ANALYSIS OF BIOGAS YIELD AND QUALITY PRODUCED BY ANAEROBIC DIGESTION OF DIFFERENT COMBINATION OF BIOMASS AND INOCULUM

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ABSTRACT: The energy conversion of waste and biomass is one of the key actions to meet the purposes of the Kyoto Protocol. The Laboratory of the Biomass Research Centre (CRB, University of Perugia) is equipped with an anaerobic digestion pilot plant, that is used to measure the yield and the composition of biogas from different substrates at different conditions. This paper presents the experimental results of the anaerobic digestion of various types of biomasses using different type of inoculum. Each test was preceded and followed by analyses for biomass characterization, carried out at the Laboratory for biomass characterization of CRB. Particular attention was focused on the productivity of various substrates, estimating daily biogas production and composition and the relative cumulative curve, especially in relations with the different inoculum utilized during the digestion process; periodic samplings and analyses of the biogas allowed to estimate the percentage of methane and, therefore, the energetic content. For the digestion process was used both animal and vegetal biomasses like chicken or cow manure and olive husk; the different type of inoculum was selected by criteria of availability, convenience and ease of use: according to this rumen fluid and the digested sludge appears the most suitable. The differences in the quantities of biogas produced for the different inoculum utilized were analyzed both to optimize the process and to estimate of the couplings biomass - inoculum, allowing the comparison of experimental results of the different substrates.

Keywords: anaerobic digestion, inoculum, methane yield

1 INTRODUCTION

EU and Italy, with Kyoto Protocol subscription, are involved in the greenhouse gases reduction; renewable energies have an important role in this process and in particular biomass could contribute in a significant way because it is a "carbon neutral" fuel. Biomass represents a complex system for solar energy accumulation by means of clorophyllos photosyntesis, in which the atmospheric Carbon Dioxide is transformed in organic substance. Biomass could be employed for energetic conversion by means of different processes, such as biochemical or thermal-chemical ones. The process choice depends on the biomass characteristics and permit to transform solid biomass in other forms (liquid and gas) to be used and stored easier.

List of Symbols	
TS	Total Solid (%)
VS	Volatile Solid (%)
OMW	Oil Mill Wastewater
HRT	Hydraulic Retention Time (day)

1.1 Anaerobic digestion process

Anaerobic process has been traditionally used for excess sludge digestion in wastewater treatment plants or for manure treatment, achieving a biogas to produce energy. Its composition is tipically 60% methane, 40% carbon dioxide with traces of hydrogen sulphide and water vapour.

The anaerobic digestion process is characterized by a series of biochemical transformations carried out by different consortia of bacteria, which could be separated into 4 stages. First organic materials of the substrate like cellulose, hemicellulose, lignin must undergo liquefaction by extracellular enzymes before being taken up by acidogenic bacteria. The rate of hydrolysis depends on pH, temperature, composition and concentration of intermediate compounds. After that soluble organic components including the products of hydrolysis are converted into organic acids, alcohols, hydrogen and carbon dioxide by acidogens. The products of the acidogenenesis are then converted into acetic acid, hydrogen and carbon dioxide. The methane is produced by methanogenic bacteria from acetic acid, hydrogen and carbon dioxide and from other substrates of which formic acid and methanol are the most important [1].

The process is complex and it is catalyzed and carried out by a consortium of microorganism (inoculum) that in a joined action convert complex macromolecules into low molecular weight compounds such as methane, carbon dioxide, water and ammonia. Nowadays the process is also convenient for generic residual biomasses, with high water content because the methane produced may be used as a renewable energy source, which can receive public funding. The technical and economical feasibility of an industrial anaerobic digestion plant is strongly dependent on methane yield and purity, which may vary considerably with biomass chemical composition and process parameters, such as temperature and retention time.

These performances, which strongly affect plant efficiencies, are often not available in the Literature, therefore increasing the risk of the investments due to excessive uncertainties in the design phase. From these premises the CRB built a laboratory scale digester [3] to derive experimentally the influence of biomass composition and process variable on methane yield.

1.2 Aim of the work

The aim of this work is to analyse the yield of biogas and methane particularly from different kind of biomass an inoculum. The inocula were selected by criteria of availability, convenience and ease of use. In according to Literature tests were carried out using previous experiments digestate and rumen fluid. The digested substrates were of two typologies: manure (chicken and cow) and agricultural residues (olive husk) at mesophilic conditions (T=35°C).

2 MATERIALS AND METHODS

2.1 Anaerobic batch reactor of laboratory

The pilot batch digester (Figure 1) is a cylindrical vessel equipped with an airtight lid. The steel AISI 304 vessel has a working volume of 17 l, with 30 cm inner diameter and a height/width ratio of 5/6.

Flexible silicon rubber heaters, with a maximum operating temperature of 260 °C and an electrical power density of 12.5 W/cm^2 (depending on temperature), are fitted on the external surface of the vessel to provide the heat necessary to maintain the feedstock at the required temperature. The heating is equipped with a AF thermocouple, connected to a PID temperature controller, introduced in the digester through a hole on the lid.

Five holes were drilled on the lid of the digester; four side holes are used to insert probes to measure temperature and pH through threaded steel adapters and rubber stoppers to avoid gas leakage. A stirring system RW 16 Basic IKA with a speed range of 40-1200 rpm was introduced to allow the mixing of the feedstock and therefore increasing biogas production, as in existing CSRT plants. Inside temperature is measured by n° 3 probes namely: one with the pHmeter, one feedbacks the heating system and a third one for redundancy. This allows a consistent confidence on temperature and also verifies its uniformity in the reactor.

Figure 1: Anaerobic digestion pilot plan

The biogas produced can be bled for measurement purposes through a tap or else is stored in a gas meter that also allows a volume measurement through an indirect measure of a liquid column height.

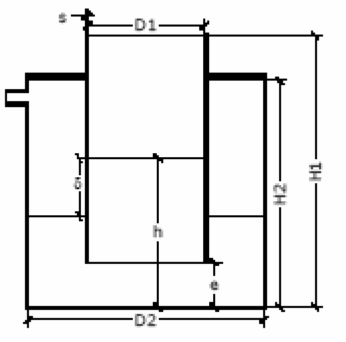

Figure 2: the structure of the gasemeter

The error on biogas volume is therefore a function of the error of the level measuring sensor, and of the ratio between the gas-meter and the liquid column diameter (Figure 2). A home made software was developed to evaluate the measure error on biogas volume as a function of the above mentioned quantities and of time [3].

2.2 Substrate

To evaluate methane yield and the behaviour of different inocula the experiments were carried out using 2 typology of biomass: animal manure (chicken and cow) and agricultural residues (olive husk).

2.2.1 Animal Manure

The process of anaerobic digestion is used usually for animal manure and many examples exist in the Literature [1,2,8,11,12,14]. In fact anaerobic digestion is a promising alternative for the treatment of these materials, as the process combines material recovery and energy production. Moreover the intensive presence in Italy and in Umbria Region of animal farming has favoured the choice of using this kind of substrates. Animal manure considered were: chicken and cow. Before the experiments tap water was added to the substrate to improve the moisture content and to favour the process according to the Literature [1,2].

2.2.2 Olive Husk

Many residues of cultivation are used in the anaerobic digestion processes (maize, vegetable waste,...) in codigestion with animal manure to improve biogas yields. Nevertheless few examples exist in the Literature [10] about the anaerobic digestion of olive husk.

In Italy olive cultivation is very wide as in the others Mediterranean Countries and the olive oil production has increased during the last 30 years.

Olive oil extraction is carried out mainly by a traditional discontinuous press process during which the olives are ground and pressed to release the oil. The manufacturing process of olive oil usually yields an oily phase (13-25%), a solid residue (37-50%), and an aqueous phase (35-50%) formed from the water content of the fruit. The oil is separated from the aqueos vegetative residues by centrifugation, oil in the husks being recovered by solvent extraction [4,5]. The wash waters combined with the olive oil waters produce a waste by product, the olive

mill wastewater (OMW). It carries important amount of organic matter (including aromatic compounds) that, in association to its high C/N ratio and low pH, compromise biological degradation processes [6]. Anaerobic fermentation of the aqueous phase, which has a high BOD value, could be a way to convert the greatest fraction of OMW organic content into biogas, a source of energy.
The olive husk is a biomass with a medium level of moisture (30-60% depending on the treatments) composed of pomace and olive ground stones.
The olive husk may be treated first with solvents to extract the residual oil and the exhausted olive husk may be compressed into briquettes and used as a solid fuel. However most current milling processes use continuous mills in which only a very small fraction of oil is left in the olive husk, making oil recovery unprofitable. If the residual oil is not extracted the olive husk putrefies and becomes a waste product. [4-5,7-9]
The possibility of producing a clean gaseous fuel together with a residue that can be used as a fertilizer richer in nitrogen content should be considered. Anaerobic digestion converts the carbonaceous matter into biogas leaving a stabilized slurry in a form suitable for reuse to land as fertilizer.
The choice of using olive husk was made considering its availability and the lacking data in the Literature as above mentioned [10].
Olive husk has a moisture value not suitable for the process, therefore tap water was added to obtain a slurry with a TS content of 5% to maximize the methane yield according to data in the Literature [10].

2.3 Inoculum

To improve the yield of biogas is necessary to add to the substrate a good inoculum.
For the olive residues anaerobic digestion process is mainly used for OMW treatment. Current methods are only applicable to highly diluted OMW and their economy is further compromised by the use of chemicals from alkalinity, pH and nitrogen contents setting. Therefore, physicochemical and biological pre-treatments have been suggested as means to reduce significantly the organic load and toxicity of OMW and, thus, to allow its biologic treatment.
In the Literature [6] the improvement of OMW anaerobic treatment, with no need for dilution or pre-treatments, and considering an effluent suitable for soil irrigation, was done using piggery effluent from an anaerobic digestion plant, therefore the same inoculum was considered.
To establish the inoculum influence on the substrate behaviour two set of experiments are carried on. The firsts using the same inoculum for different substrate (piggery manure anaerobically digested from a plant). The second set of experiment are carried on using the same substrate (olive husk and tap water, 5% TS [10]) with piggery manure anaerobically digestested [6] and in the other one using rumen microorganism.
The piggery anaerobic sludge was collected from a anaerobic plant located near the University of Perugia. A second inoculum was then considered as rumen fluid obtained by squeezing the rumen stomach, provided by a nearby slaughterhouse. The rumen is an exclusive organ of ruminant animals in which digestion of cellulose and other polysaccharide molecules occur through the activity of specific microbial populations. The capacity of cellulose digestion that these animals possess is related to the presence of anaerobic microorganisms in its rumen that convert acetate part in methane and in carbon dioxide. The potential application of rumen cultures for anaerobic digestion of lignocellulosic materials has been investigated in several papers [11-13]. The choice of this inoculum depends by the presence of ground olive stone in the olive husk than increase the level of lignin in the substrate.
The chemical and physical characteristics of substrate and inoculum were analysed at the CRB laboratory. In particular, Total Solids (TS) were determined, drying the samples at 105°C for 12 hours, in compliance with UNI 10458. Then the samples were ground and sieved, to measure the ash content in a Thermogravimetric Analyzer (TGA-701 LECO) at 600°C. Volatile components were determined as difference between TS and ash. The Nitrogen, Hydrogen and Carbon content was determined with Elementary Analyzer (Truspec CHN LECO), according to ASTM D-5373 [1,2].
Table 1 and 2 list the characteristics of the different mixture slurry assuming the same proportion between substrate/inoculum.

Table I: M1: cow manure and inoculum (piggery manure anaerobically digested), M2: chicken manure and inoculum (piggery manure anaerobically digested).

	M1($\%_{db}$)	M2($\%_{db}$)
Moisture	84.32	52.75
Ash	1.01	11.6
Volatile Solids	12.08	35.14
Fixed Carbon	1.73	0.88
C	6.86	15.39
H	6.78	9.14
N	0.44	2.80
C/N	16	5.5

Table 2: P1: olive husk and piggery manure anaerobically digested, P2: olive husk and rumen fluid

	P1($\%_{db}$)	P2($\%_{db}$)
Moisture	77.39	78.08
Ash	4.25	1.01
Volatile Solids	15.96	18.10
Fixed Carbon	2.41	2.66
C	9.52	12.68
H	6.15	8.48
N	0.17	1.99
C/N	75.85	6.4

3 RESULTS AND DISCUSSION

3.1 Biogas and Methane Yield

The amount of solid volatile content in the mixture to digest is an important parameter to evaluate the process. The biogas produced was measured and analysed to evaluate the daily methane percentage.
The experiments have different HRT summarized in the Table 3 because the experiments were carried out until a significant methane increase in percentage. The different slurries (substrates+inoculum) inserted into the digester

are characterized by a weight of Volatile Solids between 0.28-0.30 Kg VS therefore the amount of biomass and water was adjusted to reach this value of weight starting from a same weight of inoculum (1kg).
Table 4 shows the results in terms of biogas and methane yield per Kg VS. The energy produced by the gas was evaluated considering the LHV of the methane.

Table 3: HRT and Methane yield (v/v%)

	HRT(day)	Methane (v/v%)
M1	32	46.5%
M2	30	66.6%
P1	43	60.3%
P2	46	57.6%

Table 4: Biogas and methane yield

	Biogas (Nm3/Kg VS)	Methane (Nm3/Kg VS)	Energy Value (kWh/KgVS)
M1	0.15	0.04	0.40
M2	0.22	0.11	1.20
P1	0.28	0.11	1.07
P2	0.08	0.03	0.18

All the data obtained in pilot plant are comparable to the value in Literature for several biomass (Chynoweth et al, Gunaseelan) [1,2] and in particular for olive pomace (A.R.Telkin et al) for dairy manure (Morris et al.; Bryant et al) and for chicken manure (Salminen et al) as showed in the table 5.

Table 5: Methane yield in the Literature

	Methane (Nm3/kgVS)	References
Chicken Manure	0.2 – 0.3	Salminen et al [14]
Cow Manure	0.22	Morris et al. [11]
Cow Manure	0.17	Bryant et al. [11]
Olive Pomace	0.08	A.R.Tekin et al. [10]

Figure 3 shows the cumulative curves for biogas and methane production having 3 different biomasses characterized by the same value of Kg VS and the same inoculum (1 Kg piggery manure anaerobically digested).
The olive husk and piggery manure anaerobically digested is characterized by the highest biogas production that become equal to chicken manure and inoculum biogas production after thirty days. Evaluating the methane production instead chicken manure and piggery manure digested show the highest production. In this case the production begins faster than the other ones demonstrating that the coupling ckicken manure and piggery digestate is more suitable.
Figure 5-6 show the cumulative curves for biogas and methane production having the same biomass (olive husk) but different inoculum characterized by the same weight of KgVS.
The cumulative curves of biogas and methane production starting from the same substrate demonstrate that the olive husk could be a good substrate for the anaerobic digestion process if coupled with a suitable inoculum as the piggery manure anaerobically digested. The volume percentage of methane is not so different, but the biogas yield is lower.

In general the experiments are characterized by the same weight of inoculum (around 1 Kg) and by the same Kg SV to compare the results. The chicken manure and the olive husk with the same inoculum are characterized by the highest methane yield. For the chicken manure, characterized by the highest percentage of methane, it was a foreseeable result considering its common application. The methane yield of anaerobic digestion of olive husk can be less foreseeable and more interesting valuable also with the different inoculum.

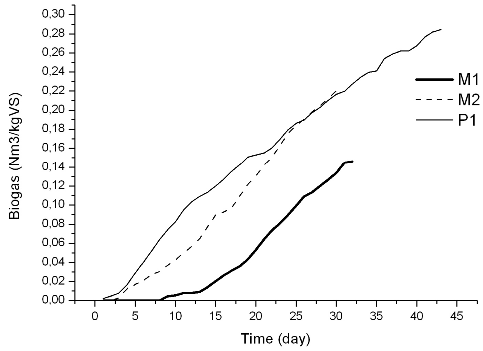

Figure 3: Biogas production from different substrates using the same inoculum

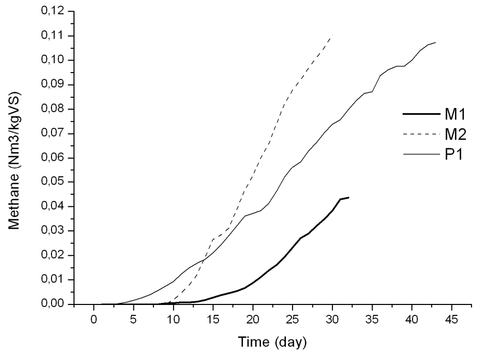

Figure 4: Methane production from different substrates using the same inoculum

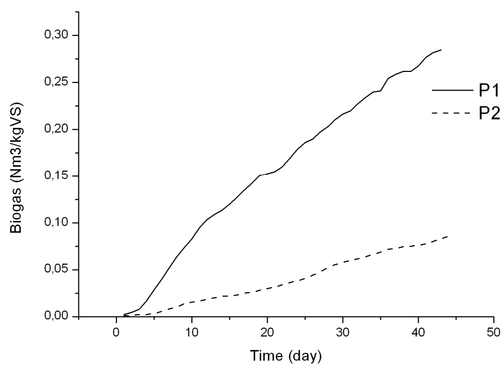

Figure 5: Biogas production from the same substrate

using different inoculum (P1 and P2).

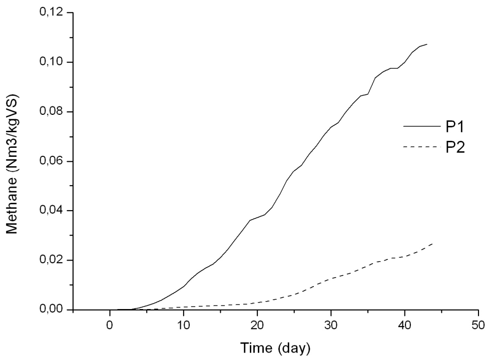

Figure 6: Methane production from the same substrate using different inoculum (P1 and P2).

4 CONCLUSIONS

The work has evaluated the influence of the inoculum in the anaerobic digestion process in terms of biogas and methane yield. The experiments were carried out in mesophilic condition in a pilot plant in the CRB Laboratory. The differences in the quantities of biogas and methane produced for the different inoculum and substrates were analyzed through two set of experiments. In the first the same inoculum (piggery manure anaerobically digested) was coupled with different substrates as olive husk (P1), cow (M1) and chicken (M2). In the second set the same substrate (olive husk) was coupled with several inoculum (P1: anaerobically digested piggery manure and P2: rumen fluid). The chicken manure and piggery manure anaerobically digested show the highest yield for the methane production while the biogas production is not higher than olive husk with the same inoculum. Starting from the same substrate the coupling of olive husk with piggery manure anaerobically digested is more suitable than with rumen fluid, the biogas and methane yield are higher. It means that a valid contribution has been done by the use of digested piggery manure as inoculum coherently with the Literature. [6].

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