



Research paper

Comparison of approaches for organic matter determination in relation to expression of bio-methane potentials



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ABSTRACT

Bio-Methane Potential (BMP) tests are used to evaluate the suitability of a biomass for anaerobic digestion. BMP data are usually presented as the amount of methane produced from a kilogram of volatile solids (VS) or chemical oxygen demand (COD) of the substrate. However, the most used methods for determination of VS and COD are not always accurate. Oven drying may underestimate VS content due to loss of volatile organic compounds, and incomplete chemical oxidation may lead to underestimation of COD content. Bomb calorimetry is an attractive alternative to COD measurements, because the physical state of the biomass sample does not influence the measurement, and because sample preparation is limited. In this study, 11 biomass samples, wet and dry, were analyzed with different methods for organic content determination. COD (determined by bomb calorimetry and by wet chemistry) and VS (by Karl Fischer titration and loss on drying; LOD) were compared, and used for determination of BMP. In general, the BMP estimated on a VS basis were higher than those estimated on COD basis. For certain biomass samples the method for VS determination also greatly influenced the results; for fishery waste the BMP was estimated as 928 L kg⁻¹ based on LOD-VS compared to 394 L kg⁻¹ based on KF-LOD. Thus, this study shows that determination of organic content is not trivial and the method of choice strongly influences the estimation of bio-methane potentials. Bomb calorimetry offers a possibility to measure energy content directly, independent of biomass composition and physical state.

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1. Introduction

Biochemical Methane Potential (BMP) tests are applied to evaluate the anaerobic biodegradability of a biomass and the effect of pretreatment technologies. For this purpose standard protocols have been proposed in an attempt to limit the variations between laboratories [1,2]. The protocols suggest that bio-methane yields are presented either on the basis of volatile solids (VS) or Chemical

Oxygen Demand (COD), and most studies report either one or both of these values. In relation to this, it is acknowledged that VS and COD determinations in biomass samples are challenging, but few studies have investigated this in detail [1,3–5].

VS refer to the amount of organic compounds in a biomass sample and are defined as the difference between dry matter (DM) and the ash content. VS is usually determined gravimetrically as the difference in the sample weight after drying at 105 °C (Loss on Drying; LOD) and subsequent burning at 550 °C (Loss on Ignition; LOI). The method assumes no evaporation of organic material at 105 °C, which is not the case for many volatile compounds. To overcome this problem Agger et al. [3] suggested using Karl Fisher titration which specifically measures water content in biomass as an alternative to LOD for DM determination. The study demonstrated that Karl Fischer titration could give accurate measures for water content in various biomass samples and thus a more accurate determination of DM and VS, in particular for samples containing true volatile compounds. Both methods uses LOI for ash determination.

Abbreviations: BCV, net biological calorific value for biological degradation; BMP, bio-methane potential; CEP, chemical energy potential; COD, chemical oxygen demand; Cr-COD, chemical oxygen demand estimated with the closed reflux method; CV-COD, chemical oxygen demand calculated from the net calorific value; DM, dry matter; GCV, gross calorific value; KF, Karl Fischer; LOD, loss on drying; RSD, relative standard deviation; SE, steam exploded; SIR, substrate to inoculum ratio; ThCOD, theoretical chemical oxygen demand; VFA, volatile fatty acids; VS, volatile solids.

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COD is a term for the experimental determination of chemical oxidation where a strong oxidizing agent is used to oxidize organic material, followed by colorimetric or titrimetric determination of the reduction of the oxidizing agent. The result from such determination is often used as an estimate of Theoretical Chemical Oxygen Demand (ThCOD). ThCOD is the stoichiometric amount of oxygen required to oxidize an organic compound to minerals, H_2O , CO_2 , NH_3 , $H_2PO_4^-$ and H_2SO_4 . However, due to the complex composition of real biomass samples, exact elemental composition is difficult to determine, thus ThCOD can often not be calculated. COD of biomass samples is commonly determined with commercial kits by chemical wet oxidation using potassium dichromate as the oxidant. Samples containing substances that are partially or completely recalcitrant to chemical oxidation by dichromate, e.g. samples containing particulate materials, make COD measurements difficult and open to uncertainty [4,5]. In addition, real inhomogeneous biomass samples are exceptionally challenging to handle for COD determinations with commercial kits, because the analysis requires highly dilute and homogeneous sample preparation, as these kits were originally conceived for liquid samples.

Another empirical method to estimate ThCOD is by oxygen bomb calorimetry, where the gross calorific value (GCV) of a sample is determined by incineration in a bomb (an oxygen pressurized chamber). Bomb calorimetry can be considered a perfectly closed system and hence the GCV can be calculated from the temperature rise in the closed chamber surrounding the bomb [6]. The energy released from the incineration is a result of the oxidation of the biomass, and the breaking and formation of chemical bonds. This is referred to as chemical energy potential (CEP). The amount of heat released depends on the type of chemical bond broken and formed, hence, the oxygen consumed and the energy released are not exactly proportional. On the other hand, oxygen consumption and released heat are correlated and a calorific-determined COD value can be derived, via the experimentally established correlation between CEP and COD (14 MJ kg^{-1} of COD) [7].

In this study we evaluate and compare the four methods mentioned here: VS calculated from DM determination by the Karl Fisher method, VS calculated from DM determination by LOD, wet oxidation COD, and bomb calorimetry determined COD for their applicability in describing the organic content in various biomass samples. Moreover, we carried out biogas batch tests of the same samples and investigated how the method for organic matter content determination affected the calculation of bio-methane yields. The general hypothesis was that the bomb calorimetrically determined COD method is the most generic method for inhomogeneous biomass samples, due to the completeness and unspecificity of the measurement, and hence should yield the most correct description for bio-methane potential estimations.

2. Materials and methods

2.1. Biomass samples

Biomass samples were selected to obtain a wide range of organic matter and energy content. An overview of the biomasses and relevant pretreatments is provided in Table 1, and includes untreated and pretreated sewage sludge, digestate, pretreated birch, cellulose, whey permeate, cow manure, food waste, pretreated food waste, slaughterhouse waste and fish waste. Pretreatment (steam explosion) was performed using the steam explosion unit (designed by Cambi AS, Asker, Norway) [8] situated at the Norwegian University of Life Sciences, in cases where the supplier did not already perform a similar kind of pretreatment. The pretreatment was performed on biomass samples that are commonly pretreated before anaerobic digestion in large scale application (sludge and

food waste), or where such treatment is needed if the biomass should be used in large scale in the future (birch). Pretreatment with steam explosion increases the amount of volatiles in the biomass, making accurate organic matter determinations challenging. As water is added in the process, some kind of organic matter determination is needed in order to evaluate whether and how much the methane yield improves due to the treatment. Both un-pretreated and pretreated biomass samples were included for the possibility of evaluating the effect of pretreatment on the organic matter determination.

2.2. BMP-test

The BMP-test was performed as previously described by Horn et al. [9], with some modifications. In brief, inoculum from a full-scale biogas plant treating cow manure (Biowaz, Tomb, Norway) was used, diluted with water, and 0.7 L added to 1-L batch bottles to approximately 8 kg m^{-3} of COD. The substrate to inoculum ratio (SIR) on a Cr-COD basis was 1:3 for most biomasses, but a lower ratio was used for substrates where the production rate was expected to be too high for daily pressure measurements, hence slaughterhouse waste and whey was dosed as 1:6 on a COD basis. Biogas production was monitored regularly until the production in all flasks was less than $0.5 \text{ L kg}^{-1} \text{ d}^{-1}$ on the basis of COD. This monitoring was carried out for 49 days by measuring pressure with a digital manometer (GMH 3161 Greisinger Electronic, Germany). The pressure in the flasks was not allowed to exceed 100 kPa measured at incubation temperature: 310.15 K. The composition of the wet biogas was analyzed by gas chromatography (3000 Micro GC, Agilent technologies, USA) equipped with a thermal conductivity detector (TCD) using helium as a carrier gas. For calibration a standard mixture of methane (650 L m^{-3}) and carbon dioxide (350 L m^{-3}) was used. Methane production was calculated using normalized methane concentrations and subtracting the endogenous methane production from the blank controls, which was in all cases lower than the bottles containing substrate. Cellulose was used as positive control. All substrates were evaluated in triplicate. All gas volumes are reported at 273.15 K and 101.3 kPa.

2.3. Chemical oxygen demand by chemical wet oxidation

Analysis of COD was performed by use of Merck Spectroquant® COD Cell Test with measuring range $0.5\text{--}10 \text{ kg m}^{-3}$, where the reaction takes place in a closed glass vial. The method corresponds to DIN ISO 15705:2002 [10]. The samples were diluted with water prior to analysis to ensure that the measured COD was within the dynamic range of the test-cell. One exception was SE birch where 0.01 g of sample was added directly to the digestion cell followed by 1 cm^3 of water. Homogenization of food waste, sewage sludge and manure samples was performed using a homogenizer (IKA T18 basic ULTRA-TORRAX) prior to analysis. Diluted samples were mixed vigorously with a magnetic stir bar while the sample for analysis was extracted. All measurements were performed in triplicate. Commercial kits were used despite the inaccuracy of such kits for some solid samples, as this method is commonly used for such samples. The abbreviation used in the following sections for the results of this assay is Cr-COD.

2.4. Chemical oxygen demand by oxygen bomb calorimetry

The gross calorific value (GCV) of the biomass was analyzed using an IKA C200 oxygen bomb calorimeter. The thermal capacity of the bomb calorimeter was found to be $10\,090 \text{ J K}^{-1}$ by analyzing five individual standards of benzoic acid. Before, during and after the testing period, standards were measured to verify that the

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