The **error propagation** in calculating the BMP of silage: **tricks to minimize it**

By Mario A. Rosato

It is common to find tables of Biochemical Methane Potential (BMP) of different biomasses both in the technical literature, as well as in the web pages of some constructors of biogas plants, and online calculators that allegedly are able to predict the methane yield of mixtures composed by several substrates. Even the European Union has financed some universities and research centers with the scope of producing databases that should represent a useful guide for investors and anaerobic digestion plants constructors in redacting business plans and selecting the optimum feedstock among many available.

Inevitably, each time a table with a collection of BMP values is published in a specialized magazine or web portal, the followers of biogas-related groups in the various social networks start to dispute the validity of the figures.

Sometimes somebody (wrongly) argues that some of said BMP tables have "official value". Somebody else immediately comments that "they are absolutely theoretical and inapplicable to real life conditions". Some self-taught "guru" of the agroenergy business, considers laboratory test "things for academicians who have not yet understood that the only results that count are those measured in the real size plant». Each one has a tiny quota of reason, and all together are quite wrong, in particular those who believe that such a complex process like anaerobic digestion can be reduced to a set of tables and linear formulas. By the way, the BMP of silage is always the one arising the hottest debates, partly because in many countries the so-called energy crops are strongly subsidized, being then the main feedstock for agricultural digesters, but mostly because the very nature of silage generates a series of procedural errors when measuring their BMP in the laboratory. If said errors are not considered, or if one is not capable of correctly estimating their magnitude, the results can be extremely misleading, as we will see in the next paragraphs.

The methods for the determination of the BMP

The BMP of a given substrate is defined as the total amount of methane produced by the anaerobic fermentation divided by the quantity of volatile solids from where said methane originated. The BMP is not an univocal figure, since a large quantity of factors can influence it, for instance: the composition of the bacterial consortium present in the digester, the grain size of the feedstock, chemical or physical pre-treatments to which the feedstock may have been submitted, the content of anti-nutrients of some feedstock, contamination with inhibiting substances like pesticides or antibiotics...

The determination of the silage's BMP is a special case, because the blind application of standard laboratory methods, which work fine for other substrates, amplifies the instrumental errors. Let's see, step by step, why.

Ensilage is a fermentative process in which naturally occurring bacteria convert the sugars and starch contained in the fresh vegetal matter into alcohol, lactic and acetic acid. Silage is stored in airtight containers, where said

products of the sugar fermentation act as natural preservatives. It is normal – and even desirable – that silage remains "moist", since said wetted appearance is not fully caused by water but also by the presence of the natural preservatives, which are all liquids at room pressure and temperature.

The first step in measuring the BMP by means of anaerobic digestion laboratory tests, is the determination of the dry weight of the biomass. The standard method for determining the dry weight of biomass consists in drying the fresh matter by placing a sample in an oven at 105ºC (or, alternatively, at 60ºC, or at 80ºC, depending on the reference protocol) , measuring the weight at regular intervals until no weight variation between two successive measures is encountered. A quicker alternative is to employ an automatic moisture analyzer, a laboratory scale specially designed for this scope. Once the sample is dry, it must be calcined at 550ºC in a muffle oven. The weight difference between the dry sample and the ash remaining after the calcination is called "Volatile Solids" (VS). VS are assumed to be the fraction of organic matter that can be degraded by the bacteria to produce biogas, hence the correct way to express the BMP is as a function of the VS concentration in the biomass (Nml of CH_4/ g of VS). The problem arising during the determination of the VS of silage is that alcohol, acetic acid and lactic acid are all liquids characterized by a boiling point lower than 105ºC, hence they evaporate together with the sample's moisture. Since during the anaerobic digestion process both alcohol and volatile fatty acids are the immediate precursors of methane, they should be considered as "volatile solids" -even if they are liquids- and hence it is not correct to compute them as moisture. By grouping alcohol and VFA in the moisture content, the total VS of the silage is underestimated, and this error propagates to the calculation of the BMP. By definition, the latter is the quotient between the total net amount of methane produced by the anaerobic digestion of a biomass sample and the quantity of VS contained in said sample. Hence, an underestimated VS value translates into an overestimated BMP value. In extreme cases this overestimation can result in a BMP up to 50% higher than the value calculated with the correct amount of VS. The procedural error described before explains why many BMP values of silage published by some researchers and biomass vendors are higher than those that can be measured on the same vegetal matter before ensiling, and why the managers of biogas plants that base their calculations of the diet for their digesters on said tabulated values fail in reaching the expected energy production. In 2007 a group of German researchers even concluded, quite superficially, that the ensilage process increases the BMP of the vegetal biomasses. Said publication was of course criticized by other researchers because, by adopting the standard method in the determination of the dry matter content, the loss of VFA was not accounted for. The anecdote shows

Figure 1: Example of field laboratory to measure the BMP of silage and other substrates

how the BMP values published by the scientific and agricultural press must be taken with a high dose of caution, especially in the case of tables and databases which are just collections of literature values which disregard the context of the original papers and the curriculum of the publisher. The referenced paper also shows how the peer reviewing system sometimes fails in identifying errors in the submitted studies prior to their publication. As a result, the last version of the German norm VDI 4630 has adopted a correction method proposed by Weissbach and Strubelt ([1], [2] and [3]) to account for the content of alcohols and VFA in silage.

How to minimize the errors in the determination of silage's BMP

The correction method reported above is not the only. Many alternative methods have been proposed to avoid the problem of the VFA and alcohols evaporation together with the moisture during the desiccation of the silage's sample. One of said methods consists in adding a known amount of alkali (CaOH or NaOH) to the silage: the alkali will react with the VFA, forming salts that will not evaporate during the desiccation in the oven. Such method works fine with cereal silage because it is rich in VFA, but is not efficient when testing silage of sugar beet or similar saccharine plants, because the latter is rich in alcohol, which will not react with the alkali and will easily evaporate together with the moisture. A drying method based on the distillation with toluene can be found in older papers, but it is not advisable because of the toxicity of said solvent. Another method, already adopted as a standard in the Canadian and American industries of animal fodder, was developed for the special case of the determination of the silage's dry mass. It consists in drying the sample in a distillation balloon and collecting the condensed liquid for its further analysis and determination of the water and organic matter proportions. Said method is extremely accurate, but quite labor intensive, hence it may be acceptable for research purposes but in general it will be difficult to adopt it in industrial biogas plants. The most pragmatic method, originally proposed by two researchers, Irish and English respectively ([4]), and then re-proposed with variations by the German researchers already quoted, consists in determining the dry weight of the silage according to the Standard Methods and then applying a correction factor, obtained statistically from a large number of assays, performed on different kinds of silage with the distillation method. With said method, the maximum error in the determination of the VS of any silage is 2%.

The correct determination of the VS of energy crops silage is one of the two factors that must be taken into account in order to minimize the errors in the measure of the BMP. The second factor to be considered (not only for silage but in general for any anaerobic digestion feedstock) is the laboratory test conditions. In order to minimize the second error component in the calculation of the BMP, i.e. the net amount of methane produced by the anaerobic degradation of the sample, it is absolutely necessary to eliminate the "background noise", which is represented by the amount of methane produced by the inoculum. In order to obtain more accurate BMP values it is hence necessary to "degas" the inoculum, by pre-incubating it for at least one week before starting the BMP assay. Finally, it is necessary to know very well the calibration curve of the instrument employed to measure the volume of gas produced by the digestion, and furthermore to check if the same normalizes automatically the measured volume or not. The normalization consists in referring the volume of methane produced by the anaerobic digestion to a specific thermodynamic condition defined by a norm, in our case 0° C and 101 kPa. Instruments without real time normalization can induce up to 10% error in the BMP calculation, because the atmospheric pressure and temperature may vary a lot during the duration of the BMP assay (usually 30 or 60 days, depending on the type of biomass and protocol adopted).

Conclusions

Measuring the BMP of silage is not a difficult test in itself, and can be performed even by the technical personnel of an industrial biogas plant, on condition that the operator is adequately trained, and he/she employs an instrument with a high degree of standardization and automation, with a guaranteed maximum error in its nominal range of measure. Such instruments as the AMPTS and its industrial version, Biogas Endeavour, are characterized by

[1] Weißbach, F.; Strubelt, C.: Die Korrektur des Trockensubstanzgehaltes von Maissilagen als Substrat für Biogasanlagen. In: Landtechnik 63 (2008), p. 82–83
[2] Weißbach, F.; Strubelt, C.: Die Korrektur des Trockensubstanzgehaltes von Grassilagen als Substrat für Biogasanlagen. In: Landtechnik 63 (2008), p. 210-211
[3] Weißbach, F.; Strubelt, C.: Die Korrektur des Trockensubstanzgehaltes von Zuckerrübensilagen als Substrat für Biogasanlagen. In: Landtechnik 63 (2008), p. 354–355.
[4] Porter MG, Murray RS. The volatility of components of grass silage on oven drying and interrelationship between dry matter content estimated with different methods. Grass Forage Sci 2001; 56:405-411.

a well-defined calibration curve, high repeatability, user friendly interface and real time normalization of the gas volume. In this way, the BMP assay becomes a simple routine control task, in which the possibility of human error is almost null and the instrumental error is minimized to the order of 1% for the AMPTS and 4% for the Biogas Endeavour. If measuring the BMP of silage, the application of Porter and Murray's correction method introduces just 2% of additional uncertainty.

The most practical and reliable way to correctly and profitably manage an industrial biogas plant is to actually measure the net methane yield of the available feedstock in the plant's own conditions (same inoculum, temperature, retention time…). Basing the calculation of the digester's diet on collections of literature values of the BMP can quite often lead to lower energy productivity than expected, or, in some rare cases, to producing more biogas than necessary and hence wasting substrate.

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