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Prediction of biogas yield and its kinetics in reed canary grass using near infrared reflectance spectroscopy and chemometrics

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HIGHLIGHTS

- NIRS based models were developed for biogas yield, its kinetics, and methane yield.
- The iPLS models did not improve the models based on full spectrum data.
- The NIRS models for SBY and *k*-SBY were better than the model for SMY.
- NIRS model prediction for SMY was better than models based on chemical composition.

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ABSTRACT

A rapid method is needed to assess biogas and methane yield potential of various kinds of substrate prior to anaerobic digestion. This study reports near infrared reflectance spectroscopy (NIRS) as a rapid alternative method to the conventional batch methods for prediction of specific biogas yield (SBY), specific methane yield (SMY) and kinetics of biogas yield (*k*-SBY) of reed canary grass (RCG) biomass. Dried and powdered RCG biomass with different level of maturity was used for biochemical composition analysis, batch assays and NIRS analysis. Calibration models were developed using partial least square (PLS) regression from NIRS spectra. The calibration models for SBY (R^2 = 0.68, RPD = 1.83) and *k*-SBY (R^2 = 0.71, RPD = 1.75) were better than the model for SMY (R^2 = 0.53, RPD = 1.49). Although the PLS model for SMY was less successful, the model performance was better compared to the models based on chemical composition.

1. Introduction

Biogas production by anaerobic digestions of various agricultural crops and their residues is increasing worldwide as an alternative source of energy. Maize is the most common crop currently used for biogas production in European countries (Bruni et al., 2010; Grieder et al., 2011; Herrmann and Rath, 2012). However, perennial grasses are identified as a better option than maize as they generally have better environmental profile and require less input (Tilman et al., 2006). Moreover, cultivation of perennial grass also offers diversity in areas where monoculture of maize for biogas production is common. Reed canary grass (RCG) is identified as a suitable perennial crop to cultivate on peatlands in Denmark for biogas production (Kandel et al., 2012, 2013a,b).

Biogas yields (volume of biogas produced per unit dry matter) of RCG vary considerably. It depends on chemical compositions of the biomass such as nitrogen concentrations, the amount of structural and non-structural carbohydrates and lignification (Gunaseelan, 2007; Kandel et al., 2013a). The chemical composition is greatly influenced by factors such as variety, cultivation site, and agronomical managements including fertilization, harvest time and harvest frequency which eventually affect the biogas and methane yield (Seppälä et al., 2009; Kandel et al., 2013a). Therefore, it is important to determine the biogas and methane yield potentials of RCG prior to anaerobic digestion in order to assess its value as feedstock and also to obtain information on required feeding rate and retention time in the biogas reactor (Raju et al., 2011).

Assessment of the biochemical methane potential (BMP) by a lab procedure with small anaerobic reactors is the most common method to assess the biogas yield potential of various feedstocks (Møller et al., 2004; Grieder et al., 2011). However, it takes at least 30 days to assess the anaerobic digestion potential by this batch method. Biomass with higher percentage of fibrous components can even take longer time (Triolo et al., 2011; Kandel et al., 2013a). Moreover, the test is also labor and resource intensive (Grieder et al., 2011). As the BMP assay is time consuming, it is

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not a practical method for assessing biogas yield potential of biomass at industrial scale (Lesteur et al., 2011). Therefore, a more rapid method is needed to assess the quantity of biogas and methane that may be produced from different kinds of substrate as the biogas industry is booming in Northern Europe and other parts of the world.

Various methods have been used to assess the biogas production as an alternative to the BMP assays (Lesteur et al., 2010). Modelling biogas or methane yield based on chemical composition of the biomass is one of the common methods (Gunaseelan, 2007; Triolo et al., 2011). The BMP models based on chemical composition analysis can estimate the biogas or methane yield in shorter duration as compared to the fermentation assays and they provide an insight on factors responsible for decomposition of substrates. However, modelling still needs information on the chemical composition itself, and this analysis can be expensive and labor intensive. In vitro organic matter digestibility assay (IVOMD) (Raju et al., 2011) and Dynamic Respiration Index (DRI) (Scaglia et al., 2010) are relatively faster methods as compared to BMP assays but they are also time and labor intensive methods.

Near infrared reflectance spectroscopy (NIRS) may be a method for faster assessment of anaerobic digestion potential of feedstocks (Raju et al., 2011; Lesteur et al., 2011; Grieder et al., 2011). NIRS is a non-invasive method, and time and labor requirement in this method is significantly lower as compared to the BMP assays. NIRS has already been proved to be a powerful tool to determine the chemical composition of various plants parts (Gislum et al., 2004; Shetty and Gislum, 2011). As the chemical composition of the biomass determines BMP of the feedstocks and NIRS can determine the chemical composition, some attempts were already made to directly predict BMP from various kinds of biomass using NIRS. Those studies include BMP potential of municipal solid wastes (Lesteur et al., 2011), meadow grass (Raju et al., 2011) and maize (Grieder et al., 2011). Although these studies have shown certain ability of NIRS on predicting BMP, further studies are needed to make the technique applicable to a wider ranges of biomasses and to identify the reasons to lack of good model fitting. This study investigated NIRS as a tool to predict specific biogas yield (SBY), specific methane yield (SMY), and kinetics of biogas yield (*k*-SBY) of RCG biomass with different level of maturity and chemical composition.

2. Methods

2.1. Plant materials

The plant materials used for this study were 98 samples of RCG from an earlier study (Kandel et al., 2013a). RCG was grown on a peatland located in Nørre Å river valley near to Viborg, Denmark. Environmental conditions during crop cultivation, soil properties and design of the field experiment are described in details by Kandel et al. (2012, 2013b). The experimental site consisted of three plots of RCG established in 2009 which were divided into two subplots (18 × 12 m). Biomass was sampled (1 m^2 area in each sampling) from those subplots in 2 week intervals from April to September in 2011. Similarly, regrowth of biomass in one of the summer harvests was harvested again in September for a two-cut management strategy with or without additional fertilization after the first cut. The biomass was separated into leaf and stem, and oven dried to constant weight. Subsequently, the biomass was ground in a mill to pass through a 1 mm sieve. The ground samples were divided into three parts used for biochemical composition analysis, BMP assays and NIRS analysis.

2.2. Biogas reference data

Biochemical methane potential (BMP) of RCG was determined using a method described by Møller et al. (2004). In brief, 4 g of dry, ground sample was digested at mesophillic condition (35 °C) in a batch reactor (500 ml) filled with inoculum (200 g) obtained from a mesophillic (25 °C) post digestion tank. Three batch reactors without addition of RCG were used as control. The volume of the biogas produced was measured every week at the beginning of the batch assay and then gradually at longer time intervals using an acidified (pH < 2) water displacement method. Total biogas produced from the biomass samples during the batch assay period (69 days) were corrected to normal conditions (0 °C and 1.013 bar) and presented as specific biogas yield (SBY) [NL biogas (kg VS)$^{-1}$]. Methane concentration in the biogas was analyzed by gas chromatography (HP 6890 series; Agilent Technologies, Copenhagen, Denmark). Total methane yield was calculated as the product of SBY and methane concentration and presented as specific methane yield (SMY) [NL CH_4 (kg VS)$^{-1}$].

To determine the kinetics of biogas yield, a simple first order degradation model (e.g., Gunaseelan, 2007) was used for measurements from individual batch reactors:

$$B = B_0(1 - \exp^{-kt}) \quad (1)$$

where B is the cumulative biogas yield at time t, B_0 is the ultimate biogas yield and k is the first order rate constant. Here, k is used as kinetics of biodegradation or biogas yield and presented as *k*-SBY. Biomass with low *k*-SBY degrade over a long time period with lower rate of biogas production while the biomass with high *k*-SBY degrade immediately in batch reactor with high rates of biogas formation at the beginning of the batch assay.

2.3. Near infrared reflectance spectroscopy

The grass samples were measured by NIRS spectroscopy (Q-interline Spectroscopic Analytical Solutions, QFAflex, Roskilde, Denmark) in reflectance mode where $\log(1/R)$ was recorded from 1100 to 2498 nm, equivalent to 4000–9091 cm^{-1}. Each sample was scanned 128 times using 16 cm^{-1} resolution.

2.4. Multivariate data analysis

Exploratory data analysis of all samples using principal component analysis (PCA) and leverage plots of the NIRS spectra revealed a few obvious outliers which were removed before partial least squares regression (PLS) models were developed on full spectra. The full dataset was divided into a calibration and validation dataset where data were arranged in increasing order and every third sample was used for test set validation. Data in the test set was

Table 1
Reference data parameters. Specific methane yield (SMY), specific biogas yield (SBY) and kinetics of biogas yield (*k*-SBY).

Parameters	SBY	SMY	*k*-SBY
Calibration			
n	69	69	69
Min	431	264	0.038
Max	699	401	0.082
Mean	564	337	0.059
S. Dev	68	32	0.010
Validation			
n	22	22	22
Min	440	272	0.040
Max	673	396	0.087
Mean	563	338	0.061
S. Dev	55	29	0.011