# Anaerobic Digestion of Coffee waste

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## Abstract
The anaerobic co-digestion of five different by-products from instant coffee substitutes production was studied in mesophilic conditions. The co-substrate was the excess of sewage sludge from the wastewater treatment plant located in the same coffee factory. Four of the tested wastes produced methane in the range of 0.24-0.28 $m^3CH_{4(STP)}/kgVS_{initial}$ . Reduction of 50-73% in total solids and 75-80% in volatile solids were obtained and the hydrolysis rate constants were in the range of 0.035-0.063 $d^{-1}$.
After 40 days, one waste, composed of 100% barley, achieved a methane yield as low as 0.02 $m^3CH_{4(STP)}/kgVS_{initial}$ and 31% and 40% total and volatile solids reduction, respectively,. Two different strategies were applied to enhance the biodegradability of this waste. An alkaline hydrolysis pre-treatment, that increased the methane production up to 0,22 $m^3CH_{4(STP)}/kgVS_{initial}$ and the total and volatile solids reductions up to 67 and 84%, respectively. A co-digestion with kitchen waste, that increased the methane production up to 0,36 $m^3CH_{4(STP)}/kgVS_{initial}$ and the total and volatile solids reductions up to 61 and 67%, respectively.
**Keywords:** alkaline hydrolysis pre-treatment, biogas, hydrolysis rate constant, instant coffee substitutes, kitchen waste.

## Introduction
The EU legislation through the Council Directive 1999/31/EC imposes that the amount of biodegradable organic waste that is disposed in landfills should be decreased by 65%, relatively to the total amount of organic fraction of municipal solid waste produced in 1995, by July 2016. Anaerobic technology is placed as one of the best available technologies to face the problem of organics disposal (Mata-Alvarez, 2003). Nevertheless, some organic solid wastes present a low biodegradability in spite of the high COD content and, therefore, studies to enhance the biomethanation process of such wastes are still required. Coffee waste is a typical example of such kind of wastes.

Instant coffee production process comprises roasting the beans and extracting the soluble fraction with hot water, giving rise to the generation of large amounts of a dark coloured liquid waste containing about 20% of insoluble solids. When instant coffee substitutes are produced the raw material contains barley, rye, malted barley, chicory and coffee, the relative amount of each depending on the specific substitute to be produced. Due to the different raw matter used to produce the different substitutes, the waste composition changes sequentially, being important to evaluate their individual performance as far as the anaerobic digestion (AD) process is concerned. Whatever the raw material used, the waste is mainly composed of carbohydrate fibbers such as cellulose, hemi-cellulose and also lignin (Dinsdale *et al*., 1996). Lignin is highly recalcitrant and its degradation is considered the limiting step in the decomposition of lignocellulosic substrates (Pavlosthatis and Girald-Gomez, 1991).

The aim of this work was to study the anaerobic biodegradation of five wastes from the instant coffee substitute production, under mesophilic conditions, in co-digestion with the excess of activated sludge from a wastewater treatment plant located in the same coffee factory.

With the objective of enhancing the methane production from the waste composed by 100% barley, two different approaches were used: an alkaline pre-treatment before the co-digestion with sewage sludge and the co-digestion with kitchen waste.

The alkaline hydrolysis at ambient temperatures has been proposed as the chemical pre-treatment more compatibly with the AD process, since the bioconversion generally requires an adjustment of pH by increasing alkalinity (Pavlosthatis and Gosset, 1985). On the other hand,

the co-digestion with biodegradable wastes has also been successfully and increasingly applied to several agricultural and industrial organic wastes (De Baere, 2000).

## Materials and methods

### Waste source

The five wastes (W#) from the instant coffee substitute production were obtained from the Nestlé factory in Avanca, Portugal. About 40 ton/day (dry matter between 13 and 22%) of waste are, in average, produced in this factory. A wastewater treatment plant is installed in the same factory, producing an excess of activated sludge (S) of about 3.9 ton/day with a dry matter content of 22%.

The kitchen waste (KW) was a composed sample (one week based) from the waste produced in the restaurant of the University of Minho, located in "Campus de Gualtar", Braga, Portugal. Table 1 shows the composition of the five wastes, W1 to W5, as well as the characterization in total solids (TS), volatile solids (VS) and COD of the excess activated sludge and the kitchen waste.

**Table 1** Composition of the insoluble matter of the five instant coffee substitute wastes studied and characterization of each type of waste used in TS, VS and COD

| Waste # | Coffee (%) | Barley (%) | Rye (%) | Malted barley (%) | Chicory (%) | TS ($g/kg_{waste}$) | VS ($g/kg_{waste}$) | COD ($g/kg_{waste}$) |
|---|---|---|---|---|---|---|---|---|
| W1 | 0 | 40 | 5 | 30 | 25 | 131±4 | 127±4 | 111±4 |
| W2 | 45 | 32 | 0 | 0 | 23 | 217±5 | 215±5 | 208±9 |
| W3 | 0 | 100 | 0 | 0 | 0 | 214±2 | 208±2 | 123 ±1 |
| W4 | 20 | 45 | 0 | 0 | 35 | 144±8 | 141±8 | 130 ± 6 |
| W5 | 20 | 45 | 0 | 0 | 35 | 139±11 | 136±11 | 109±9 |
| S | - | - | - | - | - | 7±1 | 6±1 | 6 ±1 |
| KW | - | - | - | - | - | 238±1 | 214±7 | 327±73 |

### Inoculum

The inoculum was an anaerobic granular sludge collected from an upflow anaerobic sludge blanket reactor treating a brewery effluent located in Oporto, Portugal. The production of methane due to the residual substrate present in the inoculum was 0.020 ±0.001 $m^3CH_4/KgVS_{sludge}$.

The quantification of the residual methane production was performed using a pressure transducer technique (Colleran *et al*., 1992). The test involves the monitoring of the pressure increase developed in sealed vials without substrate. Strict anaerobic conditions were maintained, by using an anaerobic basal medium composed of cysteine-HCL (0.5 g/L), $NaHCO_3$ (3 g/L), with the pH adjusted to 7.0-7.2. Rezasurin was added as an indicator of redox potential. This basal medium was prepared by boiling the medium before adding the bicarbonate. The hand held pressure transducer used was capable of measuring a pressure increase or decrease of two atmospheres (0 to ± 202.6 kPa) over a range of -200 to +200 mV. The methane content in the headspace was determined. The tests were performed in 25 ml vials, in triplicate. The volume of methane produced was corrected to the standard temperature and pressure (STP) conditions.

### Analytical methods

COD, TS and VS, were determined according to Standard Methods (APHA, AWWA, WPCF (1989)). The methane and carbon dioxide content of the biogas was measured by gas chromatography using a Porapack Q (180 to 100 Mesh) column, with He as the carrier gas at 30 ml/min and a thermal conductivity detector. Temperatures of the detector, injector and oven were 110, 110 and 35 ºC, respectively. VFA (acetate, propionate, iso-butyrate, n-butyrate and valerate) were determined by high-performance liquid chromatography using a chrompack column (300x6.5 mm) and a mobile phase of sulphuric acid 5mM at 0.7 ml/min. The column was set at 60 ºC and the detection was by spectrophotometry at 220 nm.

### Methane production assays

The methane production assays were performed in duplicate, with the wastes W1 to W5 in co-digestion with the excess of sewage sludge, in 160ml vials. The methane production assays were performed in 160 ml vials, in duplicate. A constant ratio of 7 $gTS_{coffeewaste}/gTS_{sludge}$ was kept in the assays, which reflect the relative daily production of the two waste streams. In each assay, the ratio substrate/inoculum was kept constant at 2.3 $gTS_{substrate}/gTS_{inoculum}$. The pH was corrected to 7 and 0.75 $gNaHCO_3/gTS$ was added to promote suitable alkalinity. The vials were then incubated at 37 ºC under stirring conditions (150 rpm) and the pressure increase was monitored using the above mentioned pressure transducer device. At regular time intervals, the vials were depressurised and the biogas composition was analysed for $CH_4$ and $CO_2$ content. The batch assays had a total solid content in the range 6 to 9 %. The volume of methane produced was corrected to STP conditions.

*Liquid composition assays.* Parallel assays, with 500 ml working volume, were set up to assess the liquid composition, in terms of soluble COD and VFA.

### Alkaline hydrolysis pre-treatment

For the alkaline hydrolysis pre-treatment the barley waste (W3) was left overnight in a solution of 0.3 $gNaOH/gTS_{W3}$, at 25º C. The batch assays were set up afterwards, keeping the same conditions as described for the first set of methane production assays.

### Co-digestion of kitchen waste and barley waste

These assays were performed in 100 L digesters intermittently stirred, in batch conditions. Two digesters were set: in digester I, the waste initially loaded to the reactors was composed by 60% KW and 40% W3. For comparative purposes, 100% KW was fed in a second digester (II), which was run in the same conditions as was the digester I.

In both digesters the solid content (TS) of the waste was 22% and the ratio substrate/inoculum was kept constant at 2.3$gTS_{substrate}/gTS_{inoculum}$. To provide suitable alkalinity 5 $gNaHCO_3/L$ were added. Once a week, the reactors content was sampled for pH, soluble COD, VFA, TS and VS.

The cumulative biogas production and the corresponding methane content were determined continuously in all the assays. The results from the biomethanation process were expressed in terms of methane yield ($m^3CH_4/kgVS_{initial}$) and in terms of % methanation, which corresponds to the percentage of methane produced relative to the biochemical methane potential (0.350 $m^3CH_4$(STP)/kgCOD).

## Results and Discussion

### Methane production assays

Figure 1 shows the methane production curves obtained for the different assays of the sewage sludge and the by products of instant coffee waste (SW#). Table 2 shows the methane yield, the percentage of methanation, the reduction of TS, the reduction of VS and the hydrolysis rate constant obtained in each assay, after the correction of the methane production due to the residual substrate present in the inoculum (blank assays). Among the different wastes, the SW2 showed the highest methane yield, 0.28$m^3/kgVS_{initial}$, which agrees with the higher VS reduction (80%) and the higher initial COD content of this waste. This assay also achieved 85% of the theoretical methane production, although it took 144 days to attain the “plateau”.

In the assays SW1, SW4 and SW5 similar methane yields were obtained (0.24-0.25 $m^3/kgVS_{initial}$), the VS reduction was in the range 75-79% and the percentage of methanation in the range 75-89%. The assay SW1 was faster than the others, since it stabilised after about 50 days, whereas the other assays needed about 100 days.

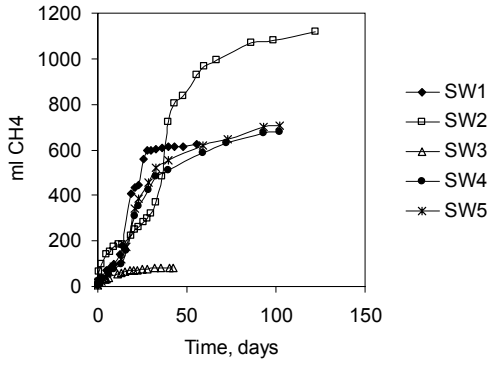


**Figure 1** Cumulative methane production during the co-digestion assays of coffee waste and sewage sludge.

The methane yield achieved in the assay SW3 was very low (0.02 m3/kgVSinitial), which corresponded to only 11% of the theoretical methane production. The lowest values of TS and VS reduction were obtained. This is not surprising because carbohydrates from barley are about 69% composed by fiber (http://www.nutritiondata.com/facts-001-02s04dq.html), being about 6% indigestible fiber (Potter and Hotchkiss, 1995).

Figure 2 shows the time course of methane, VFA and soluble COD, all expressed as COD. The assay that reached the higher concentration in VFA was SW2 (29 g/l) and this value did not seem to inhibit the subsequent methanogenic process. The poor methane yield of the assay SW3, was likely due to the presence of products from the hydrolysis of complex heterocyclic compounds rather than to the levels of VFA which peaked at 22 g/l, value lower than in assay SW2. All the other assays achieved VFA concentrations around 13-15 g/l. The final pH in all the assays was in the range of 7.3 to 7.8 indicating that irreversible acidification did not occur. At the end of the assays, the VFA concentration was very low (almost near zero in some of the assays), except for SW3 that was still at 20g/l, 41 days after beginning the test.

Figure 3 shows the cumulative methane as COD, hydrolysed COD and acidified COD for all the assays. From this Figure, the relative kinetics of hydrolysis, acidification and methanation can be assessed. In general, it is accepted that hydrolysis of particulate organic matter is the rate-limiting step in the anaerobic digestion of particulate substrates. However, in the present work this did not occurred, since the curve of cumulative hydrolysed COD increased at a higher rate than the corresponding cumulative methane production curve. For all the wastes, 84 to 97 % of the initial COD was hydrolysed, but the percentage of methanation was lower, in the range 75-89%, with the exception of SW3 where only 11% of methanation was observed.

Although the rate of hydrolysis is a function of pH, temperature, concentration of hydrolytic bacteria, and type of particulate organic matter (Pavlostathis and Girald-Gomez, 1991), it is not well understood how the physicochemical properties of particulate organic substrates quantitatively affect the rate of hydrolysis (Veeken and Hamelers, 1999).

In this study all the mentioned above parameters were the same in all the assays, except the physicochemical properties of the organic waste. The hydrolysis rate constant for each assay was determined, assuming a first order kinetics (Table 2).

**Table 2** Methane yield, % of methanation, % reduction of TS, % reduction of VS and Hydrolysis rate constant of different coffee wastes in the batch assays.

| ASSAY# | Methane Yield ($m^3CH_{4(STP)}/KgVS_{Initial}$) | % of methanation | Reduction of TS (%) | Reduction of VS (%) | Hydrolysis rate constant ($d^{-1}$) |
|---|---|---|---|---|---|
| SW1 | 0.24 | 76 | 73 | 78 | 0.063 |
| SW2 | 0.28 | 85 | 67 | 80 | 0.035 |
| SW3 | 0.02 | 11 | 31 | 40 | 0.084 |
| SW4 | 0.25 | 75 | 50 | 79 | 0.040 |
| SW5 | 0.25 | 89 | 54 | 75 | 0.036 |

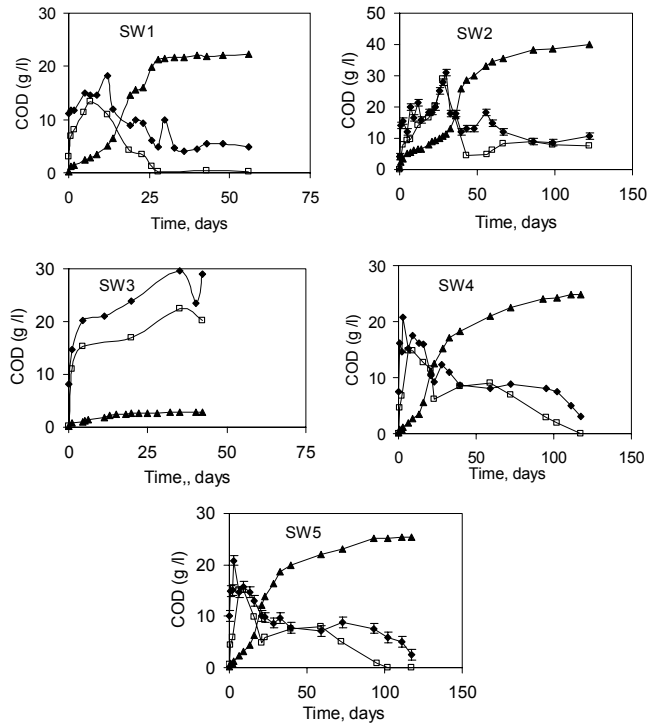


**Figure 2** Time course of soluble COD (◆), volatile fatty acids COD (□) and Methane COD (▲).

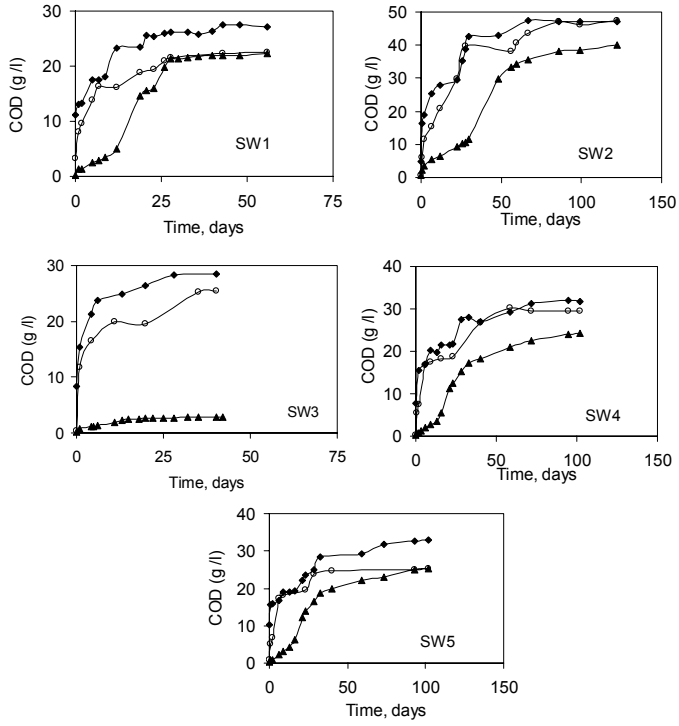


**Figure 3** Cumulative hydrolysed COD (◆= methane +soluble COD), acidified COD (○= methane+VFA) and methane COD (▲).

Figure 4 shows a negative correlation between the hydrolysis rate constant and the methane yield for all the assays. This indicates that when hydrolysis was faster, the methane yield was lower, likely because the faster hydrolysis induced a more important accumulation of intermediates potentially toxic to the methanogenic population.

Veeken and Hamelers (1999), when studying the anaerobic biodegradability of six components of biowaste containing lignocellulosic material found that grass was less biodegradable (≈ 47%) than leaves (≈ 35%), although having a higher hydrolysis rate constant in mesophilic conditions.

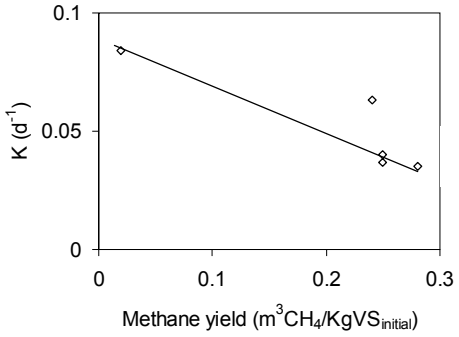


**Figure 4** Linear correlation between the hydrolysis constant rates and the methane yields.

According to Tong et al. (1990), the biodegradability depends on the structure of the lignocellulosic complex. Cellulose is readily degradable but becomes less degradable or even refractory when incorporated in a lignocellulosic complex. Moreover, Azhar and Stuckey (1994) studied the influence of chemical structure of instant coffee wastes on anaerobic catabolism and found that the individual chemical structure of compounds greatly influences and determines the rate and mechanisms of methanogenic degradation.

## Alkaline hydrolysis pre-treatment

Figure 5 presents the results of the cumulative methane production obtained in the co-digestion of the pre-treated barley waste with sewage sludge. The alkaline hydrolysis pre-treatment of the W3 increased the methane production up to 0.22 $m^3CH_{4(STP)}/kgVS_{initial}$, achieving 100 % of the theoretical methanation. Furthermore, this pre-treatment improved the reduction of the TS as well as VS to 67 and 84%, respectively.

The pre-treatment of lignocellulosic materials with dilute alkali leads to an important chemical reaction, which consists of a saponification of esters of uronic acid associated with xylan chains (Data, 1981). The effect of saponification is a breaking of cross-linking. Consequently, there occurs a marked increased in the swelling capacity and pore size. This increase not only provides an increased diffusivity for the hydrolytic enzymes but also facilitates/improves enzyme-substrates interactions. Hence, acidogenic bacteria can ferment the pre-treated lignocellulose even though no delignification or cellulose hydrolysis occurs during the pre-treatment (Data, 1981).

The present results show that the alkaline pre-treatment of wastes like barley is beneficial, because it significantly improved the anaerobic biodegradability.

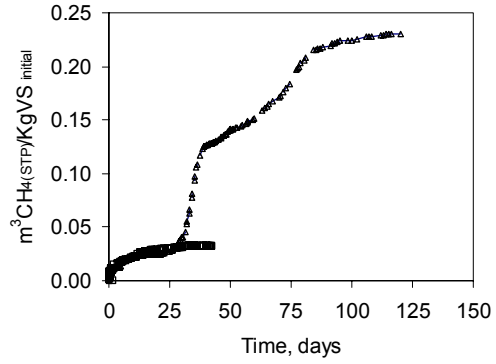


**Figure 5** Cumulative methane production during the co-digestion assays of W3 with (△) and without pre-treatment (□).

In the assay without pre-treatment, it was observed that hydrolysis was not the rate limiting step in the anaerobic biodegradation of the barley waste. The observed inhibition on the methane production was likely caused by the sub-products of the natural hydrolysis process (first step of AD process) that were not suitable for the methanogenic population. The outcome from these assays elicits the conclusion that the products of the alkaline hydrolysis are less toxic and/or inhibitory for the subsequent stages of the AD process.

## Co-digestion of kitchen waste and barley waste

The results obtained for the weekly monitoring of pH, TS, VS and soluble COD are presented in Figure 6. All the studied parameters presented an identical behaviour in both digesters.

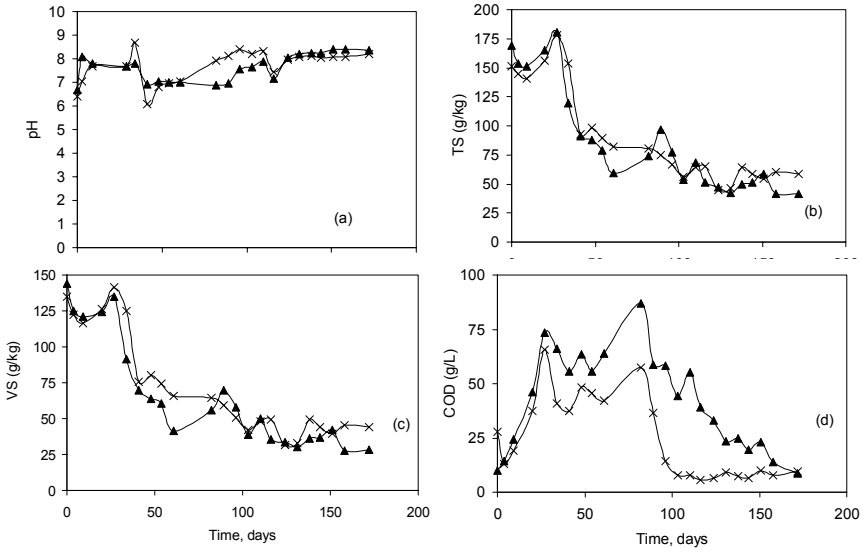


**Figure 6** Time course of the pH (a), TS (b), VS (c) and soluble COD (d) in the anaerobic digester I (×) and II (▲)

The results obtained for the weekly monitoring of pH, TS, VS and soluble COD presented an identical behaviour in both digesters. The profile of soluble COD was different for the two assays. In digester I, the soluble COD values were systematically lower than in the digester II and attained a residual value of 8 g/l around day 100, while in digester II this was only attained by day 172. This indicates that the co-digestion process of barley waste and kitchen waste was faster than the single digestion of the kitchen waste. Such behaviour can be observed in the cumulative methane production curves (Figure 7(a)), as well as the methane content of the biogas produced (Figure 7 (b)). The methane content is somewhat different for the two digesters.

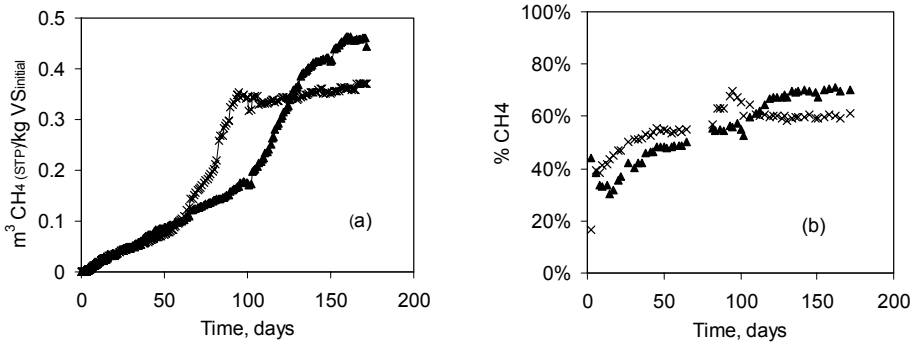


**Figure 7** Cumulative methane production (a) ($m^3CH_{4(STP)}/KgVS_{initial}$) and methane content (b) (%) and in the anaerobic digester I (×) and in the anaerobic digester II (▲).

In the single digestion of kitchen waste (digester II), the methane content is about 11% lower than in the co-digestion process (digester I), until day 100. However, thereafter, the biogas from the digester II presented a methane content about 15% higher than the one of the digester I.

Around day 100 the cumulative methane production of the digester I stabilized in the final value that was, at that time, about 99% higher than the observed in digester II. Nevertheless, at the end, the cumulative methane production was about 20% higher in digester II when compared to the digester I. The digester I attained a methane production of 0.36 $m^3CH_{4(STP)}/kgVS_{initial}$ (92% of the theoretical methanation), TS as well as VS reduction of 61 and 67 % respectively. The digester II attained a methane production of 0.43 $m^3CH_{4(STP)}/kgVS_{initial}$ (83% of the theoretical methanation), TS as well as VS reduction of 75 and 80 %, respectively.

## Conclusions

When studying the methanation ability of five coffee wastes from the production of instant coffee substitutes, methane yields in the range of 0.24-0.28 $m^3CH_{4(STP)}/kgVS_{initial}$ were obtained with the exception of a barley rich waste (SW3) that achieved only 0.02 $m^3CH_{4(STP)}/kgVS_{initial}$. Four of the five wastes (SW1, SW2, SW4, SW5) also presented TS and VS reductions in the ranges of 50-73% and 75-80%, respectively and the methane yield attained 75-89% of the theoretical methane potential. Hydrolysis constant rates in the range of 0.035-0.063 $d^{-1}$ were obtained.

The SW3 waste achieved a methanation of 11% and reduction of TS and VS of 31 and 40%, respectively. However, this waste presented the highest hydrolysis rate constant (0.084 $d^{-1}$), indicating that hydrolysis was not, in this case, the rate limiting step in the anaerobic digestion process.

When the barley waste was submitted to an alkaline hydrolysis pre-treatment before the co-digestion with sewage sludge, the methane production increased up to 0.22 $m^3CH_{4(STP)}/kgVS_{initial}$ and the total and volatile solids reductions increased to 67 and 84%, respectively. When this waste was co-digested with kitchen waste (40% Barley waste, 60% kitchen waste), the methane production obtained was 0.36 $m^3CH_{4(STP)}/kgVS_{initial}$ and the total and volatile solids reductions were, 61 and 67%, respectively. Compared with the alkaline pre-treatment, the co-digestion with Kw attained more 64% of methane production. However, the TS and VS reductions were 9% and 20% lower, respectively.

From the results of these two approaches, it seems that no inhibition of methanation occurred, conversely as it happened when the barley waste was co-digested with sewage sludge and without pre-treatment. So, it is feasible to suppose that different intermediates, likely presenting a lower toxicity to the methanogenic populations, were formed in the two approaches studied in the present work.

The decision about the management of the coffee waste should be based on economic analysis. In case of decision about the construction of an AD plant to treat the coffee waste it is advisable to apply a pre-treatment to the barley waste being the alkaline hydrolysis a clear possibility. However if an AD plant for kitchen waste exists in the proximity, the delivery of this waste to such plant could also be consider. The co-digestion of the barley waste with the OFMSW seems to be attractive from an integrated solid waste management point of view, because it only decreases the methane production in about 20%, reducing the amount of wastes to be landfilled.

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