The value of agro-industrial by-products for biogas production: BMP (Biochemical Methane Potential) test

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Abstract
The CRPA Lab (Environment and Energy Section), part of Technopole of Reggio Emilia, has development a systems to establish the Biochemical Methane Potential (BMP) of different biomass. The parameter expresses the amount of biogas/methane potential obtained from biomass degradation, expressed as Nm$^3$ kgVS$^{-1}$. The paper reports the results obtained from BMP tests of various residues and by-products generated by the agro-food industry. These biomasses are suitable for use in anaerobic digestion and they also represent an interesting alternative to energy crops.

Introduction
Anaerobic digestion is an energy process which allows the highly efficient exploitation of biomass which can be of vegetable or animal origin, derived from waste or dedicated production and wet or dry without distinction, producing a valuable biofuel (biogas/biomethane). Every anaerobic digestion plant has its own equilibrium depending on the type of biomass loaded and the plant/process parameters adopted (organic load, hydraulic retention time, process temperature, type of heating and mixing technique, pre-treatment etc.). The basic element which has the greatest influence on any kind of analysis, representing the point of departure for any feasibility study for the construction of an anaerobic digestion plant, is the knowledge of the Biochemical Methane Potential (BMP) [1]. We have set out below a summary of the results obtained from BMP analysis of biomasses from organic residue and by-products comes from agro-food industry. These biomasses are of considerable interest because of the high level of organic matter and the absence of unwanted fractions. They are suitable for use in the anaerobic digestion, itself representing a possible solution for their recycling. In addition they may represent an interesting alternative to energy crops whose use in anaerobic digestion is currently the source of considerable controversy [2].

Material and Methods
Static Methanogenic potential
The analysis of static BMP (discontinuous or batch analyses) was conducted in the CRPA Lab laboratory. The biomass to be assessed was first analysed and then mixed with a “hungry” inoculum, that is a pre-digested organic substrate coming from biogas plant which already uses the biomass to be evaluated, and a salt solution (to buffer the production of acids and provide micro-nutrients which are essential for the proper development of the bacteria). The ratio between the volatile solids of the substratum for analysis and those in the inoculum must at least be greater than 0.5. The mixture is put into a 48 small digestors, glass bottles with a total volume each of about 2,200 ml (about 60% full). This is then placed in a thermostatic cabinet where the process temperature (mesophilic or thermophilic process) is kept constant.

At the same time a batch test is carried out using the inoculum alone so as to be able to subtract the effect of the residual inoculum production of biogas from that produced by the mixture. Two measurement techniques are used to establish the quantity of biogas produced, one with a pressure gauge and the other measuring mass. In the first case the measurement is effected directly in the digestor, measuring the increase in pressure in the free space at the top of the bottle due to the production of carbon dioxide (CO$_2$) and methane (CH$_4$). In the second case the measurement is effected at the moment of the analysis of the quality of the biogas using a thermal dispersion mass sensor (measuring the mass of the biogas flow through a correlation between the dissipation of heat from a heated surface, corrected for the specific composition of the biogas analysed). In addition to the measurement of the volume, the test also includes the analysis of the quality of the biogas produced.
The static BMP test is normally continued until the marginal daily production is less than 1% of the entire accumulated production. Measurements are continued and the accumulated production curve also provides important information relating to the degradation speed [3, 4].

**Test description**

The maximum methanogenic potential depends on the chemical composition of the biomass (mainly carbon, hydrogen, oxygen and nitrogen), while the effective potential depends on the presence of recalcitrant molecules which reduce the degradability, on the availability of all the chemical-physical conditions which allow the bacteria to reproduce and by the presence of inhibiting factors [5].

All the above factors have considerable influence, as well as on the effective productivity and, thus, on the economic value, also on some kinetic parameters of the process that may be usefully applied to verify the compatibility of use of the biomass in the biogas plant or better to optimize the design [6].

The kinetic parameters derivable from the tests can be of great help for the feasibility of the plants and to assess the quality of the biomass. From the analysis of the curves of production can be processed, the following kinetic parameters:

- **Kmax**: time to reach the maximum speed of production (days);
- **Fmax**: maximum percentage of volatile solids degradable (%);
- **F50%**: time to reach 50% of production (days);
- **F90%**: time to achieve 90% production (days).

CRPA Lab has characterised different biomasses from agro-food residues and by-products industry as well as analysing their methanogenic potential. The biomasses analysed can be classified in the following categories:

- **By-products from the food industry**: organic residue coming from the fruit processing industry, produced by the baking (bread and sweets) industry, coffee roasting residues, brewing residue...
- **Vegetable residues**: residues from fruit, vegetables, tobacco, corn cobs, tomato skins, coffee husks, olive residues, rape-seed cake, vine trimmings, pressed beet pulp, residues from oranges, potatoes, onions, fennel, soya husks, sugar-beet molasses and straw.
- **Milling products**: flour, waste flour, various different types of bran and chaff
- **Animal by-products (ABP)**: by-products deriving from slaughterhouse and milk processing (not for human consumption): blood, ruminal content, milk, serum...
- **Organic waste**: civil and agro-industrial treated sludge
- **Fine grain or crop silage**: products derived from dedicated crops, high energy density, high quality and excellent degradability. The choice of the phenological stage of the crop, the cutting and storage method can greatly affect the biogas yield.

**Results**

Table 1 shows the average values of biogas/methane yield, degradability and degradation rate of the different category of biomass analysed.

<table>
<thead>
<tr>
<th>Category</th>
<th>n° samples</th>
<th>Methane yield (Nm³ t VS⁻¹)</th>
<th>Kmax (days)</th>
<th>Fmax (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop silages</td>
<td>81</td>
<td>348 (36)</td>
<td>6.5 (1.9)</td>
<td>81.6 (6.8)</td>
</tr>
<tr>
<td>Animal by-products (ABP)</td>
<td>11</td>
<td>409 (46)</td>
<td>7.0 (2.0)</td>
<td>72.0 (8.9)</td>
</tr>
<tr>
<td>By-products from food industry</td>
<td>17</td>
<td>407 (184)</td>
<td>5.7 (3.4)</td>
<td>85.8 (21.7)</td>
</tr>
<tr>
<td>Livestock manure</td>
<td>46</td>
<td>208 (86)</td>
<td>7.1 (3.6)</td>
<td>43.5 (15.7)</td>
</tr>
<tr>
<td>Vegetable residues</td>
<td>37</td>
<td>318 (125)</td>
<td>7.3 (4.0)</td>
<td>65.1 (24.0)</td>
</tr>
<tr>
<td>Milling products</td>
<td>8</td>
<td>361 (28.1)</td>
<td>3.4 (3.4)</td>
<td>81.3 (5.2)</td>
</tr>
</tbody>
</table>
The table 2 shows the analysis of three biomasses from agro-food industry, with different chemical characteristics, but with a good amount of organic substance and therefore suitable for use in anaerobic digestion: the sugar beet molasses pulp (by-product consisting of the syrupy residue collected during the manufacture and/or refining of sugar beets), a processing residue of soybean and olive press cake (solid residue of olive pressing, in plant “2-step” continuous type).

Table 2. Methane yield and kinetic parameters of the three biomasses analysed: average values

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Methane yield (Nm$^3$/t VS$^{-1}$)</th>
<th>$K_{max}$ (days)</th>
<th>$F_{max}$ (%)</th>
<th>$F_{50}$ (days)</th>
<th>$F_{90}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar beet molasses</td>
<td>393</td>
<td>2.8</td>
<td>69</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>Soya bean residue</td>
<td>437</td>
<td>7.6</td>
<td>82</td>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>Olive press cake</td>
<td>201</td>
<td>11.2</td>
<td>32</td>
<td>11</td>
<td>20</td>
</tr>
</tbody>
</table>

The kinetic parameters are important to assess the quality and the stability of the biomass: a biomass very easily degradable, such as beet molasses, consisted of simple carbohydrates, has a $K_{max}$ value lowest of a biomass hardly degradable such as a fibrous fraction, such in olive cake. The average degradation speed of the biomass is evaluated with the coefficients $F_{50\%}$ and $F_{90\%}$: a biomass very degradable has values of $F_{50\%}$ and $F_{90\%}$ lower than an hardly degradable one. The knowledge of these parameters, therefore, allows to evaluate dimensional compatibility of the digester with the biomass that will be used: once known the hydraulic retention time of a plant is possible to understand whether this is compatible with the times of degradation proceeds with the BMP test. The figure 1 and figure 2 shows the typical curve of cumulative biogas production of the three BMP tests, and the degradation curve of volatile solids obtainable as a result of biogas transformation.

Figure 1 - Biogas production curve trend

The graphs show differences in the curves trend due mainly to the origin and concentration of organic molecules, with different biodegradability, contained in the organic matter present in the biomass tested. In fact the hydrolytic enzyme activity determines the overall speed of the process. It is observed that the hydrolysis of proteins (mainly contained in the soybean) and lipids (present in the olive cake) is slower than that of carbohydrates (contained in beet molasses). In general an organic matrix composed of simple and soluble organic substances is quickly and completely converted into biogas, compared to a more heterogeneous substance.
Conclusion and perspectives

The food industry produces organic residues and by-products in considerable quantities which are of excellent quality and suitable for use in anaerobic digestion. Their use in biogas production allows small plant using only livestock effluent to increase production and, on the other, allows larger plant to reduce dependence on energy crops. The management times for the different by-products vary greatly from one type to the other and depend on the chemical characteristics of the individual organic matrices. The BMP test provides a great deal of information regarding the use and compatibility of co-digestion. In addition to the methane production potential, the main purpose of the test, the production curves can be used to check the presence of possible latencies, inhibition, the speed of degradation (that is, the hydraulic retention time required) and compatibility with the inoculum used, that is, the digestate present in the reference plant. Therefore, to ensure the proper functioning of the plant, the co-digestion of by-products must always be effected following the confirmation of the compatibility of the different matrices used while also observing all minimum process conditions for biomass with the greatest energy and economic value. From the point of view of formalities, great attention must be given to the way in which the flows of these matrices are introduced into an agro-livestock biogas plant, ensuring they are in the form of “by-products” pursuant to Legislative Decree 152/2006 as subsequently amended and supplemented (which is the transposition of the European Directive 2008/98/CE), complying with all the conditions laid down by the Decree. In default the flows may be classified as “waste” with all the negative repercussions which this entails [7].

References