

## Anaerobic digestion of onion and fennel scraps

A. Poletti <sup>1</sup>, L. Poletti <sup>2</sup>, R. Poletti <sup>2</sup>, S. Santini <sup>1</sup> F. Ascani <sup>2</sup>

**1 Laboratory of Chemical Sciences and Technologies for the Environment, University of Perugia (LCSTE). Italy**

**2 Sereco Biotest snc. Perugia. Italy**

### Introduction

Literature search clearly shows that there are not updated information regarding the process of anaerobic digestion of vegetable waste from **fennel (F)** and **onions (O)**. The only international scientific paper related to this topics concerns a work done on **Anaerobic Digestion (AD)** of onion scraps enlighting the fact that the methane yield is rather low and that it can be improved only if the **AD** is carried out in co-digestion with sludge derived from wastewater treatment plants. The lack of data on the **AD** of fennel - onion mixture has urged a thorough study that went beyond the mere technical aspects connected to the standard parameterization of an **AD** process. The first part of the experiment involved the analytical determination of the chemical and physico-chemical parameters of the materials that were previously collected from an industry involved in the processing of this kind of vegetable. The second part focused on the evaluation of the **AD** performance parameters connected to biogas and methane yield for the aforementioned mixture in the proportion of 80 % **F** and 20% **O**. This experiment appears to be an unprecedented case of **AD** carried out on both substrates (O and F) in which to assess the existence of catalytic and / or inhibitors effects that could impair and/or enhance the stability and yield of the process. Tests were also performed in the presence of other biomass substrates in order to verify the possibility of getting higher methane yields. This requirement is necessary when materials and / or mixtures whose the behavior in an anaerobic environment is unknown are used. It should be emphasized that mono- digestion, with the exception of few cases, has always to be considered extremely critical and unstable, so that it has been often suggested to find, also occasionally, other waste feedstock such as those commonly believed to be the most suitable such as manure, slaughterhouse wastes, other vegetable substrates such as straw, shredded sorghum, triticale and corn. These types of substrates, beside increasing the percentage yield of methane in the biogas, are known for providing supplementary nutrients and micronutrients and are useful in order to overcome the toxic or inhibitors effects arising out of the presence of particular substrates present in the mixture. Thus, the study herewith described was able to cover aspects still unknown for these two specific substrates.

### Material and methods

#### Chemical characterization of the substrates

The materials received from the processing facility looked extremely coarse and rough and therefore, without interfering with the cleaning or washing operations, were immediately crushed and sealed under nitrogen in PE bags. It should be noted that a few pieces of fennel showed mold colonies and soil residues. On the basis of the analytical data collected on the samples it can be stated as follows:

- a. pH of both substrates was found to be quite low to demonstrate that the waste materials received as such were already in the hydrolytic and acidogenic phase .
- b. The content of **TS** and **VS** are in modest percentage whilst reaching a **VS/TS** ratio compatible to **AD**.
- c. The concentration of the nutrients N and P is mildly deficient ; that of micronutrients K, Zn, Fe, Mn is satisfactory, with the exception of Cu, which is rather poor.
- d. On "fresh" samples of fennel ( **F** ) and onions ( **O** ) found at a local market, collected from fields for no more than four days, shredded and added with water to a solid concentration of 7%, then left at room temperature for 5 days, the pH value decreased from **6.06 (F)** and **5.98 (O)** to **4.66** and **4.22** respectively. With reference to the standard conditions of anaerobic treatment, the materials examined, with proper precautions and supplements, are to be considered eligible to be submitted to **AD**.

**TABLE 1 Analytical data of fennel sample**

pH		4,16
Total Solid TS	g/Kg a.s.	92 (9,2%)
Volatile Solid VS	g/Kg a.s.	74 (7,4% t.q.)
Organic C on dry matter	%.	28,4%
SV/ST Ratio		80%
NTK	g/Kg a.s.	1,18
Fats	g/Kg a.s.	1,6
Ammonia-N	mg/l	0,11**
Nitric-N	mg/l	1,6**
P	g/Kg a.s.	420
K	g/Kg a.s.	3600
Zn	g/Kg a.s.	1,66
Cu	g/Kg a.s.	0,05
Fe	g/Kg a.s.	6,53
Mn	g/Kg a.s.	1,73

\* a.s. = *as sampled* thus followed by grinding, \*\* tests executed after of the aqueous solution at 10% the homogenized material as sampled

**TABLE-2 Analytical data of onion sample**

pH		4,28
Total Solid TS	g/Kg a.s.	79 (7,9%)
Volatile Solid VS	g/Kg a.s.	67 (6,7% t.q.)
Organic C on dry matter	%.	35,6%
SV/ST Ratio		85%
NTK	g/Kg a.s.	1,03
Fats	g/Kg a.s.	0,86
Ammonia-N	mg/l	0,2
Nitric-N	mg/l	0,96**
P	g/Kg a.s.	230
K	g/Kg a.s.	1160
Zn	g/Kg a.s.	1,51
Cu	g/Kg a.s.	0,86
Fe	g/Kg a.s.	2,6
Mn	g/Kg a.s.	2,1

\* a.s. = *as sampled* thus followed by grinding, \*\* tests executed after of the aqueous solution at 10% the homogenized material as sampled

## Type of reactors, sample preparation and running of experimental tests

The tests were carried out using four completely mixed glass reactors (CSAR) (Fig.1) with the following characteristics :

- useful hydraulic volume: 4 liters; gas phase volume: 1.5 liters; mechanical agitation with variable speed and timing; thermostat with double wall glass at  $37^{\circ}\text{C} \pm 1^{\circ}$
- measurement of the biogas produced by means of eudiometers water saturated with  $\text{CO}_2$

The tests were performed in batch. Each fermentation test had a 28 days duration.

On the basis of analytical data and values of **TS** and **VS** reported in **Table 1** and **2** (weight ratio of **F** = 80.65 % and **O** = 19.35 %), and different mixes have been used for testing by keeping the ratio of available materials **H/C** at 0.24. The tests, named from **A** to **E**, were carried out using different mixtures as set out further below

**A) without dilution** (mix with components such as solid **9%** ), **F** 2,42 kg, **O** 0.58 kg, **TS%** 8,95

**B) Mixture F/O** with **8%** solids, solid weight 0.24 kg, 0.47 liter water, material quantity 2.53 kg ,  
**F** 2,04 kg, **O** 0.49 kg , **TS%** 8.95

**C) Mixture F/O** with **6%** solids, solid weight 0.21 kg, 0.87 liter water, material quantity 2.13 kg ,  
**F** 1,72 kg, **O** 0.41 kg, **TS%** 6

**D) Mixture F/O** with **5%** solids, solid weight 0.18 kg, 1.32 liter water, material quantity 1.68 kg ,  
**F** 1,35 kg, **O** 0.33 kg **TS%** 5

**E) Mixture B) + 2 % TS v/v pig manure effluent**

## Test running

The first two tests were run in parallel with total solid loads ranging from 5% to 6% , using a primer of activated sludge extracted from an anaerobic digester fed with corn silage and showing an excellent biogas production. The purpose of the tests at different loads of **TS** and **VS** was the assessment of:

- solid loading
- potential toxicity and inhibiting factors
- organic load on the hydrolysis and acidophilic steps

The activated sludge acclimated by the first two trials was used for the subsequent tests .

The experimental tests highlighting the aims for which they were performed, are listed below:

- testing in a completely mixed reactor with feeding batches heated at  $37^{\circ}\text{C}$
- collection of key data in order to evaluate the kinetics and potential of the methanogenic mixture **F+O**
- evaluation of possible inhibitory effects attributable to nutrient deficiencies and / or to the presence of toxic metabolites.
- testing in the presence of substrates such as livestock pig manure
- assessment of biogas composition in terms of **CH<sub>4</sub>**, **H<sub>2</sub>** and **H<sub>2</sub>S** over the different tests.

The length of the batch tests was standardized to 28 days, but the ultimate end of the tests was dragged on to asymptote when production reached 5% of the biogas production at the 28th day. This constrain has made it possible to directly use the mixed liquor from activated sludge for the subsequent tests. During the tests, phenomena of reduced production of biogas were highlighted and were probably due to the imbalance of nutrients. Therefore, the introduction of nutrients was decided by using small amounts of exhausted anaerobic digestate rather than chemicals. Only on one occasion urea was used to make up for a significant lack of nitrogen thus avoiding the introduction of large amount of livestock manure that could alter the results in an unpredictable way. The pH value was checked twice a day and corrected when the values fell below 6.5 to 6.7, with small additions of calcium hydroxide powder. The total alkalinity was checked every five days, using a potentiometer.

The analytical methods used are the official IRSA – CNR 64 " Analytical methods for sludge" 1985. The analysis of the biogas for **CH<sub>4</sub>**, **CO<sub>2</sub>** and **H<sub>2</sub>S** was carried out by gas chromatography equipped with a thermal conductivity detector.

## Results

### Calculation and application of consistent kinetic production

Given the complexity of the overall reaction of biomethanization and its dependence on a large number of factors, it is not possible to obtain kinetic data as accurate as for the study of chemical reactions. Hence, here it was used the criteria of the volume produced in infinite time, which, in this case, is been brought to coincide with that accumulated up to the time when the production of biogas can be considered technically finished. In this test this infinite time was established as the 28th day of the test

run. Therefore, if we consider, with good approximation, that the process of biogas production follows a kinetic law of the first order, integrating, we obtain as follows: where  $V_t$  is the value of the volume of biogas produced at time  $t$ ,  $V_\infty$  is the volume of gas produced at the end of experiment (in our case the 28th day). To this volume is added normally a 5 % extra production, to take into account the fact that the infinite time should coincide with the time at which the production of biogas becomes actually zero.  $k$  is the rate constant of the process expressed as 1/time unity ( usually " day - 1 "). If  $V_t$  is reported as 1 kg of VS (or UOM, Unit Organic Matter) added , the value of  $k$  will allow to calculate the biogas volume that can be produced in a given time following the addition of a given quantity of VS. This approach is particularly suitable in the study of anaerobic processes and the data obtained this way can be used, with precautions, for the designing real-scale plants.

## Biogas production

The **ICP** (net) dry biogas at **SCP** at a proportion of 60%, which is considered as a standard for cogeneration (see e.g. GE Jenbacher ) is 5 kWh/m<sup>3</sup> (18 MJ/m<sup>3</sup>). The biogas obtained in the experiment has an average concentration of methane around **63-64 %** and then an average **ICP** of 19 MJ / m<sup>3</sup> . The total amount of biogas produced during the 27 days of trial is shown, normalized to 1 kg of slurry evaluated as such and as UOM. The experimental results are reported in Table 3, as technic unit **mc biogas/t SV**.

**TABLE 3 – RISULTS of the gasification tests  
mc biogas / t S.V. and %CH<sub>4</sub> content**

TEST	MATERIAL	ST %	SV %	biogas mc/t SV	% CH <sub>4</sub>
1	Only FENNEL	9,2	7,4	155	54
2	Only ONION	7,9	6,7	102	51
3	MIX A	9	7,4	132	56
4	MIX B	8	7,3	145	55
5	MIX C	6	7,4	138	58
6	MIX D	5	7,1	148	58
7	MIX.E	+2% pigs	7,6	186	61

The biogas production was computed as the total gas volume obtained as the asymptotic value at 24°- 25° day, without consider the residual productivity esteemed nearly 5%.

The substrates conversion show an anomalous behavior, as the 80% of biogas production is realized between the 4°-5° day of the test.

## CONCLUSIONS

Fenel proved to be a satisfactory substrate for a 3-step AD process. The process implemented in this study showed that it was extremely advantageous for the process yield that the hydrolytic and acidogenic phases were carried out separately from the methanogenic phase. This brought about an higher overall efficiency, with respect to a 1-step experimental tests as standard methodology reference. Moreover, the use of other types of substrates, because of the characteristics of the adopted process, easily allow an appreciable increase in biogas production by assuring stability and efficiency to the process. On the other hand, the low amount of nitrogen present in olive wastes (sansa), makes it easier to manage soluble nitrogen in the outlet digestate in comparison to the use of other substrates, with obvious advantages in terms of plant engineering and process economics . Furthermore, when the analysis of biogas is taken into account, it worthy to note that a rather low value of ammonia has always been detected. This finding may be regarded as a remarkable technical advantage that avoids possible toxic effects that high concentrations of ammonia could produce .

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