Requirements for measurement and validation of biochemical methane potential (BMP)*

Christof Holliger, Hélène Fruteau de Laclos, Sasha D. Hafner, Konrad Koch, Sören Weinrich, Sergi Astals, Madalena Alves, Diana Andrade, Irini Angelidaki, Lise Appels, Samet Azman, Alexandre Bagnoud Urs Baier, Yadira Bajon Fernandez, Jan Bartacek, Federico Battista, David Bolzonella, Claire Bougrier, Camilla Braguglia, Pierre Buffière, Marta Carballa, Arianna Catenacci, Vasilis Dandikas, Fabian de Wilde, Sylvanus Ekwe, Elena Ficara, Ioannis Fotidis, Jean-Claude Frigon, Agata Gallipoli, Jörn Heerenklage, Pavel Jenicek, Judith Krautwald, Ralph Lindeboom, Jing Liu, Javier Lizasoain, Rosa Marchetti, Florian Monlau, Mihaela Nistor, Hans Oechsner, João Vítor Oliveira, André Pauss, Sébastien Pommier, Francisco Raposo, Thierry Ribeiro, Christian Schaum, Els Schuman, Sebastian Schwede, Mariangela Soldano, Anton Taboada, Michel Torrijos, Miriam van Eekert, Jules van Lier, Isabella Wierinck

October 7, 2020

Document number 100. File version 1.7. This document is from the Standard BMP Methods collection. †

*Recommended citation: Holliger, C.; Fruteau de Laclos, H.; Hafner, S.D.; Koch, K.; Weinrich, S.; Astals, S.; Alves, M.; Andrade, D.; Angelidaki, I.; Appels, L.; Azman, S.; et al. Requirements for measurement and validation of biochemical methane potential (BMP). Standard BMP Methods document 100, version 1.7. Available online: https://www.dbfz.de/en/BMP (accessed on September 7, 2020).
Or see https://www.dbfz.de/en/BMP for a BibTeX file that can be imported into citation management software.

†For more information and other documents, visit https://www.dbfz.de/en/BMP. For document version history or to propose changes, visit https://github.com/sashahafner/BMP-methods.

1 Introduction

This document presents the minimal requirements for measurement and validation of biochemical methane potential (also called biomethane potential) (BMP) in batch tests, and represents the consensus of more than 40 biogas researchers. The list of requirements is based on Holliger et al. [2016], with some recent modifications of validation criteria as described in Hafner et al. [2020c] and additional details on calculation standardization. For details and many additional recommendations, see these papers [Holliger et al., 2016, Hafner et al., 2020c].

2 Requirements for BMP measurement

2.1 Analysis of substrate and inoculum

Volatile solids (VS) content of inoculum and substrate is needed to determine quantities for a selected inoculum-to-substrate ratio (ISR) and for calculation of BMP. Details on measurements of TS and VS can be found elsewhere (including a detailed free document from the US EPA [EPA, 2001], as well as Strach [2016] and Baird et al. [2017]).

1. Total solids (TS). Measure for the inoculum and all substrates, by drying until constant weight at 105°C in triplicate.

2. Volatile solids (VS). Measure for the inoculum and all substrates by combusting the dried sample at 550°C until constant weight in triplicate.

2.2 Test setup and duration

1. Samples. All BMP trials must include three types of samples: batches with only inoculum ("blanks"), with inoculum and microcrystaline cellulose as a positive control[1], and with inoculum and substrate.

2. Replication. All tests must include at least 3 batches (bottles) for each condition[2]. The minimum number of batches used in a BMP test with one substrate is therefore 9 (3 blanks, 3 cellulose, 3 substrate).

3. Duration. Terminate BMP tests only after daily CH_4 production from individual batches during 3 consecutive days is $< 1.0\%$ of the net accumulated volume of methane from the substrate (substrate batch minus average of blanks). For manual or other methods where measurements are not made every day, termination can take place at the end of the

[1] Other positive control substrates could be used in the future, but only cellulose has had extensive testing that was used to develop the validation criteria described below in Section 4 [Hafner et al., 2020c].

[2] If a bottle is lost through, e.g., breakage, resulting in $n = 2$ for any condition, results cannot be validated. Therefore it is prudent to include 4 replicates, especially for blanks. Outliers can be eliminated if there is good reason to suspect there was an error in measurement (e.g., leakage) but the remaining number of replicates must be at least 3.

first measurement interval of at least 3 days where the rate of production drops below the 1% maximum (or two or more intervals that sum to at least 3 days, all with rates below the 1% maximum). If different substrates are tested, each substrate can be terminated when the slowest of the 3 replicate batches has reached the termination criterion. Blanks must be continued as long as the slowest (latest) batch with substrate. Continuing tests beyond this 1% net duration is acceptable and can help ensure that validation criteria are met (Section 4).

3 Calculations

1. Data processing. Standardized CH_4 volume (dry, 0°C, 101.325 kPa) is calculated from laboratory data using standardized methods.[3]

2. BMP units. BMP is expressed in standardized CH_4 volume (dry, 0°C, 101.325 kPa, referred to as "normal" volume) per unit mass of substrate organic matter added (typically VS but sometimes chemical oxygen demand (COD)) (often written as $NmL_{CH_4}\ g_{VS}{}^{-1}$).

3. Calculation of BMP. BMP of all substrates (including cellulose) is calculated by subtracting inoculum CH_4 production (determined from blanks) from gross (total) CH_4 production from substrate with inoculum, and normalizing by substrate VS mass. Any differences in inoculum or substrate mass among batches must be reflected in calculations. Calculations must follow a standardized approach[4].

4. Calculation of BMP standard deviation. The standard deviation associated with each mean ($n = 3$) BMP value must include variability from both blanks and batches (bottles) with substrate and inoculum, along with uncertainty in the mass of substrate VS added[5].

4 Validation criteria

BMP results that meet *all* the following criteria can be described as "validated".[6] Otherwise, results are not validated, and tests must be repeated.

1. All required components of the BMP measurement protocol listed above (Section 2) are met (including duration) and calculations are done as described above (Section 3).

[3] Detailed descriptions of calculations are available for the following measurement methods in the Standard BMP Methods collection (https://www.dbfz.de/en/BMP): volumetric (document 201) [Hafner et al., 2020f], manometric (document 202) [Hafner et al., 2020a], gravimetric (document 203) [Hafner et al., 2020g], and gas density (document 204) [Hafner et al., 2020d].

[4] Calculation of BMP is described in detail in document 200 Hafner et al. [2020b].

[5] See document 200 Hafner et al. [2020b].

[6] The criteria listed above are duplicated in document 101 [Hafner et al., 2020e], which was created to simply make it easier to find these required criteria.

2. Mean cellulose BMP is between 340 and 395 $NmL_{CH_4}\ g_{VS}{}^{-1}$.

3. Relative standard deviation for cellulose BMP (standard deviation, including variability in blanks, substrate bottles, and added substrate VS, divided by mean BMP) is no more than 6%.

References

R. B. Baird, A. D. Eaton, and E. W. Rice. *Standard Methods for the Examination of Water and Wastewater*. American Water Works Association, 2017. ISBN 978-1-62576-240-5.

EPA. Method 1684 Total, Fixed, and Volatile Solids in Water, Solids, and Biosolids. Technical Report EPA-821-R-01-015, U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303), Washington DC, 2001. URL https://www.epa.gov/sites/production/files/2015-10/documents/method_1684_draft_2001.pdf.

S. D. Hafner, S. Astals, P. Buffiere, N. Løjborg, C. Holliger, K. Koch, and S. Weinrich. Calculation of Methane Production from Manometric Measurements. Standard BMP Methods document 202, version 2.6., 2020a. URL https://www.dbfz.de/en/BMP.

S. D. Hafner, S. Astals, C. Holliger, K. Koch, and S. Weinrich. Calculation of Biochemical Methane Potential (BMP). Standard BMP Methods document 200, version 1.6., 2020b. URL https://www.dbfz.de/en/BMP.

S. D. Hafner, H. Fruteau de Laclos, K. Koch, and C. Holliger. Improving Inter-Laboratory Reproducibility in Measurement of Biochemical Methane Potential (BMP). *Water*, 12(6):1752, June 2020c. doi: 10.3390/w12061752. URL https://www.mdpi.com/2073-4441/12/6/1752.

S. D. Hafner, C. Justesen, R. Thorsen, S. Astals, C. Holliger, K. Koch, and S. Weinrich. Calculation of Methane Production from Gas Density-Based Measurements. Standard BMP Methods document 204, version 1.6., 2020d. URL https://www.dbfz.de/en/BMP.

S. D. Hafner, K. Koch, H. Fruteau de Laclos, and C. Holliger. Validation criteria for measurement of biochemical methane potential (BMP). Standard BMP Methods document 101, version 1.0., 2020e. URL https://www.dbfz.de/en/BMP.

S. D. Hafner, N. Lø jborg, S. Astals, C. Holliger, K. Koch, and S. Weinrich. Calculation of Methane Production from Volumetric Measurements. Standard BMP Methods document 201, version 1.9., 2020f. URL https://www.dbfz.de/en/BMP.

S. D. Hafner, B. K. Richards, S. Astals, C. Holliger, K. Koch, and S. Weinrich. Calculation of Methane Production from Gravimetric Measurements. Standard BMP Methods document 203, version 1.1., 2020g. URL https://www.dbfz.de/en/BMP.

C. Holliger, M. Alves, D. Andrade, I. Angelidaki, S. Astals, U. Baier, C. Bougrier, P. Buffière, M. Carballa, V. de Wilde, F. Ebertseder, B. Fernández, E. Ficara, I. Fotidis, J.-C. Frigon, H. Fruteau de Laclos, D. S. M. Ghasimi, G. Hack, M. Hartel, J. Heerenklage, I. Sarvari Horvath, P. Jenicek, K. Koch, J. Krautwald, J. Lizasoain, J. Liu, L. Mosberger, M. Nistor, H. Oechsner, J. V. Oliveira, M. Paterson, A. Pauss, S. Pommier, I. Porqueddu, F. Raposo, T. Ribeiro, F. Rüsch Pfund, S. Strömberg, M. Torrijos, M. van Eekert, J. van Lier, H. Wedwitschka, and I. Wierinck. Towards a standardization of biomethane potential tests. *Water Science and Technology*, 74(11):2515–2522, 2016. doi: 10.2166/wst.2016.336.

K. Strach. Determination of total solids (dry matter) and volatile solids (organic dry matter). In J. Liebetrau, D. Pfeiffer, and D. Thrän, editors, *Collection of Methods for Biogas*. DBFZ, Leipzig, Germany, 2016. URL https://www.dbfz.de/projektseiten/chinares/downloads/.