Prediction of several constituent contents in the compost of glycerol by-product from biodiesel fuel production

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Introduction

Compost fermentation is one of the key technologies for waste treatment of glycerol by-product from biodiesel fuel (BDF) production. It is important to control the constituents of the compost for conducting good compost fermentation. Glycerol by-product contains several constituents such as oil (BDF), methanol and glycerol. In this study, near-infrared (NIR) spectroscopy was applied to determine the oil and glycerol contents of the compost during the compost fermentation of the glycerol by-product.

Materials and methods

Compost fermentation process

Compost reaction was started after mixing saw-dust, glycerol by-product of BDF production, a nitrogen compound (urea), hydrochloric acid and microbial seed, and adjusting the water content at about 50%. The fermentation was carried out at 50°C.

Conventional methods

Oil and glycerol contents in the compost were measured using the Soxhlet extraction method, and an enzyme method (F-kit glycerol, R-Biopharm AG) as a conventional method, respectively.

Near infrared spectroscopy

For the NIR method, the compost was packed in a sample cup (Foss NIRSystems Inc.) and the cup was put into a spectrophotometer (NIRS 6500SPL, Foss NIRSystems Inc.) to measure the spectrum. The second derivative of absorbance was obtained at a gap of 0 nm and segment of 20 nm. Simple or multiple linear regression (SLR or MLR) analysis using the least-squares method was conducted on the second derivatives of the NIR spectral data, A_λ regressed against the oil or glycerol contents obtained by the conventional methods, C_{act}. The ranges in contents of oil and glycerol in the calibration and validation sample sets were 1.57–38.9 and 2.14–37.7 (g-oil kg-dry compost^{-1}) and 0.03–26.8 and 0.24–26.6 (g-glycerol kg-dry compost^{-1}), respectively.

Results and discussion

Compost fermentation process

Figure 1 shows the time courses of oil and glycerol contents of the compost during compost fermentation.

Second derivative NIR spectra of compost and glycerol solution.

Second derivative NIR spectra of composts and glycerol solutions are shown in Figure 2.

The absorption bands observed at 1418 nm and 1906 nm in Figure 2(a) are well-recognized as being due to the absorption of H_2O. For Figure 2(b), the band observed at 1714 nm may be assigned to BDF and the band at 1814 nm may be assigned to cellulose (a constituent of the compost).[1] Accordingly, the wavelengths of 1714 nm and 1814 nm were used as the first and second wavelengths to formulate a calibration equation for the oil and cellulose contents, respectively.

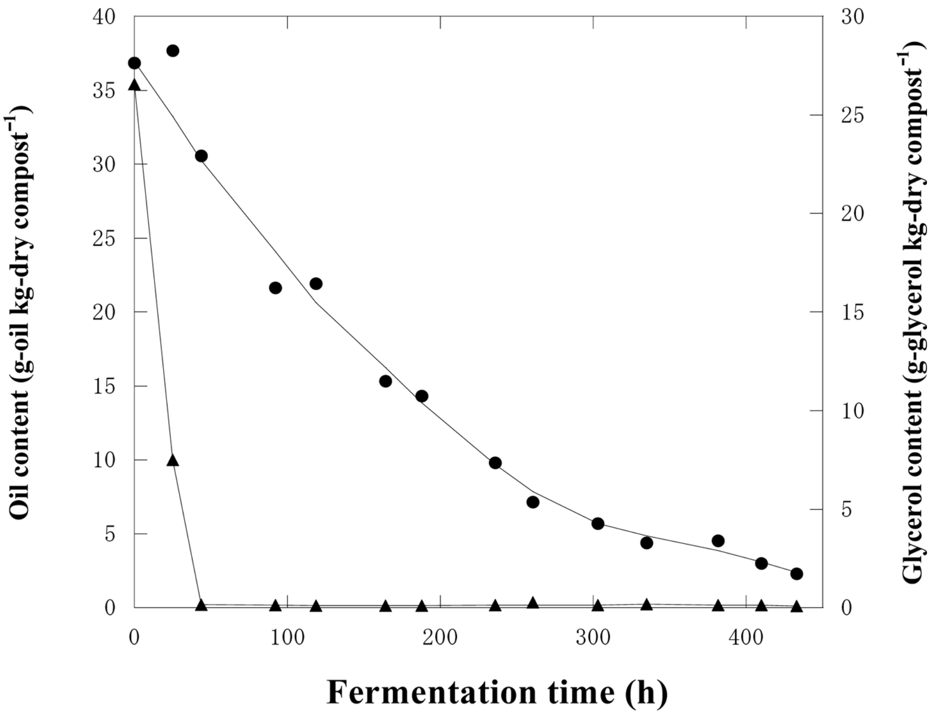

Figure 1. Time courses of oil content (•) and glycerol content (▲) of the compost during compost fermentation.

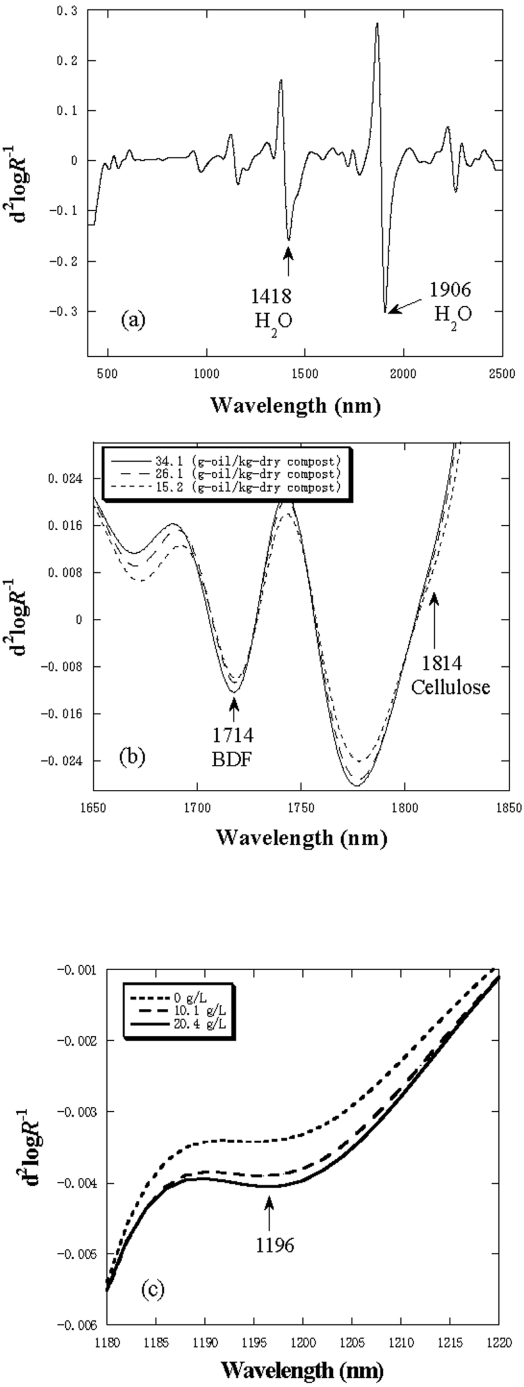

Figure 2. Second derivative NIR spectra of composts from 400 nm to 2500 nm (a) and that from 1650 nm to 1850 nm (b), and second derivative NIR spectra of glycerol solutions (c).

To select the wavelength to make a calibration equation for glycerol, the second derivative NIR spectra of glycerol solutions were studied. For Figure 2(c), the peak observed at 1196 nm is assigned to a C-H bond. The wavelength of 1196 nm was used as the first wavelength to formulate a calibration equation for the glycerol content.

Calibration and validation for determining oil and glycerol contents in the compost

SLR or MLR analysis were conducted on the second derivative NIR spectra and C_{act} for oil content in the compost. The following calibration equations were obtained.

$$C_{pre}\,(\text{g-oil kg-dry compost}^{-1}) = 1.774 – 2471.62A_{1714} \tag{1}$$

The r^2 value and *SEC* were 0.837 and 6.69 g-oil kg-dry compost^{-1}, respectively.

$$C_{pre}\,(\text{g-oil kg-dry compost}^{-1}) = –23.906 – 2762.406A_{1714} + 2504.298A_{1814} \tag{2}$$

The r^2 value and *SEC* were 0.968 and 3.13 g-oil kg-dry compost^{-1}, respectively.

Validations of Equations (1) and (2) were carried out by predicting the oil content in the prediction sample set ($n = 30$), which was not used for calibration, and by comparing with the values of C_{act}. The results for Equation (2) are shown in Figure 3(a).

SEP was 2.16 g-oil kg-dry compost^{-1} and good agreement between the conventional method and the NIR method was observed with $r^2 = 0.954$.

SLR or MLR analysis was also conducted on the second derivative NIR spectra and C_{act} for glycerol content in the compost. The following calibration equations were obtained. The wavelength of 2284 nm as the second wavelength may be assigned to C-H bond (methanol or cellulose) and the wavelength of 2236 nm, as the third wavelength, may be assigned to N-H bond (urea).[1]

$$C_{pre}\,(\text{g-glycerol kg-dry compost}^{-1}) = -44.115\text{-}4140.438A_{1186} \tag{3}$$

The r^2 value and *SEC* were 0.669 and 7.06 g-glycerol kg-dry compost^{-1}, respectively.

$$C_{pre}\,(\text{g-glycerol kg-dry compost}^{-1}) = –35.238 – 5986.563A_{1186} – 4380.205A_{2284} \tag{4}$$

The r^2 value and *SEC* were 0.874 and 4.67 g-glycerol kg-dry compost^{-1}, respectively.

$$C_{pre}\,(\text{g-glycerol kg-dry compost}^{-1}) = -87.733\text{-}3639.265A_{1186} – 5102.572A_{2284} + 2164.234\,A_{2236} \tag{5}$$

The r^2 value and *SEC* were 0.929 and 3.59 g-glycerol kg-dry compost^{-1}, respectively.

Validations of Equations (3), (4) and (5) were carried out by predicting the glycerol content in the prediction sample set ($n = 31$), which was not used for calibration, and by comparing the NIR predicted results with the values of C_{act}. The results for Equation (5) are shown in Figure 3(b). *SEP*

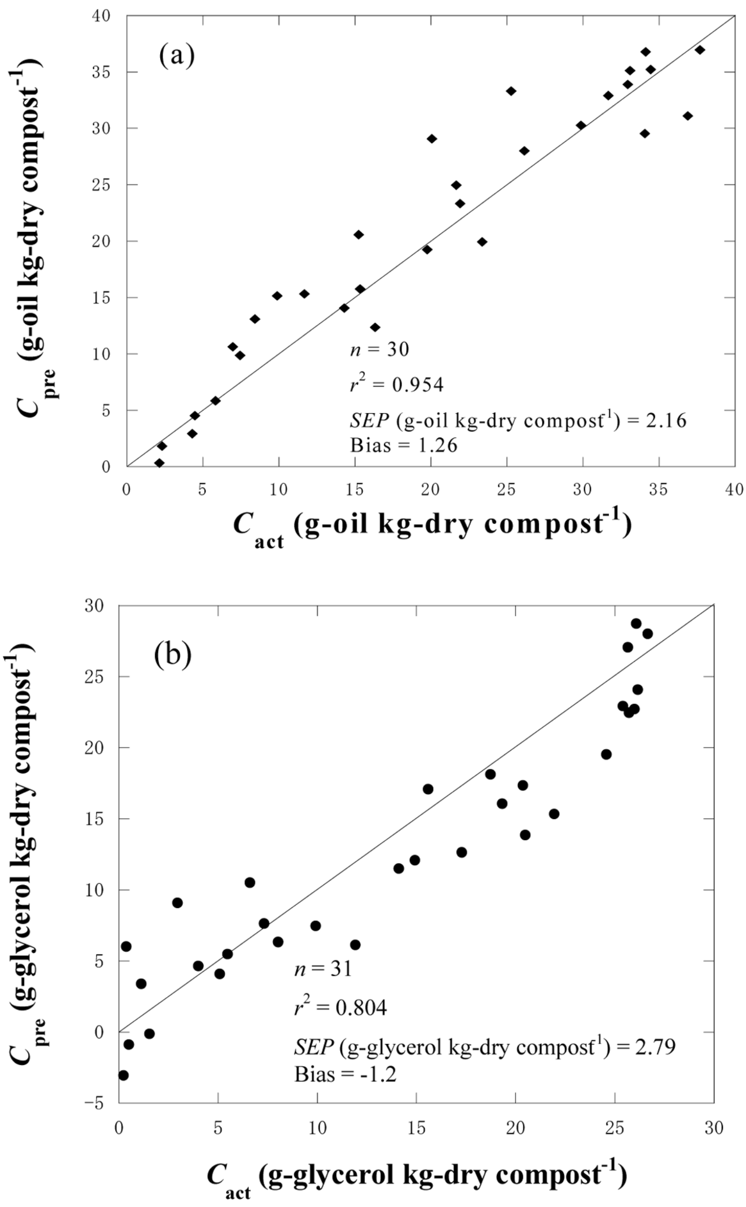

Figure 3. Validation results on oil and glycerol contents prediction. Correlation between oil content measured by Soxhlet extraction method, C_{act}, and that predicted by NIR method, C_{pre}. Solid line represents $C_{act} = C_{pre}$ (a). Correlation between glycerol content measured by enzyme method, C_{act}, and that predicted by NIR method, C_{pre}. Solid line represents $C_{act} = C_{pre}$ (b).

Table 1. Calibration and validation results for the oil (BDF) and glycerol contents in the compost.

Constituent	Wavelength (nm)	Calibration (*n*=50)		Validation (*n*=30)		
	λ_1 λ_2	r^2	*SEC* (u-oil)	r^2	*SEP* (u-oil)	Bias
Oil	1714	0.837	6.69	0.877	3.93	−0.52
	1714 1814	0.968	3.13	0.954	2.16	1.26
Constituent	Wavelength (nm)	Calibration (*n*=52)		Validation (*n*=31)		
	λ_1 λ_2 λ_3	r^2	*SEC* (u-gly)	r^2	*SEP* (u-gly)	Bias
Glycerol	1186	0.669	7.06	0.781	7.19	–1.46
	1186 2284	0.874	4.67	0.946	4.52	–1.62
	1186 2284 2236	0.929	3.59	0.804	2.79	–1.20

r^2: Correlation coefficient, *SEC*: Standard error of calibration
SEP: Standard error of prediction

was 2.79 g-glycerol kg-dry compost^{-1} and good agreement between the conventional method and NIR method was observed with $r^2 = 0.804$.

The results of calibration and validation for determining the oil and glycerol contents in the compost are summarized in Table 1.

The units of *SEC* and *SEP* shown by u-oil or u-gly represent g-oil kg-dry compost^{-1} and g-glycerol kg-dry compost^{-1}, respectively.

Conclusion

Rapid measurement of several constituents of compost was examined, using NIR spectroscopy, and good results were obtained.

The results of this study suggest that NIR spectroscopy is a potentially useful method for prediction of oil and glycerol contents in the compost of glycerol by-product from BDF production process. The measurement of other constituents of the compost, such as nitrogen and methanol, using NIR spectroscopy will be studied in the future.

Acknowledgements

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Reference

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