Interlaboratory assay in anaerobic digestion: A Brazilian case study

R. L. R. Steinmetz*, A. Kunz*, A. C. do Amaral**, D. C. Tápparo**, V. Gressler*, M. L. B. da Silva*, H. M. Soares***

* Embrapa Swine and Poultry, Brazilian Agricultural Research Corporation, BR 153 km 110, Concórdia, Santa Catarina, 89700-000, Brazil
(E-mail: *ricardo.steinmetz@embrapa.br; airton.kunz@embrapa.br; vanessa.gressler@embrapa.br; marcio.busi@embrapa.br*)
** Western Paraná State University, UNIOESTE, R. Universitária, 1619 - Universitário, 85819-110, Cascavel, Paraná, Brazil
(E-mail: *andrec.doamaral@gmail.com; deisictapparo@gmail.com*)
***Federal University of Santa Catarina, UFSC, Campus Universitário Reitor João David Ferreira Lima, Trindade, 88040-900, Florianópolis, Santa Catarina, Brazil
(E-mail: *soares@enq.ufsc.br)*

Abstract
Brazil has a high potential of substrates to be used for biogas production and a data base of biogas and methane potential is urgent to enable new policies and new business. To improve the accuracy methods to produce reliable technical results, the BiogásFert Network promoted an Anaerobic Digestion (AD) Interlaboratory Study. This work describes the experience with Brazilian laboratories participation in the AD interlaboratorial activities in 2014. Cellulose was used as reference standard. Up to 69% of the laboratories obtained satisfactory results in the solid analysis, but only 38% obtained the same classification for specific biogas production assay. To improvement in AD results, was identified necessity to acclimate the mesophilic inoculum to the substrate (sample) and the conditions of the anaerobic batch test.

Keywords
Specific Biogas Production; Specific Methane Production; harmonization method

INTRODUCTION

The biogas scenario is changing in Brazil. In the last years the waste management policies has been more restrictive and has pushing the use of alternative strategies to mitigate the environmental impact. In the same way new energetic supplies are emergency, and recently the National Agency of Petroleum, Natural Gas and Biofuels has published a law resolution with definition of rules for biomethane use as fuel (ANP, 2015).

Brazil has a high potential of substrates to be used for biogas production due to the huge amounts of wastes originating from cities, agriculture, livestock and food industry. A brazilian data base of biogas and methane potential from wastes and from energy crops is urgent to enable new policies and new business. But for this, it is necessary laboratories with accuracy methods to produce reliable technical results (i.e. specific biogas production [SBP] and specific methane production [SMP] by batch test).

Interlaboratory studies (e.g. proficiency test ring) are recommended as analytical tool to improve the laboratories efficiency. In 2014, the BiogásFert Network has promoted a interlaboratory study in anaerobic digestion (AD) with the following purpose: a) to know the currently methodology in use by the Brazilian's laboratories; b) to know the accuracy of each laboratory; and c) to establish a initial information to assist the process of harmonizing AD methods. This work describe the experience with the AD interlaboratory study from BiogásFert Network, which happened in 2014 with Brazilian laboratories.

MATERIAL AND METHOD

Interlaboratorial description

The interlaboratory study was conducted in two rounds. The first round happened between May and July, and de second between September and November. At each round, 40 g portion of sample was send to the laboratories. The laboratories could analysed the samples in 3 replicates and express the results for total solids (TS), volatile solids (VS), SBP and/or SMP.

Laboratories participation

The participation of laboratories was voluntary, 13 laboratories accept the invitation and enrolled in the study. Eight participants were academic & research laboratories from Universities, four were from research & technical institutions and one from a private company. To maintain confidentiality and to avoid bias, each laboratory was identified by a number. All data processing and results were identified by this number. Table 1 show the methods used by each laboratory to analyse the samples in fermentative batch test.

Samples

As synthetic sample microcrystalline cellulose (20 μm, Sigma, Germany) was used. According to the literature, microcrystalline cellulose could be used as internal standard and can produce 740 to 750 mL_N of biogas for each g_{VS} of sample. In the Laboratory of Biogas Studies from Embrapa Swine and Poultry, in aleatory way, 13 portions of 40 g sample were weighted and packed in plastic bags, under vacuum atmosphere. Other 5 aleatory samples were used to check the homogeneity and stability, according described in the AD Interlaboratory Study Report from the BiogásFert Network (EMBRAPA, 2015). Each sample was sent by express post service (SEDEX), which took between 1-5 days to be delivered to each laboratory.

Statistical analysis

It was used robust statistics method. The statistic analysis was based on ISO 13528 (2005), with adaptations. The criterion of z-score performance to evaluate the accuracy was used as the following equation:

$$\boldsymbol{Z = \frac{(x_i - x^*)}{s^{**}}}$$

where, Z is the score performance (if $|Z| \leq 2$ the result is satisfactory; if $2 \geq |Z| \leq 3$ the result is suspicious; if $|Z| \geq 3$ the result inadequate), x_i is the arithmetic mean of the results obtained by the laboratory, x* is the robust mean of the results of all laboratories, s** is the robust standard deviation.

RESULTS

Although 13 laboratories register for participation in the study, not all succeeded to send the results at the end of all rounds. The laboratories Nº 4 and 10 did not send the results of the first round. The laboratories Nº 4, 5 and 11 did not send the data of the second round. The laboratory Nº 13 only participated in the second round (not enrolled at the first round) but did not send the results. Others laboratories sent partial results (e.g. only for solids analysis). Some participants did not sent the results from the three replicates. These factors affected in part the statistical evaluation.

After the end of the ring test, some particular characteristics were observed. The number of decimal was stipulated by the study, but still several laboratories expressed decimal above the requested. In these cases the quantities do not express better resolution or low uncertainty. Some labs expressed the results in different units that were requested. E.g. the laboratory Nº 7 probably expressed the solid results in g_{TS} per100 g of fresh sample.

The z-score distribution obtained from statistical analysis of TS and VS (data not shown)

evidence that 69% of the laboratories obtained satisfactory results in all study ring. In Figure 1 is shown the specific biogas recovery in SBP assay for the cellulose sample. According the VDI 4630 (2006), the cellulose could produce 740 to 750 mL_N of biogas per g_{VS}. Recoveries above 80% of this amount (> 600 mLN/gVS) represent a satisfactory activity of the mesophilic inoculum. The Figure 1A shows that 46% of laboratory results succeeded above the 80% of biogas recovery from cellulose. As shown in Figure 1B only 38% of laboratories had satisfactory results for the evaluation of z-score results ($|Z| \leq 2$). In both cases the laboratories that show better accuracy was the same that used some acclimation process for the mesophilic inoculum before the batch test.

CONCLUSIONS

Interlaboratorial assay in AD methods was a new experience for the participants of this study. The performance improvement of laboratories depends on adjustments in the methods of solid analysis and more attention by laboratory workers in the expression of results. To improvement in AD results, was identified necessity to acclimate the mesophilic inoculum to the substrate (sample) and the conditions of the anaerobic batch test.

Table 1. Methods used by the laboratories in the fermentative batch test.

Laboratory Nº	Digestion			Gas analysis		pH measurement
	Inoculum	w or v based	T_{test} (°C)	volume measurement	gas composition	
1	Swine manure + cow manure; acclimated	weight	37	Eudiometer tube	Electrochemical sensor	In the beginig and the end of test
2	Swine manure	volume	37	Pipette tube	Gas chromatography	NI
3	Swine manure + cow manure + food industry sludge; acclimated	weight	37	Eudiometer tube	Electrochemical sensor	In the beginig and the end of test
4	NI	NI	NI	NI	NI	NI
5	WWTP sludge	volume	35	Automatic sensors	Gas chromatography	NI
6	Food industry sludge	weight	35	Automatic sensors	Electrochemical sensor	In the beginig and the end of test
7	NI	NI	NI	NI	NI	NI
8	WWTP sludge	weight	35	Syringes	Gas chromatography	NI
9	NI	NI	NI	NI	NI	NI
10	Swine manure + cow manure + food industry sludge; acclimated	weight	37	Eudiometer tube	NI	In the beginig and the end of test
11	WWTP sludge	weight	35	Liquid displacement cylinder	NI	NI
12	Cow manure	weight	37	Eudiometer tube	Electrochemical sensor	NI
13	NI	NI	NI	NI	NI	NI

WWTP = Wastewater treatment plant

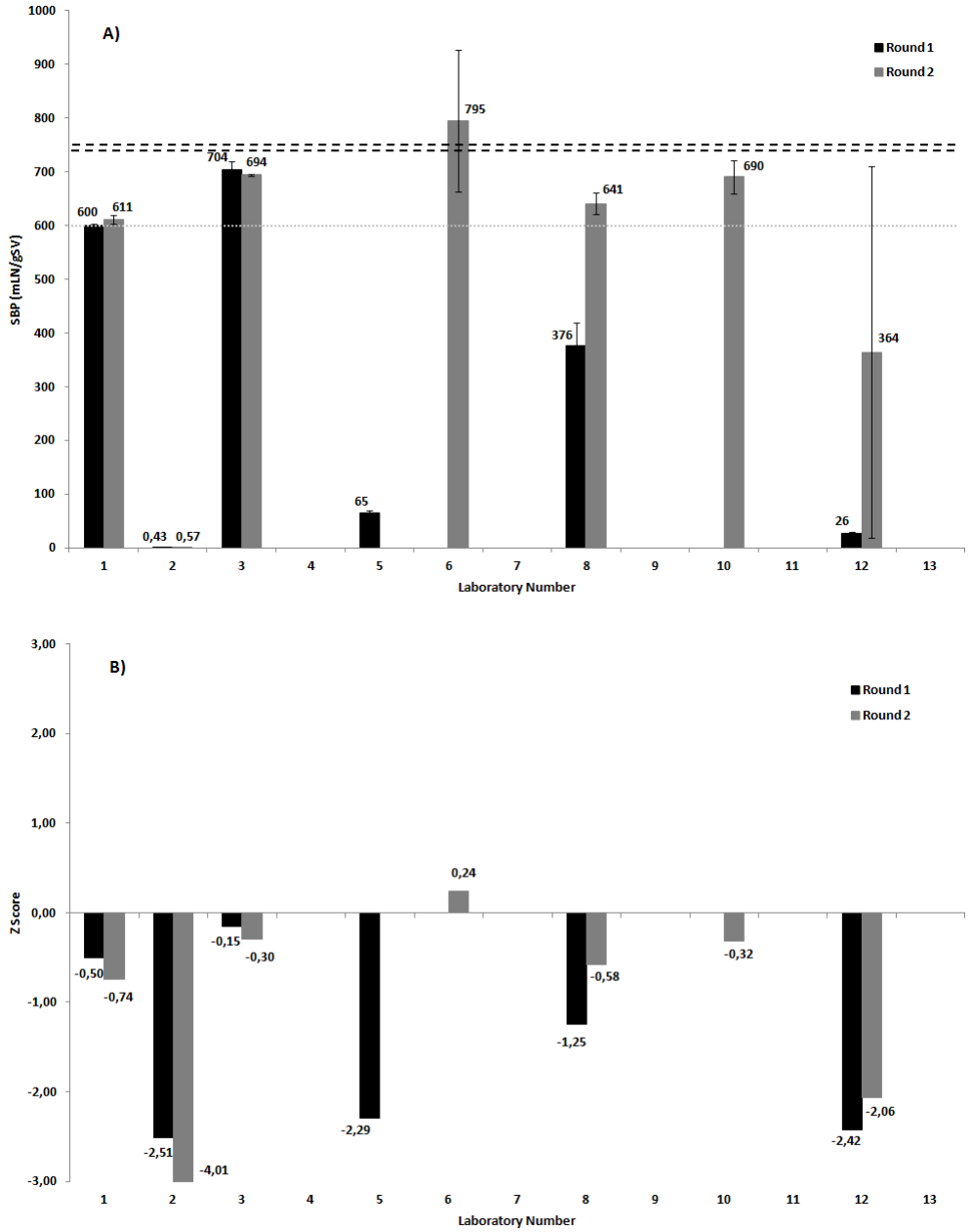

Figure 1. Graphical results of the cellulose sample: A) specific biogas recovery; B) z-score distribution. Discontinuous lines represent reference values for cellulose (740-750 mL_N/g_{VS}), point line represent 80% of biogas recovery from cellulose.

ACKNOWLEDGEMENTS

Acknowledgments to all laboratories that contributed for this study; and to Embrapa and Itaipu Binacional for the BiogásFert Network financial support.

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