Applied Energy 116 (2014) 52–57

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Near Infrared Reflectance Spectroscopy (NIRS) for rapid determination of biochemical methane potential of plant biomass

Jin M. Triolo [a,*], Alastair J. Ward [b], Lene Pedersen [a], Mette M. Løkke [b], Haiyan Qu [a], Sven G. Sommer [a]

[a] Department of Chem. Eng., Biotechnology and Environmental Tech., Faculty of Engineering, University of Southern Denmark, Niels Bohrs Allé 1, DK-5230 Odense M, Denmark
[b] Aarhus University, Dept. of Biosystems Engineering, AU Foulum, P.O. Box 50, DK-8830 Tjele, Denmark

HIGHLIGHTS

- We tested PLS model for a rapid determination of BMP using NIRS.
- The challenge is using data from a reference method which has high uncertainty.
- The NIRS model was nevertheless satisfactory and could be an alternative method.
- The best model could provide moderately successful computation of BMP.

ARTICLE INFO

Article history:
Received 2 July 2013
Received in revised form 25 September 2013
Accepted 1 November 2013

Keywords:
Anaerobic digestion
Predicting BMP
Multivariate data analysis
Biogas production

ABSTRACT

Determination of biochemical methane potential (BMP) by fermentation tests is time-consuming and costly, and therefore not useful for operators of full-scale biogas digesters. A great advantage of NIRS in determining BMP is the reduction in measurement time from at least one month for chemical determination to a couple of minutes for production of near infrared spectroscopy (NIRS) spectra. An innovative NIRS method that can be used as an alternative to current BMP tests was developed in this study. We tested the Partial Least Squares (PLS) model for a rapid determination of BMP using NIRS by applying a series of pre-processing methods with caution. A total of 88 plant biomass samples of a wide variety were used for model prediction. The standard error of the best PLS model was 37 CH_4 NL kg^{-1} VS, where BMP of the test set was between 136.2 and 477.9 CH_4 NL kg^{-1} VS. Coefficient of determination (R^2) and residual prediction deviation (RPD) were 0.84 and 2.49, respectively. This shows that the new NIRS model is moderately successful in application and could be an alternative modern tool to overcome the problems of current BMP methods.

1. Introduction

The world is running out of fossil fuels, in particular fuels for transport. Biogas production can replace fossil energy, including fuels used in the transport sector, and is the most socio-economically cost-efficient technology for reducing greenhouse gas (GHG) emissions and for recycling plant nutrients and recalcitrant carbon [1,2].

Animal manure is used as feed for biogas digesters, but due to the low biogas production potential the manure is co-digested with industrial organic wastes [3]. Due to limited availability of organic waste, digesters are also fed with crops which could otherwise be used as feed or food. Therefore this practice may not be considered ethical or sustainable. Alternatives to industrial organic waste or crops could be plant biomass from areas not being used for crop production or from highly productive species.

The biomass produced by these sources is known to have relatively low biochemical methane potential (BMP) due to its high content of lignocellulosic biopolymers, which have low anaerobic biodegradability [4]. However, recent studies have shown that cheap biomass types such as garden waste and wild grasses from meadows have rather high BMP and can be attractive and economical feedstocks for biogas production [5]. The lignocellulose composition of these biomass forms varies considerably between plant species. This is one of the most significant sources of variability and causes great problems for the management of the digesters and also when pricing the biomass at the gate. BMP can be determined by a fermentation test [6,7], which is time-consuming and costly and therefore not feasible for operators of full-scale biogas digesters. Thus, it is of paramount importance to develop new techniques and methodologies that are more efficient in terms of time and costs as alternatives to the classic BMP method of fermentation of substrate. First-generation alternative technologies comprise chemical analysis, which relates BMP to the degradation of organic components [8]. However, these methods do not provide a high

* Corresponding author. Tel.: +45 4117 8867; fax: +45 6550 7354.
E-mail address: jmt@kbm.sdu.dk (J.M. Triolo).

0306-2619/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2013.11.006

positive correlation to BMP, due to either large regression model error or poor model validation. Moreover, the chemical analysis is still time-consuming and the cost of analysis is often higher than the fermentation test. Compared with destructive methods (i.e. fermentation-based and chemical analysis methods), non-destructive and real-time measurements using spectroscopic methods such as Near Infrared Reflectance Spectroscopy (NIRS) are more promising. NIRS has been widely applied by other industries and is generally accepted as an instrument-based method giving fast measurement that can be used for process control and testing of raw material quality [9]. During the past decade, NIRS has also been used for biofuel technology [10–13]. Only three pioneering studies regarding the application of NIRS to the prediction of BMP and biogas production rate and their correlation to NIRS have been reported to date. Two of these are based on a wide variety of substrates such as municipal solid wastes (MSW) [14,15]. Lesteur and co-workers [14] strictly built a single-substrate model, Doublet and co-workers [15] combined MSW and agro-industrial wastes [15] and Raju and co-workers [16] used meadow grass as a very specific substrate. To our knowledge, no publications have presented a precise model for assessing the BMP of a wide range of plant biomass types using NIRS spectra. Therefore, the aim of this study was to develop a robust model that can predict BMP of a wide range of plant biomass sources from their NIRS spectra.

2. Materials and methods

2.1. Sample collection

A total of 88 plant biomass samples were included in the present study. The samples were collected in Funen and Jutland, Denmark, from July 2011 to April 2012, which gave a range of vegetation ages in the sample archive. Vegetation age is important in BMP where shorter age has higher BMP, because as vegetation age increases, the fraction of lignin increases which is non-degradable under an anaerobic environment, while other cell components such as cellulose and hemicellulose decrease (lignification) [5]. By collecting the various vegetation ages, we obtained various BMP profiles within the same plant species. Detailed information on the collected samples is provided in Table 1. A wide range of plant biomass samples with various BMP levels was included, e.g.: municipal green wastes such as lawn grasses and hedge trimmings; plants from both non-agricultural land and agricultural land, such as meadow grass and reed canary grass; and energy crops such as maize, sugar beet, wheat straw, short rotation coppice (*Salix b. and Salix a.*), short rotation forestry (*Betula*), and broad-leaved coppice (*Platanus* sp.). In order to improve the analytical precision, the collected samples were homogenised by grinding to a maximum size of 1 mm after drying at 60 °C prior to analysis, since most of the collected samples were heterogeneous, consisting of a distinct plant body, i.e. leaves, stem, fruit bodies and occasionally branches. According to our previous study [17], the procedure of drying at 60 °C and grinding does not affect BMP and other biogas production characteristics ($p > 0.05$). On the other hand, this homogenisation pre-treatment could have improved the analytical precision in BMP tests.

2.2. Characterisation of samples

2.2.1. BMP assay

BMP was determined according to VDI 4630 [3] using triplicate 1.0 l (working volume) batch infusion digesters. Inoculum was obtained from Fangel biogas plant (Funen, Denmark), which receives 80% animal slurry and 20% industrial organic wastes from the food processing industry and operates in mesophilic conditions (37 °C). The inoculum was degassed for two weeks at 37 °C prior to the BMP tests. Inoculum and each substrate were mixed in a ratio of 3:1 on a dry matter (DM) basis in each triplicate reactor and 100 mL of anaerobic buffer solution with medium were added to the inoculum substrate mixture [6,7]. Inoculum alone was included as a blank. Digestion was carried out at mesophilic conditions (37 °C). Digestion was terminated when only small amounts of gas were released, when daily biogas production per batch was less than 1% of cumulative gas production according to VDI 4630 [6], corresponding to approximately 60 days of batch fermentation. The concentration of methane (CH_4) in the biogas was measured by gas chromatograph (HP 6890 series). For quality control of the batch test, microcrystalline cellulose (Avicel PH-101 cellulose) was tested as a standard material. Based on the BMP of standard materials, the results of batch BMP tests qualified according to VDI 4630 [6], which states that actual BMP must reach at least 80% of theoretical BMP (which is 416 CH_4 NL kg^{-1} VS).

2.2.2. Biochemical and physico-chemical analysis

All analyses were carried out in duplicate. Volatile solids (VS) were determined according to standard procedures [18] (APHA, 2005). The concentration of lignocellulose was determined by applying the Van Soest characterisation method according to Mertens and co-workers [19], where neutral detergent fibre (NDF) was identified as lignocellulose [8].

2.3. NIRS analysis

A Bomem QFA Flex Fourier Transform spectrometer fitted with an InAs detector (Q-interline A/S, Copenhagen, Denmark) was used to obtain reflectance spectra. The spectra obtained were averaged from the results of 200 scans. Each of the dried and ground samples was placed in a 120-ml glass bottle, which was filled to approximately 70% of the volume. A rotating powder sampler was used, since the plant materials tested were heterogeneous.

2.4. Partial Least Squares (PLS) modelling

The Eigenvector Research Inc. PLS Toolbox (vers. 7.02) with MatLab (vers. R2012a) was used for data analysis. Variable ranges were set to between 4000 and 10,000 cm^{-1}, which corresponds to a wavelength range from 1000 to 2500 nm with respect to removing the noise regions. Principal component analysis (PCA) was

Table 1
Details of the 88 plant biomass samples used for the model in the study.

Biomass type	Sample used
Energy crop	$n = 33$ (birch tree (8); plane tree (5); weeping willow (5); sharpleaf willow (5); cypress (3); maize leaves (2); maize corn (2); wheat straw (1); sugar beet (2)
Lawn grasses	$n = 15$ (Short blue grass (2); meadow grass (5); lawn cuttings mixture (8)
Hedge trimmings	$n = 19$ (oval-leaved privet (5); Ivy (4); chokeberry (7); Beech hedge (1); Ground-elder (2)
Wild plants	$N = 21$ (reed canary grass (5); common reed (6); bamboo (2); chrysanthemum (2); tufted hair grass (2); dandelion (2); northern bluegrass (1); green foxtail (1)

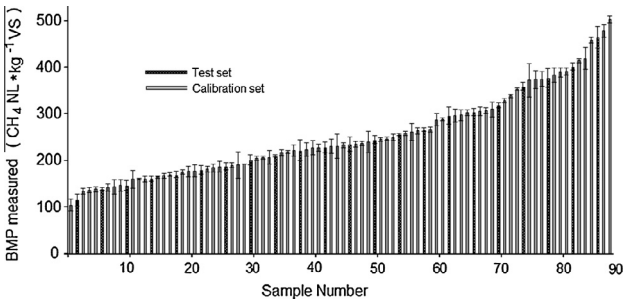

Fig. 1. Profile of measured BMP by increasing order. The dark bar indicates the test set and the light bar indicates the calibration set. Error bars indicate standard deviation of triplicate.

performed to examine data pattern of entire samples, and to identify possible outliers. A total of 88 samples were separated into calibration and test sets, in which 66 datasets were used for calibration and 22 for testing the models.

Fig. 1 shows the BMP profile of calibration and test sets included for PLS calibration and validation. As can be seen from Fig. 1, every 4th sample following the order of BMP value was chosen for the testing set in order to ensure that all the samples used for testing the model were within the BMP range of the calibration set samples. In addition, calibration and testing sets were well distributed with respect to BMP value. In detail, BMP of the test set was between 136.2 and 477.9 CH_4 NL kg^{-1} VS, with mean BMP being 254.9 (±92.0) CH_4 NL kg^{-1} VS, whereas BMP of the calibration set ranged from 104.0 to 502.3 CH_4 NL kg^{-1} VS, with similar mean and standard deviation as the test set (251.1 ± 91.5 CH_4 NL kg^{-1} VS).

The coefficient of determination (R^2) and root mean square error of prediction (RMSEP) were used to assess the quality of the PLS models in optimising pre-processing of the spectra. Residual prediction deviation (RPD), which is the ratio of standard deviation to RMSEP, and RMSEP were applied to assess the quality of the model and also to compare it with other alternative models.

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{n}(P_i - O_i)^2}{n}} \quad (1)$$

where O_i is the measured value, P_i is the predicted value and n is the number of data points.

Relative root mean square error of prediction (rRMSEP (%)) [12] was chosen for assessing relative model error and compared with precision of reference measurement. In the latter, repeatability relative standard deviation (RSD_r) was used according to the practical guide for ISO 2005 [20] to estimate the precision of BMP tests [21,22].

$$\mathrm{rRMSEP}\ (\%) = \frac{\mathrm{RMSEP}}{\overline{O}} \times 100 \quad (2)$$

where $\overline{O}$ is the overall mean and RMSEP is root mean square error of prediction.

$$\%\mathrm{RSD}_r = \frac{\mathrm{SD}_r}{\overline{\overline{X}}} \cdot 100\% \quad (3)$$

where $\overline{\overline{X}}$ is the mean of triplicate values and SD_r is repeatability standard deviation from triplicate results.

3. Results and discussion

3.1. Characteristics of samples

The methane concentration in dry biogas ranged between 51.7% and 66.5%, which is within the range expected, taking the organic composition of biomass into account. Average methane concentration was 57.3(±2.8)%, with low variability from sample to sample. The VS of all the samples measured was in the range 858–986 g kg^{-1} DM (mean 930 g kg^{-1} DM). The variation in VS was low, with a standard deviation (SD) of 26.5 g kg^{-1} DM. A high concentration of VS in dry matter compared with other municipal solid biomass types is positive for the profitability of biogas production, although the quality of VS may be critical due to low anaerobic biodegradability of lignocellulose [8], which is abundant in much plant biomass. However, not all the plant residues tested had a high lignocellulose concentration, as indicated by the large variation in concentration within samples (mean 613 g kg^{-1} VS, variation 163 g kg^{-1} VS) (Table 2).

Table 2
Methane (CH_4) concentration in biogas, volatile solids (VS) content and lignocellulose concentration of the samples used in the study.

		Mean	Min	Max	SD
CH_4 in dry biogas	%	57.0	52.5	66.5	3.2
VS	% of DM	92.2	86.7	96.2	2.9
Lignocellulose	% of DM	56.5	8.6	75.5	13.4
Lignocellulose	% of VS	61.3	9.2	78.5	16.3

BMP determined by fermentation tests was close to the Gaussian distribution, with a high density of samples in the range 200–400 CH_4 NL kg^{-1} VS (Fig. 1). The range of BMP observed (Fig. 1) was comparable to results emerging from recent studies (Table 3), and narrower than the data range presented by Doublet and co-workers [15].

A wide range of BMP may have an advantage in model precision by spanning the variability of PLS regression models. On the other hand, PLS models are significantly affected by extreme values, so there is a risk of the models being highly dependent on the uncertainty of a few extreme values, which might increase the model error in prediction.

3.2. Optimisation of pre-processing methods

Pre-processing was performed in two categories of light scatter correction methods and spectral derivatives (Fig. 2).

The pre-processing setup of standard normal variate (SNV), Detrend and Savitzky–Golay (SG) led to the best model, which agreed with the recommendation for optimal pre-processing for NIRS spectra by Rinnan et al. [23]. Table 4 shows the PLS models applying different pre-processing methods and the progress of model improvement according to pre-processing. The models varied slightly using the SG methods as affected by window size, polynomial order and derivative degree (Table 4). In SG, the number of data points allowed for the best results was 11. Furthermore, the polynomial degree 2 and second derivative in the SG method gave the best model. The optimal window size (data point 11) in SG modelling was found to be much smaller than reported previously by Jacobi et al. [24]. A possible reason could be that the reflectance spectra were obtained with the lower resolution (32 cm^{-1}) in the present study.

Possible outliers were examined simultaneously with the procedure of pre-processing optimisation. Among the energy crop samples, two sugar beet samples had a distinctly different pattern from the rest of the samples in PCA and PLS analysis. The spectra of these sugar beet samples also differed visually from the other spectra, indicating that they might be possible outliers (Fig. 2c). This could be due to a significantly different cell wall composition of these samples, which had a very low content of lignocellulose fibres (8.6% and 13.0% of DM) and high soluble carbohydrate concentrations. Hence, the PLS models was built including all samples and without these outliers, respectively.

Table 3
Compilation of NIRS calibration in predicting biochemical methane potential reported in previous studies.

Literature	Substrate	Variable range (nm)	PC	*n*	R^2	VE	RPD	Min[a]	Max[a]	Mean[a]	SD	Pre-processing
[14]	Municipal solid waste	1668–2500	7	53	0.76	27	2.36	23	400	234	66	SNV-DT
[16]	Meadowgrass	833–2500	13	95	0.69	37	1.75	51	406	288	66	Mean normalisation
[15]	Organic substrate	999–2500	7	243	0.85	40	2.61	0	1344	291	179	SNV-DT, SG(15, 2, 2)

Variable range: wavelength (nm).
PC: principal component.
N: number of calibration sets.
R^2: coefficient of determination in prediction.
VE: validation error (RMSEP) (CH_4 NL kg VS^{-1}).
RPD: residual prediction deviation.
SNV: standard normal variate; DT: detrend; SG(15, 2, 2): Parameters used of the Savitzky–Golay derivation method, i.e. the number of points used to calculate the polynomial (window size), polynomial degree and derivative degree used, respectively.
[a] In terms of biochemical methane potential (BMP), with units CH_4 NL kg VS^{-1}.

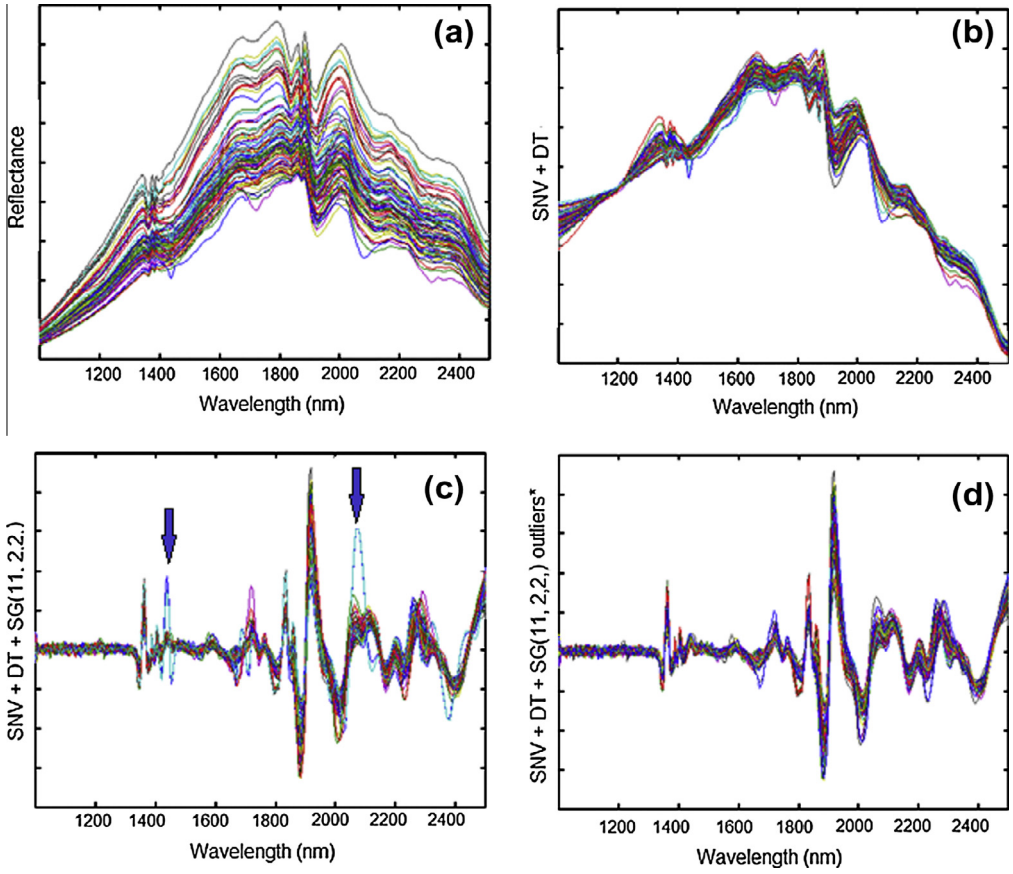

Fig. 2. Reflectance obtained with (a) no pre-processing, (b and c), pre-processed spectra and (d) pre-processed spectra excluding two potential outliers of the 88 samples within wavelength 1000–2500 nm.

3.3. PLS model results

The precision of the PLS model was best when all samples were included, giving an RMSEP value of 37 CH_4 NL kg^{-1} VS, R^2_{PRED} of 0.84 and RPD of 2.49 (Fig. 3).

When the two sugar beet samples were excluded from the model, the model error was RMSEP 40 CH_4 NL kg^{-1} VS and RPD decreased to 2.30. Thus including the sugar beet spectra resulted in a trend of higher model precision through all the pre-processing methods applied. The reason for this could be that the sugar beet samples contributed to an increase in the variability of scores, with their pronounced spectra and highest BMP values. Jacobi and co-workers [24] reported that including samples with extreme values improved the model, with a shift in R^2 from 0.85 to 0.94, and in RPD from 2.59 to 4.33. The number of PLS components (PC) used in this study (range 6–7; Table 4) seemed to be acceptable considering the complexity of samples and was similar to that in earlier studies.

The RPD of the best model in this study was acceptable compared to that reported for digestibility of biomass feed to ruminants, where RPD was 1.3 [25] and 1.7 [26]. The RPD obtained in this study seems to be moderately successful in relation to the criterion that a moderately successful model must have a RPD in the range 2.25–3 [27]. However, none of the studies known to us which have predicted BMP by NIRS have successfully produced an RPD above 3 (Table 3). R^2 of the prediction model was 0.84, which is moderately successful according to Malley and co-workers [27]. Moreover the R^2 obtained in our best model was comparable with values reported in previous studies, as shown in Table 3. The bias of the predicted values was 6 NL CH_4 kg^{-1}

Table 4
Statistical parameters of the PLS models produced.

Model no.	All samples included	n_{CAL}	n_{TES}	PC	RMSE	RMSEP	R^2_{cal}	R^2_{PRED}	Bias	RPD
1	Reflectance spectra (no pre-processing)	66	22	7	42	45	0.79	0.74	−4	2.04
2	SNV	66	22	8	32	42	0.88	0.79	3	2.19
3	SNV + DT	66	22	8	33	43	0.87	0.78	3	2.14
4	SNV + DT + SG(15, 2, 2)[a]	66	22	6	29	40	0.90	0.84	8	2.30
5	SNV + DT + SG(11, 2, 2)[a]	66	22	6	19	37	0.96	0.84	6	2.49
Excluding two sugar beet samples										
6	Reflectance Spectra (no pre-processing)	64	22	6	42	51	0.74	0.68	−5	1.80
7	SNV	64	22	6	38	44	0.79	0.75	−2	2.09
8	SNV + DT	64	22	6	38	45	0.79	0.75	−3	2.04
9	SNV + DT + SG(15, 2, 1)[a]	64	22	6	34	39	0.83	0.81	2	2.36
10	SNV + DT + SG(11, 2, 2)[a]	64	22	6	22	40	0.92	0.83	5	2.30

PC: number of PLS components.
n_{CAL}: number of calibration sets.
n_{TES}: number of testing sets.
R^2_{cal}: coefficient of determination in calibration.
R^2_{PRED}: coefficient of determination in prediction.
RMSE: root mean square error of calibration (CH_4 NL kg VS^{-1}).
RMSEP: root mean square error of prediction (CH_4 NL kg VS^{-1}).
RPD: residual prediction deviation.
SNV: standard normal variate.
DT: detrend.
SG*(11, 2, 2): Parameters used of the Savitzky–Golay derivation method, i.e. the number of points used to calculate the polynomial [a](window size), polynomial degree and derivative degree used, respectively.

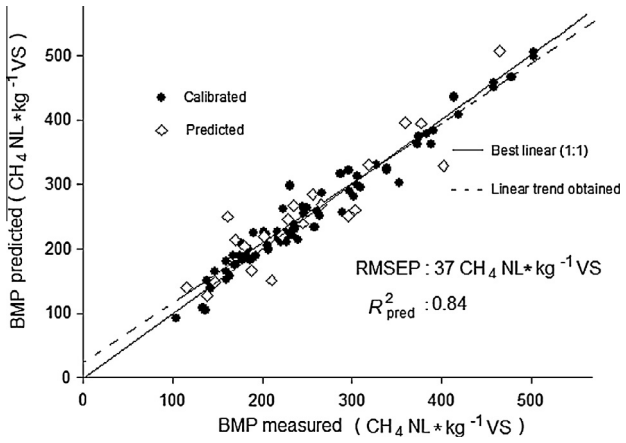

Fig. 3. BMP predicted versus BMP measured from the best model (Model 5). The dotted line indicates the linear trend obtained using the test set. The solid line indicates the best linear relationship (1:1).

VS, due to a slight under-estimation of higher BMP samples and over-estimation of lower BMP samples. This pattern is frequently seen when the samples used for calibration have a Gaussian distribution [28]. This means that as many samples as possible should be included at the calibration border space, in order to reduce the leverage. Nevertheless the predicted BMP correlated very well with the measured values (Fig. 3) at the level of bias obtained in this study. The standard error of the best model (Model 5) was in line with that reported in studies by Raju and co-workers [16] (37 NL CH_4 kg^{-1} VS) and Doublet and co-workers [17] (40 NL CH_4 kg^{-1} VS). Overall, the results of the present work demonstrate that the NIRS-based model can be used to assess the methane potential of plant biomass, which has high variability in anaerobic biodegradability.

3.4. Perspectives for improving the predictions

Standard model error with respect to the mean value of BMP can be calculated by dividing RMSEP by mean BMP of the testing set and expressing the result as a percentage [12]. In this study, rRMSEP (%) of the best model was found to be 14.6%. It is known that the square of model error in prediction is the sum of the square of PLS algorithm error and the square of the reference method error. This means that the error of model prediction is theoretically always larger than the error of the reference method, which highlights the importance of high precision of reference data collection. In this study the repeatability standard deviation (SD_r) of each sample replicate was 16 CH_4 NL kg^{-1} VS in the BMP fermentation tests, which corresponded to an RSD_r of 6.6%. SD_r is slightly lower than that of BMP tests in the study by Doublet and co-workers [15], who reported a mean SD_r of 19 CH_4 NL kg^{-1} VS. Raju and co-workers [16] concluded that the lower precision of the BMP model prediction is probably also due to lower precision of BMP tests caused by heterogeneity of samples. Compared with carrying out BMP measurements, it is easier to obtain NIRS spectra that overcome the analytical error from heterogeneity of samples, simply by averaging many spectra as part of the measurement protocol. Moreover, the BMP test suffers from many difficulties regarding heterogeneity of inocula, environmental conditions etc. and management quality, which results in low comparability of BMP data generated by different researchers and laboratories [22,29]. As a result, interlaboratory studies of BMP have found low reproducibility of BMP measurements carried out by different researchers, indicating poor comparability of BMP data [30]. Thus BMP batch measurements have to be carried out using standard protocols giving precise and reproducible results. Collating data from high quality databases could also help improve the model predictions, especially for biomasses with high or low BMP.

4. Conclusion

The BMP prediction model involves indirect PLS modelling, and the methane producing capacity of biomass samples depends on the characteristics of the organic fraction of the samples, such as groups of proteins, lipids and carbohydrates, and the concentration of non-degradable lignin, slowly degradable lignocellulosic cellulose and hemicellulose. The NIRS spectra of biomass samples contain information on the vibration modes of these molecules, and thus include all information regarding the composition of the samples. With a well-established PLS model, information can be extracted from the NIRS spectra and can be correlated with

the methane producing capacity of the biomass samples. Therefore the advantage of NIRS spectra methods compared with the existing BMP determination by chemical analysis is that no additional model is needed to transform biomass characterisation into biogas production potential, and BMP is indicated directly. The challenge lies in building a model using data from a reference method which has high uncertainty. The great diversity of various substrates and their heterogeneous chemical characteristics also make robust calibration difficult. Nevertheless, the precision of the best model in the present study was satisfactory and the model can be used for a first-hand estimation of BMP, providing moderately successful computations.

Acknowledgements

This study was supported by a grant from Energi Fyns Udviklingsfond and by a grant from the Danish Council for Strategic Research under the work program "Optimization of Value Chains for Biogas Production in Denmark" (BioChain). The authors are responsible for the content of this publication.

References

[1] Sommer SG, Petersen SO, Møller HB. Algorithms for calculating methane and nitrous oxide emissions from manure management. Nutr Cycl Agroecosys 2004;69:143–54.
[2] Ding W, Niu H, Chen J, Du J, Wu Y. Influence of household biogas digester use on household energy consumption in a semi-arid rural region of northwest China. Appl Energy 2012;97:16–23.
[3] Raven RPJM, Gregersen KH. Biogas plants in Denmark: successes and setbacks. Renew Sustain Energy Rev 2007;11:116–32.
[4] Monlaua F, Latrillea E, Da Costa AC, Steyer J, Carrèrea H. Enhancement of methane production from sunflower oil cakes by dilute acid pretreatment. Appl Energy 2013;102:1105–13.
[5] Triolo JM, Pedersen L, Qu H, Sommer SG. Biochemical methane potential and anaerobic biodegradability of non-herbaceous and herbaceous phytomass in biogas production. Bioresour Technol 2012;125:226–32.
[6] VDI. 2006. VDI 4630. Fermentation of organic materials. In: Characterisation of Substrate. Sampling. Collection of Material Data. Fermentation Tests.
[7] ISO 1995. ISO 11734: Water Quality – Evaluation of the 'Ultimate' Anaerobic Biodegradability of Organic Compounds in Digested Sludge Method by Measurements of the Biogas Production. Geneva: International Organization for Standardization.
[8] Triolo JM, Sommer SG, Møller HB, Weisbjerg MR, Jiang X. A new algorithm to characterize biodegradability of biomass during anaerobic digestion: influence of lignin concentration on methane production potential. Bioresour Technol 2011;102:9395–402.
[9] Huang HB, Yu HY, Xu HR, Ying YB. Near infrared spectroscopy for on/in-line monitoring of quality in foods and beverages: a review. J Food Eng 2008;87:303–13.
[10] Ward AJ, Bruni E, Lykkegaard MK, Feilberg A, Adamsen APS, Jensen AP, et al. Real time monitoring of a biogas digester with gas chromatography, near-infrared spectroscopy, and membrane-inlet mass spectrometry. Bioresour Technol 2011;102:4098–103.
[11] Ward AJ, Hobbs PJ, Holliman PJ, Jones DL. Evaluation of near infrared spectroscopy and software sensor methods for determination of total alkalinity in anaerobic digesters. Bioresour Technol 2011;102:4083–90.
[12] Madsen M, Ihunegbo FN, Holm-Nielsen JB, Halstensen M, Esbensen KH. On-line near infrared monitoring of ammonium and dry matter in bioslurry for robust biogas production: a full-scale feasibility study. J Near Infrared Spec 2012;20:635–45.
[13] Zhang W, Yuanb W, Zhang X, Coronado M. Predicting the dynamic and kinematic viscosities of biodiesel–diesel blends using mid- and near-infrared spectroscopy. Appl Energy 2012;98:122–7.
[14] Lesteur M, Latrille E, Maurel VB, Roger JM, Gonzalez C, Junqua G, et al. First step towards a fast analytical method for the determination of biochemical methane potential of solid wastes by near infrared spectroscopy. Bioresour Technol 2011;102:2280–8.
[15] Doublet J, Boulanger A, Ponthieux A, Laroche C, Poitrenaud M, Cacho Rivero JA. Predicting the biochemical methane potential of wide range of organic substrates by near infrared spectroscopy. Bioresour Technol 2013;128:252–8.
[16] Raju CS, Ward AJ, Nielsen L, Møller HB. Comparison of near infrared spectroscopy neutral detergent fibre assay and in vitro organic matter digestibility assay for rapid determination of the biochemical methane potential of meadow grasses. Bioresour Technol 2011;102:7835–9.
[17] Triolo JM, Sommer SG, Pedersen L. Influence of subfreezing and reducing particle size on determination of biochemical methane potential of solid organic waste. Environmental engineering and management; 2013 (accepted for publication).
[18] APHA. Standard methods for the examination of water and wastewater. 21st ed. Washington, DC: American Public Health Association; 2005.
[19] Mertens D et al. Gravimetric determination of amylase-treated neutral detergent fiber in feeds with refluxing in beakers or crucibles: collaborative study. J AOAC Int 2002;85:1217–40.
[20] ISO 2005. ISO/TR 22971: Accuracy (Trueness and Precision) of Measurement Methods and Results. Practical Guidance for the Use of ISO 5725–2:1994 in Designing, Implementing and Statistically Analysing Interlaboratory Repeatability and Reproducibility Results. TC 69/SC 6. Geneva: International Organization for Standardization.
[21] Hansen TL, Schmidt JE, Angelidaki I, Marca E, Jansen JC, Mosbæk H, et al. Method for determination of methane potentials of solid organic waste. Waste Manage 2004;24:393–400.
[22] Pham CH, Triolo JM, Cu TTT, Pedersen L, Sommer SG. Validation and recommendation of methods to measure biogas production potential. Asian Austral J Anim Sci 2013;26:864–73.
[23] Rinnan Å, Berg FBD, Engelsen SB. Review of the most common pre-processing techniques for near-infrared spectra. Trends Anal Chem 2009;28:1201–22.
[24] Jacobi HF, Ohl S, Thiessen E, Hartung E. NIRS-aided monitoring and prediction of biogas yields from maize silage at a full-scale biogas plant applying lumped kinetics. Bioresour Technol 2012;103:162–72.
[25] Cozzolino D, Fassio A, Fernandez E, Restaino E, La Manna A. Measurement of chemical composition in wet whole maize silage by visible and near infrared reflectance spectroscopy. Anim Feed Sci Technol 2006;129:329–36.
[26] Liu X, Han L, Yang Z, Xu C. Prediction of silage digestibility by near infrared reflectance spectroscopy. J Anim Feed Sci 2008;17:631–9.
[27] Malley DF, McClure C, Martin PD, Buckley K, McCaughey WP. Compositional analysis of cattle manure during composting using a field-portable near-infrared spectrometer. Commun Soil Sci Plant Anal 2005;36:455–75.
[28] Bellon-Maurel V, Fernandez-Ahumada E, Palagos B, Roger J-M, McBratney A. Critical review of chemometric indicators commonly used for assessing the quality of the prediction of soil attributes by NIR spectroscopy. Trends Anal Chem 2010;29:1073–81.
[29] Browne JD, Murphy JD. Assessment of the resource associated with biomethane from food waste. Appl Energy 2013;104:170–7.
[30] Raposo F, Fernández-Cegrí V, De la Rubia MA, Borja R, Béline F, Cavinato C, et al. Biochemical methane potential (BMP) of solid organic substrates: evaluation of anaerobic biodegradability using data from an international interlaboratory study. J Chem Technol Biotechnol 2011.