Prediction of methanol content in the compost of the glycerol by-product from biodiesel fuel production

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Introduction

Recently, there are many environmental problems, so there is a need to achieve sustainable development without environmental damage. Biodiesel fuel (BDF) is an important energy resource. BDF is formed in a trans-esterification reaction with triglyceride and an alcohol, such as methanol or ethanol. After trans-esterification, a by-product (called glycerol by-product) containing glycerol, BDF and methanol is discharged. To form a recycling, intensive system with zero emissions, the glycerol by-product is re-used by compost fermentation. Because methanol inhibits microbial growth, measurement of the methanol content in the compost is important.

Materials and methods

Measurement and prediction of methanol content

The experimental compost, composed of 625 g dry saw-dust, 25 g of dry microbial seed, 5 g of urea as a nitrogen compound, and 100 g of glycerol by-product was incubated at 50°C after adjusting the water content at around 50%. The water content of the compost was measured, and water was added to keep the water content at around 50%. Twenty grams of wet sample were added to 100 mL water, for extraction with water at room temperature for 30 minutes, and the methanol content was measured in the filtrate of the aqueous extraction by gas chromatography (GC). Eight grams of wet sample were packed into a standard sample cup and the NIR spectra measured at room temperature by a NIR spectrophotometer (NIRS Model 6500SPL, NIRSystems). Calibration equations for prediction of methanol content in the compost by NIRS were calculated and evaluated.

To study the effects of the weights of sample packed in the standard sample cup (called packed weight) on the second derivative NIR spectra, the NIR spectra of about 2 g, 3 g, 4 g, 5 g, 6 g, 7 g, 8 g, 9 g or 10 g of sample of compost at the adjusted water content of around 50% were measured at room temperature.

Results and discussion

Second derivative spectra of aqueous solution of methanol

The second derivative spectra of water, aqueous solutions of methanol (5 and 10%) and methanol are shown in Figure 1.

The absorption at 2276 nm in the spectrum of methanol was shifted to the lower wavelength, 2264 nm, in the spectra of the aqueous solutions of methanol. The peak at around 2264 nm may be due mainly to the absorption of $–CH_3$.[1,2]

Calibration and validation results

The calibration equations were calculated using second derivative values at 2264 nm, 1754 nm and 2326 nm or 1804 nm as first, second and third wavelength, respectively. The value of u shown below is the weight of methanol [g kg of dry compost^{-1}] and $A_{\lambda x}$ is the value of the second derivative spectra at λ_x nm.

$$C_{\mathrm{NIR}}(\mathrm{u}) = -30.780 - 595.341\, A_{2264} \quad (1)$$

$$C_{\mathrm{NIR}}(\mathrm{u}) = 1.712 - 473.582\, A_{2264} - 3723.475\, A_{1754} \quad (2)$$

$$C_{\mathrm{NIR}}(\mathrm{u}) = 3.496 - 580.624\, A_{2264} - 4624.285\, A_{1754} + 583.182\, A_{2326} \quad (3)$$

$$C_{\mathrm{NIR}}(\mathrm{u}) = 5.037 - 509.366\, A_{2264} - 4172.595\, A_{1754} + 2533.911\, A_{1804} \quad (4)$$

The results of evaluating the calibration equations are shown in Table 1.

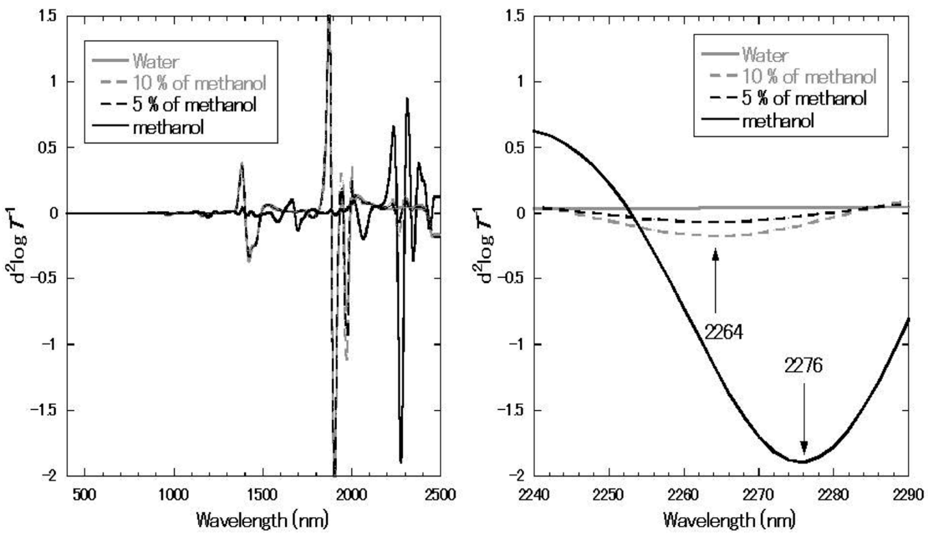

Figure 1. Second derivative spectra of methanol and aqueous solutions of methanol.

Table 1. Calibration and validation results using calibration equation.

Wavelength [nm] λ_1, λ_2, λ_3	Calibration (n=54)		Validation (n=42)		
	R^2	SEC(u)	r^2	SEP(u)	Bias
2264	0.762	1.450	0.646	1.590	0.544
2264, 1754	0.913	0.922	0.699	1.490	0.296
2264, 1754, 2326	0.939	0.783	0.792	1.270	0.199
2264, 1754, 1804	0.930	0.840	0.754	1.370	0.481

The result observed at Equation (1) was not good, although very good results had been obtained in the previous study on liquid samples.[1] Because the compost is a heterogeneous solid fermentation, the effects of the weight of the compost packed in the standard sample cup, and the water content of the compost may not be negligible. These effects were also studied. The best correlation between methanol concentration in the compost and that predicted by NIR spectroscopy was obtained with Equation (3). It was considered that the methanol content of the compost could be predicted using NIR spectroscopy.

Effect of the packed weight in the sample cup on the absorbance

Figure 2 shows the effect of the packed weight on the absorbance. The packed weight had little effect on the measurement of values of λ_1, λ_2 and λ_3.

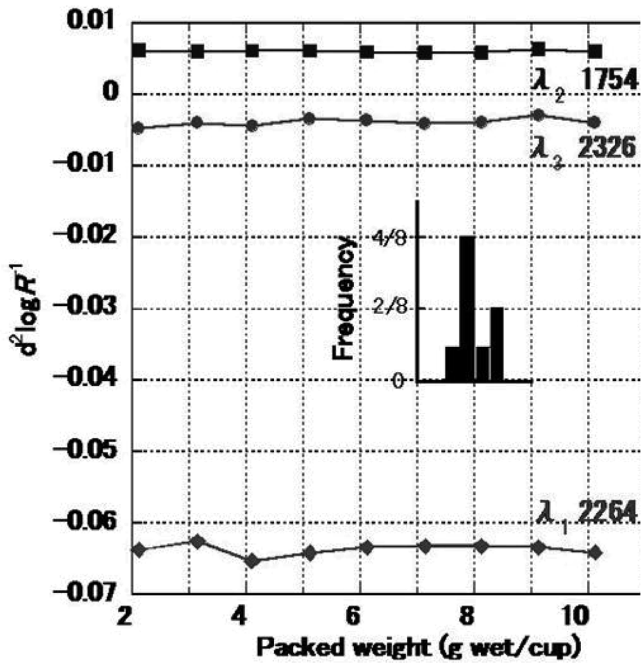

Figure 2. Second derivative absorbance at various packed weight.

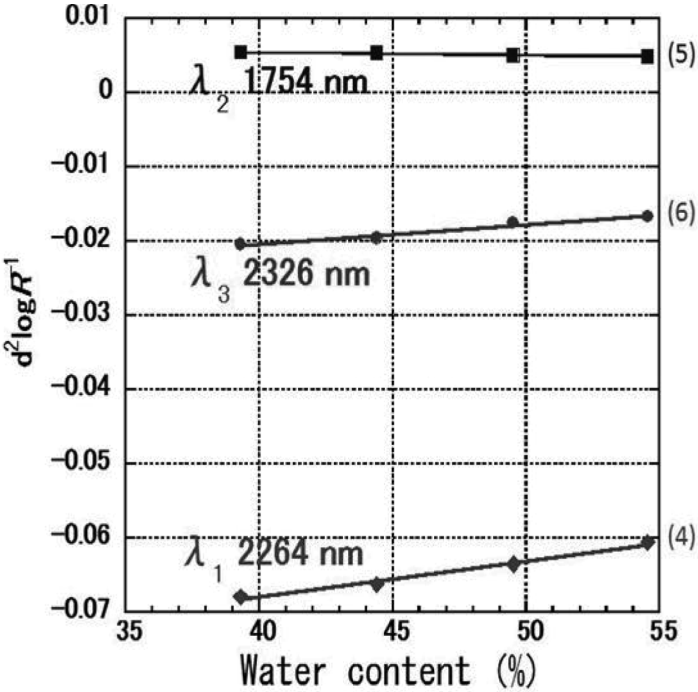

Figure 3. Effect of the water content on the second derivative absorbance.

Effects of the water content of the compost on the absorbance

The effect of water content on the absorbance values of λ_1, λ_2 and λ_3 were studied. NIR spectra of four kinds of the compost with different water content, 39.3%, 44.3%, 49.5% and 54.6%, were measured. As the water content increased, the values of second derivative absorbance at 2264 nm and 2326 nm increased (Figure 3).

The water content varied from about 42% to about 53% during composting, and affected the measurement of methanol. The effect of the water content was not negligible. The degree to which the water content affects the prediction of methanol content is calculated in the next section.

The effect of the water content on the prediction of methanol content

The contribution of water content on the prediction of methanol content in the compost at each wavelength is given by the following equations:

$$A_{2264} = -8.7463 \times 10^{-2} + 4.8689 \times 10^{-4} \times W_c \quad (4)$$

$$A_{1754} = 7.1736 \times 10^{-2} - 4.0948 \times 10^{-5} \times W_c \quad (5)$$

$$A_{2326} = 3.0679 \times 10^{-2} + 2.5867 \times 10^{-4} \times W_c \quad (6)$$

Here, W_c is the water content (%).

When the water content changed by 10%, the methanol content was affected to the extent of 2.8270 g kg^{-1}, 1.8936 g kg^{-1} and 1.5085 g kg^{-1} dry compost, at A_{2264}, A_{1754} and A_{2326}, respectively. The water content affected the values of absorbance at λ_1, λ_2 and λ_3. The difference of 2.4419 g kg^{-1} dry compost was estimated between 40% and 50% of water content. The methanol content, as predicted by NIRS, needs to be corrected for the water content.

Conclusions

Prediction of the methanol content in the compost of the glycerol by-product obtained from the BDF production process was achieved using NIR spectroscopy. The wavelength of 2264 nm was selected as the primary wavelength to ensure good calibrations. The effects of the packed weight of the compost in the standard sample cup, and of the water content of the compost on the prediction were also studied. The effect of the packed weight of the compost was negligible, while the methanol content, as predicted by NIRS should be corrected for water content of the compost.

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References

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