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A new algorithm to characterize biodegradability of biomass during anaerobic digestion: Influence of lignin concentration on methane production potential

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ABSTRACT

We examined the influence of fibrous fractions of biomass on biochemical methane potential (BMP) with the objective of developing an economical and easy-to-use statistical model to predict BMP, and hence the biodegradability of organic material (BD) for biogas production. The model was developed either for energy crops (grass, maize, and straw) or for animal manures, or as a combined model for these two biomass groups. It was found that lignin concentration in volatile solids (VS) was the strongest predictor of BMP for all the biomass samples. The square of the sample correlation coefficient (R^2) from the BMP versus lignin was 0.908 ($p < 0.0001$), 0.763 ($p < 0.001$) and 0.883 ($p < 0.001$) for animal manure, energy crops and the combined model, respectively. Validation of the combined model was carried out using 65 datasets from the literature.

1. Introduction

Biogas has been used as a source of renewable energy for more than 100 years. Its production has also played a valuable role in the sustainable management of agricultural byproducts, including animal manure. In Denmark, approximately 5% of animal manure is used for biogas production, and the aim is to use 40% of animal slurry in feedstock-to-biogas digesters by 2020 (Green Growth, 2009). Therefore it is necessary to improve profitability by enhancing methane yield in biogas production. Animal manure contains more readily degradable organic materials, such as proteins and lipids, than other agricultural byproducts, but it also has a high content of lignocellulose biofibers (40–50% of the total solids; Bruni et al., 2010). Lignocellulose consists mainly of three biopolymers: cellulose, hemicelluloses, and lignin. In lignocellulosic materials, cellulose is physically associated with hemicelluloses, and physically and chemically associated with lignin (Mussatto et al., 2008). Lignin and hemicelluloses are intermeshed and chemically bound through covalent cross-linkages such as ester or ether linkages (Jeffries, 1994). The low biodegradability (BD) of lignocellulose in biogas reactors is due to lignin being nondegradable in anaerobic environments (Mauseth, 1988) because the extracellular enzymes require oxygen to depolymerize. Furthermore, hydrolysis of cellulose in lignocellulosic materials is reduced by lignin and hemicelluloses, since these components act as a protective coat, making the cellulose resistant to enzymatic digestion (Mussatto et al., 2008). Animal manure contains high concentrations of lignin because it consists of residues from feed, where the easily degradable compounds have been taken up by the animals; therefore the biomass excreted contains mainly the slowly degradable components including lignocellulose. Ruminants are particularly efficient in using the carbon components in feed, and therefore excreta from ruminants contain high concentrations of slowly digestible organic matter.

Biochemical methane potential (BMP) has been used as the most relevant indicator for assessing BD (Lesteur et al., 2010). BMP cannot be directly related to BD, since BMP is the methane yield, reflecting the destruction of organic materials, and the methane potential of each organic component in the volatile solids (VS) pool varies widely. For example, theoretically, the methane potential of lipid is 1018 L/kg, while the methane potential of cellulose is only 415 L/kg, based on the anaerobic degradation equation suggested by Symons and Buswell (1933). BMP assessed by different researchers and institutes is usually not comparable, due to differences in equipment used, environmental conditions, and experimental protocols (Angelidaki et al., 2009). As BMP data may vary depending on the batch method used, the application of a standardized method is needed. Furthermore, since the current

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methods of determining BMP are costly and time-consuming, innovative techniques for predicting BMP or BD are of great importance. Several alternate methods of estimating BD have been suggested (Lesteur et al., 2010) and numerous studies have attempted to predict BD or BMP by measuring the content of organic components (Tong et al., 1990; Gunaseelan, 2007). Near infrared spectroscopy (NIRS) has been used to predict organic matter components (Bruun et al., 2005; Michel and Ludwig, 2010). Recently the BMP of municipal solid waste has been shown to correlate well with NIRS results (Lesteur et al., 2011). Few studies have focused on lignin as the predominant variable to predict BD or BMP for biogas production. Chandler et al. (1980) observed a strong correlation between biodegradable fraction and lignin content in VS (R^2 = 0.94) from diverse organic wastes, and Gunaseelan (2007) reported a weak relationship between the BMP and lignin content of several fractions of fruit and vegetable solids (R^2 = 0.49). It was suggested that the low correlation could be due to the narrow range of lignin content in the fruits that were tested, making it impossible to reveal a significant effect of lignin. To our knowledge there is no satisfactory model for predicting BMP using lignin as a predominant variable that can be used for animal slurries, energy crops, and a mixture of both.

The objective of this study was to examine the influence of lignin on BMP in energy crops and manure and to construct a statistical model to predict BMP and BD. The hypothesis was that lignin concentration can be used to assess BMP, and further to predict BD. The model, and the analytical procedures needed to provide data for the model, must be a cheap and fast alternative to existing methods.

2. Methods

2.1. Substrates and inoculum used

Both animal slurries and energy crops were included in the study. Fresh pig and cattle slurry samples were taken from the pre-storage tanks of 10 farms in Horsens, Denmark. Grass, maize and straw were collected from farms in central Jutland. Table 1 shows the energy crops included in the study, with harvest date, pretreatment, and particle size. Representative subsamples for characterization and for the fermentation study were stored at −18 °C. The inocula used for the BMP assay were collected from two biogas plants at Fangel and Foulum. The Fangel biogas plant is operated under mesophilic conditions (37 °C), processing pig manure from 26 animal farms mixed with industrial organic waste. The Foulum biogas plant processes cattle manure mixed with crop residues under thermophilic conditions (55 °C). Inoculum from Foulum was taken from the post storage which is running under mesophilic conditions. The inocula were degassed at 37 °C for 14 days before application. The average pH and volatile solid of inocula were 8.0 and 66 (% of dry matter), respectively. The average methane concentration of biogas released from inocula was 68.2%. The pH of animal manure ranged between 7.3 and 7.7.

2.2. BMP assay

The BMP of the animal manure and energy crops were determined using a batch technique based on methods described by Møller et al. (2004). 1100-mL infusion bottles were used as the batch digesters. Headspace was set to 30%. Inoculum to substrate was at unity or very close to unity on a VS basis (1:1). Blanks were tested using 770 g of inoculum to correct gas production. After addition of the substrate inoculum mixture, the digesters were closed with butyl rubber stoppers, sealed with aluminum crimps, flushed with N_2 atmosphere and incubated at 37(±0.5) °C. All assays were performed in triplicate. Gas volume was measured either by replacing water or using a large syringe, as described by Steed and Hashimoto (1994). Digestion was continued until no further gas production was observed (90 days). Each batch digester was mixed thoroughly by shaking to prevent dry layers and to encourage degassing on workday. Gas volumes were measured every day at the beginning of fermentation and then gradually at larger time intervals. Methane and carbon dioxide were determined simultaneously once a week by a gas chromatograph (HP 6890 series), equipped with a thermal conductivity detector and a 30 m × 0.320 mm column (J&W 113-4332). The carrier gas was helium (30 cm/s), and injection volume was 0.4 mL. Injector temperature was 110 °C, and detector and oven temperature was 250 °C. The split rate was 1:100. Methane quantification was evaluated according to VDI 4630 (2006). In detail, gas volume as read off was corrected as dry gas flow and as STP conditions (273 K, 1.013 bar). For quantification of methane concentration, simultaneously measured methane and carbon dioxide concentrations were multiplied by the same factor, being the sum of the corrected measured values as 100%, assuming that the fractions of ammonia and hydrogen sulfide are insignificant quantities (Eq. (1)).

$$C_{\mathrm{Cor}}^{\mathrm{dry}} = C_{\mathrm{CH_4}} \cdot \frac{100}{(C_{\mathrm{CH_4}} + C_{\mathrm{CO_2}})} \quad (1)$$

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

Methane volumes were calculated using corrected dry gas volume and corrected methane concentration. The methane volumes only from the substrate were calculated by subtracting the mean value of the inoculum control.

Table 1
The energy crops included in the study, with harvest date, pretreatment, and particle size.

No.	Crop	Cultivar	Pretreatment	Harvest date	Particle size (mm)
1	Perennial grass	Mixed wild types	Coarse cut	14 June	10–15
2	Perennial grass	Mixed wild types	Coarse cut	14 September	10–15
3	Dried grass	Mixed wild types	Coarse cut	NA	10–15
4	Grass	Festulolium + 20% red clover, Hykor and Amos	Coarse cut	22 October	10–15
5	Grass	Festulolium, Achilles	Coarse cut	7 August	10–15
6	Grass	Festulolium + 20% red clover, Achilles and Amos	Coarse cut	8 October	10–15
7	Maize	Anvil	None, cut during harvest	15 October	5
8	Maize	Patrick	None, cut during harvest	15 October	5
9	Maize	Aurelia	None, cut during harvest	15 October	5
10	Dried straw	Wheat straw	Coarse cut	NA	10–15

NA: not available.