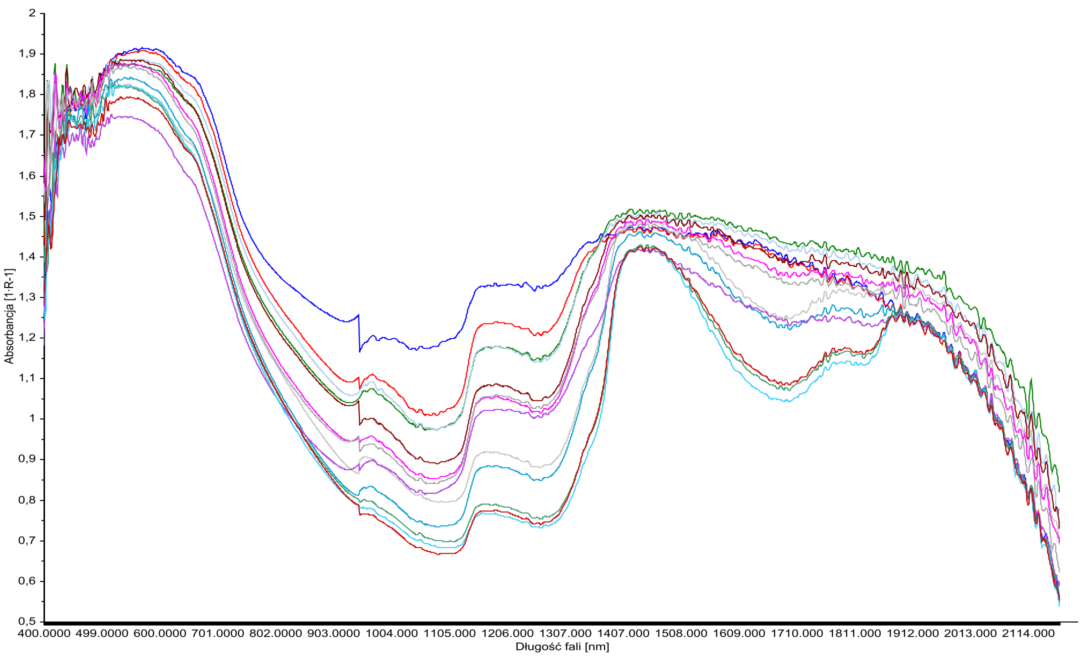

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Fig. 2. The absorption spectra of the reference samples with a dry matter content from 1% w / w to 12% w / w
Rys. 2. Widma absorpcyjne dla próbek wzorcowych o zawartości materii suchej od 1% m/m do 12% m/m

The obtained calibration models of good and very good quality parameters suggest that this method can be used to monitor the process biogassing.

4. Conclusions

Laboratory tests allowed to draw a number of conclusions and recommendations.
In the tested wavelength range (400 - 2170) for the analyzed samples changes in the characteristics of the spectra were obtained and then they were processed on a calibration model of dry matter content.

The resulting quality of the calibration model obtained from the spectra of reflection for the emitted waves in the range of 900 nm to 1300 nm can have a significant impact on the obtained noise spectrum. High interference is achieved particularly with regard to the length of the waves emitted from 952 nm to 1370 nm. In the extended-band a low quality model refers to the samples of low matter content. This is related to the head NIRON.

Detailed study of applied method of collecting spectral spectra samples of selected dry matter content indicated that the impact of sedimentation of organic and mineral material in case of reflective head can be limited and do not cause a decrease in the quality of the model.

An important element of representing conditions during the fermentation process on a technical scale was to select the research material that enabled obtention of the consistency and color of the fermenting pulp. This allows implementations of calibration model for research testing and validation.

The application of chemometric methods based on VIS-NIR spectroscopy allows a constant control of parameter values of dry matter, which indirectly determines the quality of the produced biogas. In the case of a positive validation of the presented method it will allow to monitor the parameter of loaded substrate in tract digester.

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