Bioresource Technology 197 (2015) 475–481

Contents lists available at ScienceDirect

Bioresource Technology

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

Rapid estimation of the biochemical methane potential of plant biomasses using Fourier transform mid-infrared photoacoustic spectroscopy

Georgios Bekiaris[a], Jin M. Triolo[b], Clément Peltre[a], Lene Pedersen[b], Lars S. Jensen[a], Sander Bruun[a,*]

[a] Department of Plant and Environmental Sciences, Faculty of Science, University of Copenhagen, Thorvaldsensvej 40, Frederiksberg C DK-1871, Denmark
[b] Institute of Chemical Engineering, Biotechnology and Environmental Technology, Faculty of Engineering, University of Southern Denmark, Campusvej 55, Odense M DK-5230, Denmark

HIGHLIGHTS

- Mid-infrared FTIR photoacoustic spectra identified two classes of feedstock.
- Samples with higher content in lignin and hemicellulose had lower BMP.
- The prediction of BMP was as efficient as NIR.
- Positive correlation of easily degradable compounds with BMP was found.
- Negative correlation of BMP with lignin and hemicellulose was observed.

ARTICLE INFO

Article history:
Received 9 June 2015
Received in revised form 10 August 2015
Accepted 11 August 2015
Available online 24 August 2015

Keywords:
FTIR-photoacoustic spectroscopy
Biochemical methane potential (BMP)
Prediction
Calibration model

ABSTRACT

Biochemical methane potential (BMP) is a very important characteristic of a given feedstock for optimisation of its use in biogas production. However, the long digestion time needed to determine BMP is the main limitation for the use of this assay during the operation of anaerobic digesters to produce biogas. Fourier transform mid-infrared photoacoustic spectroscopy (FTIR-PAS) was used to predict the BMP of 87 plant biomasses. The developed calibration model was able to explain 81% of the variance in the measured BMP of a selected test set with a root mean square error (RMSE) of 40 NL CH_4 kg^{-1} of volatile solids (VS) and a ratio of performance to deviation (RPD) of 2.38. The interpretation of the regression coefficients used in the calibration revealed a positive correlation of BMP with easily degradable compounds (amorphous cellulose, hemicellulose and aliphatic compounds) and a negative correlation with inhibitors of cellulose hydrolysis (lignin, hemicellulose).

1. Introduction

There is currently a great interest in bioenergy and the prospects that it provides in terms of reducing reliance on fossil fuels. A range of different conversion technologies for biomass exists including incineration to produce electricity, thermochemical conversion to produce syngas and bio-oil, and fermentation to produce ethanol. Production of biogas, mainly consisting of methane produced by anaerobic digestion, has a range of advantages over other technologies. Wet biomasses such as manure and many other waste types can be used for anaerobic digestion, while they are difficult to be used for incineration or most kinds of thermochemical conversion techniques. Anaerobic digestion is more energy efficient than bioethanol production, with a higher energy output-to-input ratio, and can be undertaken using a greater variety of feedstock (Börjesson and Mattiasson, 2008), while there is no need for a separate enzymatic hydrolysis step (Teghammar et al., 2012).

Biochemical methane potential (BMP) assays are commonly used to determine methane production from an organic substrate during its anaerobic digestion (Angelidaki et al., 2009). BMP is a very valuable characteristic that can be used by the operators of biogas plants to control the addition of feedstock. The main disadvantage of the BMP assay is the length of time it takes (30–90 days), which limits its usefulness for the optimisation and operational management of an anaerobic digester (Hansen et al., 2004). Predictions of BMP using chemical compositional analyses have been performed in previous studies (Godin et al., 2015;

---

* Corresponding author.
E-mail address: sab@plen.ku.dk (S. Bruun).

http://dx.doi.org/10.1016/j.biortech.2015.08.050
0960-8524/© 2015 Elsevier Ltd. All rights reserved.

Triolo et al., 2011). Recently, near infrared spectroscopy (NIR) was used in combination with advanced chemometrics to predict BMP (Doublet et al., 2013; Lesteur et al., 2011; Triolo et al., 2014).

To date, there have been no previous attempts to use Fourier transform mid-infrared spectroscopy (FTIR) to predict BMP. FTIR spectroscopy requires only a small quantity of the sample for the measurement, and allows the interpretation of the obtained spectra which is more complicated with NIR spectroscopy because of overlapping overtones and combination bands. FTIR-photoacoustic spectroscopy (FTIR-PAS) is not a new technique, but recent developments in extremely sensitive microphones have improved its applicability considerably. In FTIR-PAS, a traditional FTIR instrument is combined with a photoacoustic detector. A thermal wave is produced by the vibration of the molecules due to the interaction between the infrared radiation and the sample. This thermal wave results in thermal expansion and pressure oscillation in the surrounding gas which is detected as an acoustic signal by the microphone (McClelland et al., 2002). The signal is directly proportional to the amount of absorbed infrared radiation in the sample. This allows the application of this technique on dark and opaque samples as the measurement remains unaffected by the redistribution of light due to scattering effects or diffraction processes, which is one of the main limitations of reflectance or transmittance detection with traditional FTIR (Kizil and Irudayaraj, 2013).

Therefore, the main objectives of the present study were: (i) to evaluate the potential of FTIR-PAS to predict the BMP of a wide range of plant biomasses, and (ii) to identify, based on the mid-infrared spectrum, the chemical components of plant materials that are associated with BMP.

2. Methods

2.1. Sample set

A total of 87 samples together with their BMP data were retrieved from a previous study (Triolo et al., 2014) on the rapid determination of BMP using NIR spectroscopy. The samples were grouped into four different groups: crop residues (7 samples), grasses (36 samples), hedge trimmings (28 samples) and tree trimmings (26 samples). The crop residues group included maize leaves and grains as well as wheat straw samples. The grass samples originated from lawn mowing in intensively managed parks and private gardens, as well as wild grass cuttings from roadsides, wetlands etc. The hedge trimmings group included samples from ground elder, beech, oval leaf privet, ivy and chokeberry. Tree trimmings included a mixture of leaves and branches (<20 cm length) from birch, weeping willow, sharp leaf willow and plane trees.

2.2. Biochemical methane potential assay

The methane production potentials were determined as described by Triolo et al. (2014). Briefly, BMP assays were carried out in triplicate in 1.0 L batch infusion digesters and at a digestion temperature of 37 °C (mesophilic). Inoculum was obtained from the Fangel biogas plant near Odense, Denmark, which processes animal slurry (mainly pig but also some dairy slurry) as prime feedstock and industrial organic waste (max. 25%) as a co-substrate at 37 °C. The collected inoculum was degassed for two weeks at the same temperature. The inoculum-to-substrate ratio (I:S ratio) was set to 3:1 on a dry matter basis. 100 ml of buffer solution with medium was added to the mixture of substrate and inoculum, as described in VDI 4630 (VDI, 2006) and ISO Standard 11734 (ISO 11734, 1995). Nitrogen gas was flushed into each reactor to obtain an anaerobic atmosphere. Digestion was continued until the daily biogas production was less than 1% of cumulative gas production, which occurred after approximately 60 days. The reactors' contents were thoroughly mixed at least twice a day. The volume of gas produced was measured every day at the beginning of digestion and then gradually at longer time intervals, and it was corrected to dry gas at standard temperature and pressure (STP) conditions:

$$V_0^{dr} = V * \frac{(P - P_w) * T_0}{p_0 * T} \qquad (1)$$

where V_0^{dr} is the volume of dry gas in the normal state (mlN), V is the measured volume (ml), P is the pressure of the gas phase at the time of the reading (hPa), P_w is the vapour pressure of the water (hPa), T_0 is standard temperature (=273 K), p_0 is standard pressure (=1013 hPa) and T is the temperature of the fermentation gas or of the ambient space (K).

Methane and carbon dioxide concentrations in biogas samples were measured once a week using a gas chromatograph (HP 6890 series) with a thermal conductivity detector (TCD) and a 30 m × 0.320 mm column (J&W 113-4332). Injector, detector and oven temperatures were 110 °C, 250 °C and 250 °C respectively. The split rate was 1:100 and the carrier gas was helium (30 cm/s). The concentration of methane in the dry gas was calculated assuming that the amounts of ammonia and other gases were insignificant:

$$C_{Cor}^{Dry} = C_{CH_4} * \frac{100}{(C_{CH_4} + C_{CO_2})} \qquad (2)$$

where C_{Cor}^{Dry} is the corrected concentration of methane in the dry gas (%), C_{CH_4} is the measured concentration of methane in the gas (%) and C_{CO_2} is the measured concentration of carbon dioxide in the gas (%).

The methane volume from the substrate was calculated by subtracting the corrected methane volume of the inoculum from the corrected methane volume of the mixture of inoculum and substrate.

2.3. FTIR-PAS analysis

Apart from oven drying the samples at 60 °C and grinding them to a particle size of 1 mm, no other pre-treatment was performed prior to the spectroscopic analysis. The FTIR-PAS spectra were recorded by a Nicolet 6700 spectrometer (ThermoScientific, USA) equipped with a PA-301 photoacoustic detector (Gasera Ltd, Finland). The samples were packed in ring cups with a diameter of 10 mm. The detectors' chamber and the samples were purged with helium prior to and during the analysis in order to reduce the effect of the moisture evaporating from the samples during the measurement. For each sample, 32 scans in the infrared region between 4000 and 600 cm^{-1} at a resolution of 4 cm^{-1} were recorded and averaged. Prior to spectroscopic analysis, the spectra were smoothed by the Savitzky–Golay algorithm (Savitzky and Golay, 1964) [3 points each side (total window of 7 smoothing points) and a zero order polynomial], and normalised by mean using the Unscrambler X v.10.3 software (CAMO software, Oslo, Norway).

2.4. Multivariate analysis

Partial least square regression (PLSR) analysis was performed in order to calibrate a model predicting BMP from the FTIR-PAS spectra. Different transformations of the spectra (such as smoothing, normalisation by the mean, baseline correction, SNV, de-trending, first and second derivative etc.) were performed in an attempt to obtain better predictions. Prior to PLSR analysis, two outliers (both sugar beets) were removed in order to increase the model's stabil-