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Research Article

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Rapid measurement of biodiesel conversion rate by near-infrared spectroscopy

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ABSTRACT

This paper introduces a method based on the near-infrared spectroscopy for rapid measurement of the biodiesel conversion rate during the transesterification of triolein with methanol. To build the regression model between the conversion rate and the spectral date, the real conversion rate of glycerides to methyl esters was analyzed by Proton Nuclear Magnetic Resonance (^{1}HNMR) spectroscopy, and several steps were taken to the obtained spectra. Firstly, the raw spectra of all samples obtained were preprocessed by Savitzky-Golay smoothing method. Moreover, eighteen effective wavelength points were selected by successive projections algorithm (SPA). Finally, the partial least squares (PLS) model was constructed with the selected 18 wavelength points. The eventual regression model was validated and the Root Mean Square Error of Prediction (RMSEP) was 0.0115, coefficient of determination (R^2) was 0.9877. The total average absolute deviation of the measurements is 1.09%.

Keywords: near-infrared (NIR) spectroscopy, biodiesel, ^{1}HNMR, successive projections algorithm (SPA), partial least squares (PLS)

INTRODUCTION

Biodiesel is a renewable resource which mostly produced by the transesterification of triglycerides with short chain alcohol under the action of a catalyst. As one of the best solutions to solve the environmental pollution and the shortage of fossil fuel, biodiesel has attracted more and more attention[1, 2, 3, 4].

The main component of biodiesel is alkyl esters[5]. In this work, oleic methyl ester is obtained by the transesterification of triolein with methanol, in presence of KOH(as a catalyst). This transesterification is a sequence of reversible reactions, as shown in Fig.1. To optimizise the reaction conditions and improve the biodiesel quality, it is of great importance to monitor the progress of the reaction. As an indicator, the conversion rate of glycerides to methyl esters need to be measured rapidly. Recent research of biodiesel has focused on using gas chromatography (GC) or high performance liquid chromatography (HPLC) to analysis the content of biodiesel or physical parameters[6, 7, 8], which is time consuming and complicated. To shorten the analysis time, Gelbard et al[9] applied Proton Nuclear Magnetic Resonance(^{1}HNMR) spectroscopy to the measurement in biodiesel production. The analysis time is shortened significantly, however, the ^{1}HNMR spectroscopy is not the best option for online analysis since special pretreatments for samples are needed.

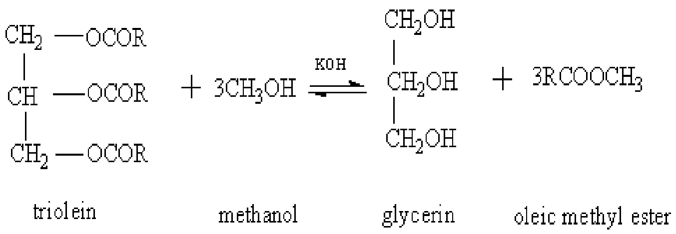

Fig.1 Transesterification reaction

Near-infrared (NIR) is a nondestructive analytical technique, which needs no complex pre-treatments. The rapidity and simplicity of this method are the key to the increasing use of NIR for quality control purpose[10]. Felizardo et al[11] predicted the methanol and water content in biodiesel by NIR method, and different preprocessing methods were discussed. Killner et al[12] established a PLS regression model in the spectral range between 5928 and 5959 cm^{-1} by using NIR spectroscopy for monitoring the biodiesel production reaction. Suzana et al[13] developed an in-line monitoring method of the transesterification reactions for biodiesel production. Gas chromatography (GC) was employed as the reference method, and the main components of the reaction mixture were quantified.

This work is focused in the development of a way to build the calibration model for biodiesel conversion rate based on the NIR spectroscopy in combination with ^{1}HNMR method. However, the strong overlapping and imperceptible distinctive features of NIR spectroscopy make it difficult to find out the imformation we concerned. Therefore, some pretreatment method and wavelength selection methods are used in this work to overcome the above problems and improve the performance of the model.

EXPERIMENTAL SECTION

Biodiesel experiment

According to Killner et al[12], 91.7g of triolein was mixed with 28.55g of methanol (6:1 M ratio), 1g of KOH was previously dissolved in methanol as a catalyst. The reaction temperature was set at 25□. The schematic diagram of experiment equipment is shown in Fig.2. The device includes a 500ml three-necked flask, a magnetic stirring thermostat water bath cauldron, a thermometer, a reflux condenser, a tube and a syringe.

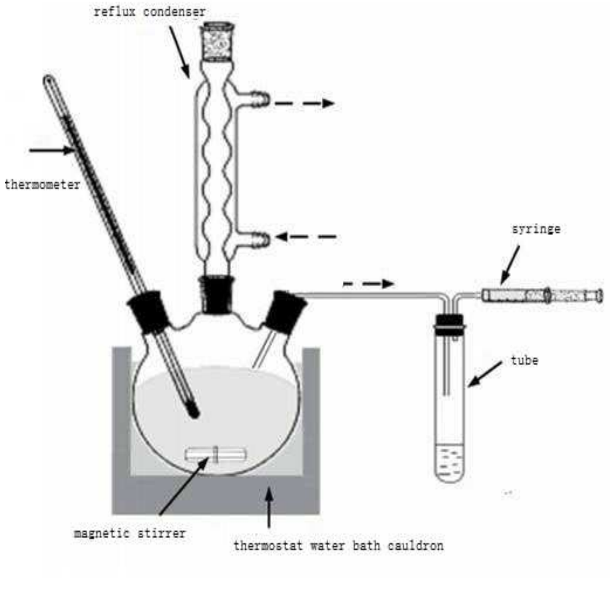

Fig.2 Schematic diagram of experiment equipment

Reference data acquisition and spectra collection

As the triolein begun mixed with methanol, the sample was taken from the solution at different times during the transesterification (from 4min to 62min). 1g of Glacial acetic acid was added in the tube to stop the reaction immediately. Finally, 28 samples were collected for analysis. According to the sampling time order, 9 samples (NO.1, NO.4, NO.7, NO.10, NO.15, NO.18, NO.21, NO.24, NO.27) were used for validation, and the remaining samples were classified to calibration set.

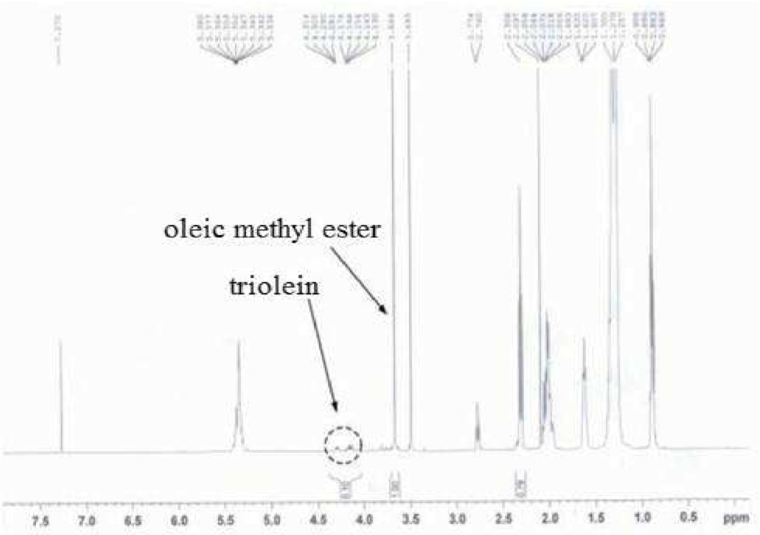

Fig.3 ^{1}HNMR spectra of the sample

The real conversion rate of glycerides to methyl esters was determined by ^{1}HNMR method. Fig.3 shows a ^{1}HNMR spectra of a sample.Knothe et al[14] proposed the equation for conversion rate calculation:

$$conv\_rate = \frac{5\times I_{me}}{5\times I_{me} + 9\times I_{tag}} \tag{1}$$

Where I_{me} is the value found for integration of oleic methyl ester (three protons with absorption at 3.669ppm), I_{tag} is value for integration of triolein (five protons with absorption between 4.130 and 4.314ppm).

The conversion rate of the samples obtained by this method was used as the reference data. NIR spectra of the samples were collected by NIR Quest-512 spectrometer (Ocean Optics, USA). All the spectra were an average of 16 scans. The wavelength range was between 900 to 2100nm, totally came to 512 points. The integration time of the spectrometer was set to 60ms. Fig.4 is the NIR spectra of the collected 28 samples.

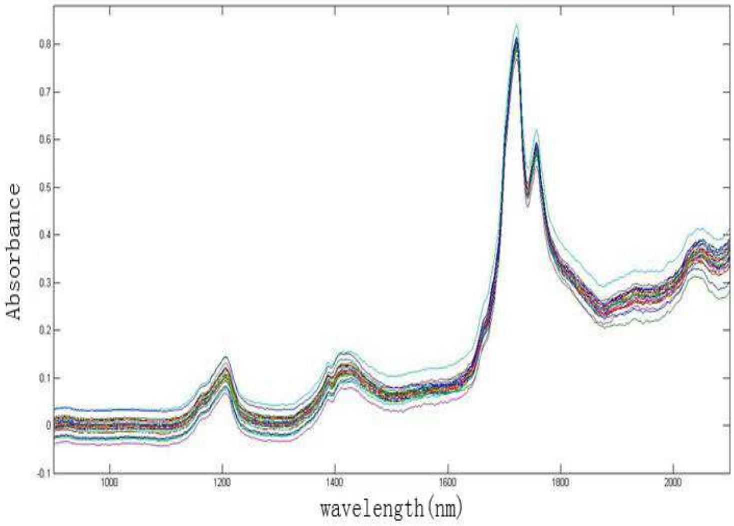

Fig.4 NIR spectra of the collected 28 samples

Successive projections algorithm (SPA)

The work by Araujo et al[15], shows the first application of SPA in the spectroscopic multicomponent analysis. The SPA is a variable selection method to find out variables with small collinearity, thus reduce the redundant of information. As a forward variable selection algorithm, new variable with maximum projection value on the orthogonal subspace of the previous selected variable is added to the selected variable set until the setting size of variable set is reached. Details steps of SPA see the reference literature [15].

Model evaluation parameters

Model evaluation parameters are the foundation for model optimization and comparison. The most commonly used parameters are Root Mean Square Error of Calibration (RMSEC), Root Mean Square Error of Prediction (RMSEP) and coefficient of determination (R^2), which are calculated as follow equations:

$$\mathrm{RMSEC} = \sqrt{\frac{\sum_{i=1}^{n}(y_{i,actual} - y_{i,predicted})^2}{n-1}} \tag{2}$$

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{p}(y_{i,actual} - y_{i,predicted})^2}{p-1}} \tag{3}$$

$$\mathrm{R}^2 = 1 - \frac{\sum_{i-1}^{p}(y_{i,actual} - y_{i,predicted})^2}{\sum_{i=1}^{p}(y_{i,actual} - \overline{y}_{actual})^2} \tag{4}$$

Where n is the number of the calibration set, p is the number of Validation set, $y_{i,actual}$ is the true value for ith sample, $y_{i,predicted}$ is the predicted value, $\overline{y}_{actual}$ is the average of the real value.

RESULTS AND DISCUSSION

The signal of NIR spectroscopy is weak and easily affected by many factors. Therefore, the processing of the spectral data is of great importance. The processing of NIR spectroscopy includes three aspects: spectral pretreatment, wavelength selection and modeling of chemometrics. First, different pretreatment methods are compared in Table.1.

Table.1 Results obtained with different pretreatment method

Modeling strategy	RMSEC	RMSEP	R^2	PLS factors
PLS/Standardization	0.0222	0.0199	0.9630	5
PLS/Savitzky-Golay smoothing (21 window points)	**0.0137**	**0.0101**	**0.9905**	**6**
PLS/first derive	0.0120	0.0157	0.9770	4
PLS/SNV	0.0095	0.0161	0.9759	5

According to the table, the pretreatment method can enhance the performance of the PLS model, especially the Savitzky-Golay smoothing with 21 window points method. The Savitzky-Golay smoothing method is used in the following study. Then, successive projections algorithm (SPA) is used to delete the uninformative wavelengths. It has been generally recognized that wavelength selection can enhance the precision of prediction and reduce the number of variables of calibration. 18 effective wavelength points (only 3.5% of the original wavelength points) are selected, as shown in Fig.5. It can be found that the effective wavelength points are not at the position of the maximum peak.

Calibration models between reference conversion rate and NIR spectra are developed by using partial least squares regression. By utilizing the 18 effective wavelength points, the result of the model is shown in Table.2. The best number of principal components (PCs) is obtained by leave-one-out cross-validation.

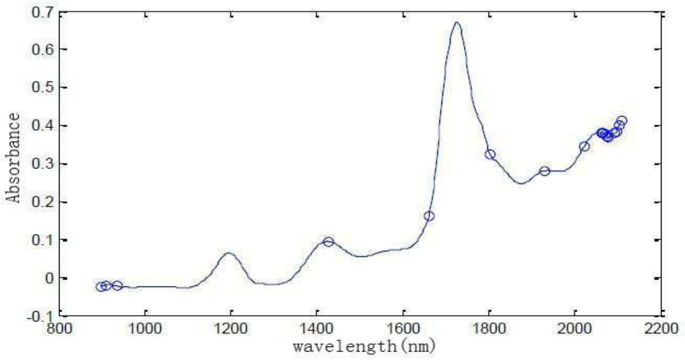

Fig.5 Distribution of the effective wavelength points

As can be seen from the Table.2, the SPA method greatly reduces the number of variables used for modeling, and the precision of the model shows little change. The RMSEC of the model is even better than the previous. Fig.6 shows the measurement result of biodiesel conversion rate. The total average absolute deviation of the measurements is 1.09%, which indicate excellent accuracy.

Table.2 Results obtained with SPA

Modeling strategy	Variables	RMSEC	RMSEP	R^2	PCs
SG+SPA +PLS	**18**	**0.0119**	**0.0115**	**0.9877**	**6**
SG+PLS	512	0.0137	0.0101	0.9905	6

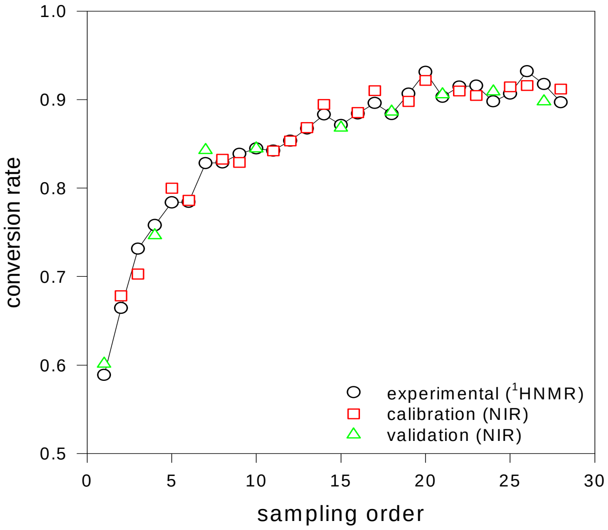

Fig.6 Conversion rate of the transesterification reaction

CONCLUSION

The NIR spectroscopy combined with ^{1}HNMR methods are successfully applied to the rapid measurement of conversion rate. Since SPA algorithm is performed to remove uninformative wavelengths effectively, the PLS model is built with only 18 wavelength points. The model is quite satisfied with a result: RMSEP= 0.0115, R^2=0.9877, and the total average absolute deviation of the measurements is 1.09%. However, more samples are needed for wider use in the biodiesel synthesis and higher measurement accurancy.

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