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Biochemical methane potential prediction of plant biomasses: Comparing chemical composition versus near infrared methods and linear versus non-linear models

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HIGHLIGHTS

- Predictions based on the NIR spectrum were most reliable to estimate the BMP.
- NIR predictions of the BMP made by local models were reliable and quantitative.
- Non-linear models gave more reliable predictions than linear models.
- Biomass presentation form did not influence the model's prediction performances.

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ABSTRACT

The reliability of different models to predict the biochemical methane potential (BMP) of various plant biomasses using a multispecies dataset was compared. The most reliable prediction models of the BMP were those based on the near infrared (NIR) spectrum compared to those based on the chemical composition. The NIR predictions of local (specific regression and non-linear) models were able to estimate quantitatively, rapidly, cheaply and easily the BMP. Such a model could be further used for biomethanation plant management and optimization. The predictions of non-linear models were more reliable compared to those of linear models. The presentation form (green-dried, silage-dried and silage-wet form) of biomasses to the NIR spectrometer did not influence the performances of the NIR prediction models. The accuracy of the BMP method should be improved to enhance further the BMP prediction models.

1. Introduction

The production of biogas by anaerobic digestion (biomethanation) of plant biomasses is of growing importance in the context of renewable energy production (Amon et al., 2007; Triolo et al., 2012). The anaerobic digestion process consists in the anaerobic conversion of the organic matter into biogas by microorganisms. The produced biogas is a mixture mainly made of methane and carbon dioxide (Duncan and Nigel, 2003). Plant biomasses such as corn (*Zea mays* L.) and meadow (e.g. *Festuca arundinacea* Schreb.) silages are commonly used feedstocks for biomethanation (Amon et al., 2007). This type of renewable energy production is socio-economically cost-efficient and environmentally efficient (e.g. reduction of greenhouse gas emissions) (Amon et al., 2007; Triolo et al., 2012). It is also a convenient source of renewable energy as it offers the possibility to use multiple feedstocks, and to meet different types of energy needs (heat, electricity, and fuel) and fertilizers for agriculture (Ward et al., 2008; Triolo et al., 2012).

The biochemical methane potential (BMP expressed as m^3 of methane per kg of organic matter) is the most relevant method

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Abbreviations: asl, above sea level; BMP, biochemical methane potential; C.-V., cross-validation; CV, coefficient of variation; DM, dry matter; eDOM, enzymatically digestible organic matter; MedRE, median standard residual error of prediction; MLR, multiple linear regression; *n*, number of samples; PLS, partial least square; NIR, near infrared; R^2Med, coefficient of determination of prediction based on median variables; RPDMed, ratio of the median standard deviation of the variable to MedRE; SD, mean standard deviation; SDMed, median standard deviation; SEL, standard error of laboratory; Val., validation; VS, organic matter (volatile solids); VST, Van Soest.

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used to determine the biogas production potential of biomasses (Grieder et al., 2011; Raju et al., 2011). It is a batch assay of 30–100 days of the sample's anaerobic biodegradation. This assay reproduces the biomethanation process conditions in a small biogas fermenter and measures the methane production (Grieder et al., 2011; Raju et al., 2011). The main drawbacks of the BMP method are that it is generally time and resource consuming. These are important burdens for industrial plant management and optimization (Grieder et al., 2011; Doublet et al., 2013). Therefore, there is a need to develop simple, fast and reliable models to predict reliably the BMP.

The gas production by anaerobic digestion depends on the feedstock's chemical characteristics such as chemical composition (contents of lignin, cellulose, hemicelluloses, starch, total soluble sugars, proteins and lipids) and anaerobic organic matter digestibility (Grieder et al., 2011, 2012; Triolo et al., 2011). The chemical composition can be determined in a cost-effective way in only a few days (Raju et al., 2011). It can be used to predict the BMP in a faster and cheaper way, as compared to the BMP measurement, if suitable prediction models can be developed. It has been shown for corn that the chemical composition (contents of lignin, hemicelluloses, total soluble sugars and lipids) enables a reliable prediction of the BMP (Rath et al., 2013). Such a model needs to be built with more than one variable to be reliable (multivariate models; Rath et al., 2013).

The anaerobic organic matter digestibility can be assessed by the enzymatically digestible organic matter (eDOM) determined by the De Boever method (De Boever et al., 1986). This relatively simple and fast method can be used to assess the suitability of plant biomasses to be converted by anaerobic digestion (Godin et al., 2013a,b,c). The eDOM can be considered as the minimum level of anaerobic digestibility of the plant biomass. Indeed, the microorganisms of the anaerobic digestion are expected to produce more enzymes in-situ and for a longer period of time compared to the enzyme cocktail used in the analysis. The eDOM can be predicted from the near infrared (NIR) spectrum of the organic matter with suitably developed models. The prediction performances of the eDOM by models based on the NIR spectrum are known to be excellent: coefficient of determination of 0.95 and ratio of the mean standard deviation of the predicted variable to the mean standard residual error of prediction of 4.6 (Decruyenaere et al., 2009).

Prediction models based on the NIR spectrum can also be very useful to rapidly, cheaply and easily predict the BMP of feedstocks. The NIR-based prediction models have been shown to be reliable for the BMP prediction of meadow grasses (Raju et al., 2011), fibrous plant biomasses, (Triolo et al., 2014) and a wide range of organic substrates (Lesteur et al., 2011; Doublet et al., 2013). The prediction models were based on the linear regression of the partial least square (PLS). However, the NIR predictions can also be made by non-linear models. The local (specific regression and non-linear) model is one of those models which are able to improve the prediction performances of a variable based on the NIR spectrum (Shenk et al., 1997). The local model builds a regression for each sample separately by selecting its most similar spectral neighbors in the used dataset. This selection is then used to develop a specific PLS model for the predicted sample (Shenk et al., 1997). While linear models are commonly used to develop prediction models from the NIR spectrum, to our knowledge, non-linear models have not been used to predict the BMP of plant feedstocks.

To have a reliable prediction model of a secondary method (NIR spectrum and chemical composition in the present study) based on the reference method (BMP and eDOM in the present study), it is important to have: (1) an accurate reference method; (2) a large variability for the values of the reference and secondary methods. The use of a multiproduct (multispecies) dataset with similar plant species helps to enlarge this variability (Berzaghi et al., 2000). The presentation form (eg. water content and particle size) of a sample to the NIR spectrometer is known to affect the prediction performances of a NIR prediction model. A higher water content and/or a bigger particle size tend to decrease the reliability of the NIR prediction model because they tend to hide the NIR spectral information (Bertrand and Dufour, 2006).

The aim of this paper is to compare the reliability of the BMP of plant biomasses predicted by models using the chemical composition or the NIR spectrum as predictor and also to use a multiproduct (multispecies) dataset, to test the influence of the state of the biomass when recording NIR spectrum (green-dried, silage-wet or silage-dried), and to assess the influence of the model used to make the prediction (linear models: PLS models and multivariate linear regression models with a linear matrix; non-linear models: local models and multivariate linear regression models with a non-linear matrix).

2. Methods

2.1. Biomass material

Miscanthus giganteus (*Miscanthus x giganteus* J.M. Greef & Deuter ex Hodk. & Renvoize), switchgrass (*Panicum virgatum* L.), spelt straw (*Triticum aestivum* L. ssp. *spelta* (L.) Thell.), fiber sorghum (*Sorghum bicolor* (L.) Moench), tall fescue (*F. arundinacea* Schreb.) with 3 harvests per year, immature rye (*Secale cereale* L.), and fiber corn (*Z. mays* L.) came from randomized block designed crop trials performed in 2008, 2009, 2010 and/or 2011 at Libramont (498 m above sea level (asl); average annual temperature: 8.6 °C; average annual precipitation: 1260 mm; 49°55′N, 05°24′E; Belgium), Gembloux (161 m asl; average annual temperature: 9.8 °C; average annual precipitation: 856 mm; 50°33′N, 04°43′E), Tinlot (255 m asl; average annual temperature: 9.7 °C; average annual precipitation: 871 mm; 50°28′N, 05°23′E; Belgium), Mötsch (330 m asl; average annual temperature: 8.4 °C; average annual precipitation: 675 mm; 49°57′N, 06°33′E; Germany) or Gerbéviller (260 m asl; average annual temperature: 9.9 °C; average annual precipitation: 1022 mm; 48°29′N, 06°31′E; France). Depending on the crop, trials were performed with different harvest periods (details in Table 1), cultivars (details in Table 1) and/or nitrogen fertilization levels (from 0 to 240 kg of nitrogen per hm^2). From plots between 9 and 24 m^2, the whole above ground biomass was harvested at 10 cm from the ground and chopped (particle size 1–2 cm). Details about the investigated plant biomasses are presented in Table 1.

For each biomass analyzed under its green-dried form, two representative subsamples were dried at 60 °C for 72 h in a forced air oven immediately after the harvest. After the drying process, the two subsamples were milled first with a 4 mm screen BOA hammer mill (Waterleau, Herent, Belgium) and then with a 1 mm screen Cyclotec cyclone mill (FOSS, Hillerød, Denmark). For the storage of the samples, airtight bags were used. They were kept at room temperature and were protected from light in a dark box.

For each biomass analyzed under its silage-wet form, one representative sample was packed in a plastic bag under vacuum. This enabled silaging of the sample. The vacuum sealed plastic bag was stored at room temperature for at least 3 weeks before the laboratory analysis. If gas was produced during silaging, the plastic bag was opened and put again under vacuum.

For each biomass analyzed under its silage-dried, one representative sub-sample of its silage-wet form was taken just before the laboratory analysis. It was dried at 70 °C for 48 h in a forced air oven. The dried sub-sample was milled with a 1 mm screen Cyclotec cyclone mill (FOSS, Hillerød, Denmark). It was then stored at room temperature in airtight bags.