Anaerobic Digestion Performance in the Energy Recovery of Kiwi Residues

Ramiro Martins 1, Rui Boaventura 2, Larissa Paulista 3

1 Department of Chemical and Biological Technology of ESTiG, Polytechnic Institute of Bragança, Campus de Santa Apolónia 5300-253 Bragança, Portugal and Associate laboratory LSRE-LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr Roberto Frias, 4200-456 Porto, Portugal
2 Associate laboratory LSRE-LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr Roberto Frias, 4200-465 Porto, Portugal.
3 ESA, Polytechnic Institute of Bragança, Campus Santa Apolónia 5300-253 Bragança, Portugal

rmartins@ipb.pt

Abstract. World production and trade of fruits generate losses in the harvest, post-harvest, handling, distribution and consumption phases, corresponding to 6.8% of total production. These residues present high potential as a substrate for the anaerobic digestion process and biogas generation. Thus, the energy valuation of the agro-industrial residues of kiwi production was evaluated by anaerobic digestion, aiming at optimizing the biogas production and its quality. Ten assays were carried out in a batch reactor (500 mL) under mesophilic conditions and varying a number of operational factors: different substrate/inoculum ratios; four distinct values for C: N ratio; inoculum from different digesters; and inoculum collected at different times of the year. The following parameters were used to control and monitor the process: pH, alkalinity, volatile fatty acids (VFA), volatile solids (VS) and chemical oxygen demand (COD). Among the tests performed, the best result obtained for the biogas production corresponded to the use of 2 g of substrate and 98 mL of inoculum of the anaerobic digester of the Wastewater Treatment Plant (WWTP) of Bragança, with addition of 150 mg of bicarbonate leading to a production of 1628 L biogas.kg⁻¹ VS (57% methane). In relation to the biogas quality, the best result was obtained with 20 g of substrate and 380 mL of inoculum from the anaerobic digester sludge of WWTP of Ave (with addition 600 mg of sodium bicarbonate), presenting a value of 85% of CH₄, with a production of 464 L biogas.kg⁻¹ VS.

1. Introduction
World fruit production and trade have steadily grown in recent decades, but it is believed that 6.8% of all production is lost during harvesting, post-harvesting, handling, distribution and consumption [1]. Most of these wastes are landfilled or incinerated [2]. However, these practices may pose a threat to the health of the population and the environment [3], because they are emitting greenhouse gases (GHG), and also attract vectors such as insects and rodents [1].
The fruit waste is characterized by a high moisture content and high concentration of easily degradable organic matter [4]. Therefore, this type of waste has been considered to be a suitable substrate for the production of methane by anaerobic digestion process (AD) [5]. This degradation process is performed by anaerobic microorganisms and includes several reactional steps which can be divided into: hydrolysis, acidogenesis, acetogenesis and methanogenesis [6]. The process final products are a stabilized sludge and biogas with high concentration of methane (50-65%), which can be used as a source for thermal or electric energy [7], [8].

Previous studies have shown that the methane yield when using fruit and vegetable residues can vary, but remains fairly high: 430 L CH₄.kg⁻¹ VS for [9], 479.5 L CH₄.kg⁻¹ VS for [10]. Gunaseelan [11] obtained 473.5 L CH₄.kg⁻¹ VS for lemon waste and 448.5 L CH₄.kg⁻¹ VS for mango waste, among others. Zhao et al. [8] reported, however, that the scientific literature contains few studies on the anaerobic digestion of fruit waste alone; in most cases it has been associated with food waste and other plant residues. Therefore, various types of fruit wastes such as from kiwi production, which have considerable annual production, have not been properly considered for anaerobic digestion.

Taking into account this fact, this study aims to recovery energy from kiwi residues by anaerobic digestion, carrying out various experiments in a laboratory scale batch reactor. Biogas production was monitored and analyzed using a continuous measurement system and other parameters such as pH, alkalinity, chemical oxygen demand (COD), volatile solids (VS) and volatile fatty acids (VFA) were also analyzed.

2. Materials and methods
A batch mixing reactor was used for the experiments, namely the BCS-CH₄biogas BlueSens system, composed of: 500 mL reactor (B) where the digestion process takes place; flowmeter (C), which measures the volume of biogas generated; sensor (D), which measures the quality of the biogas (% CH₄); and, accessories for the interconnection of these components (A, E and F) (Figure 1). The biogas volume (mL) and methane content (%) are processed every 20 seconds and plotted on a chart by using the supplied software. The reactors were placed on magnetic stirring plates to maintain the same concentration at all points as a result of the stirring caused by the rotation of a magnetic bar. Also, a heating tape was used to maintain the temperature inside the reactors in the mesophilic range (35°C).

![Figure 1. Materials used to assemble the BCS-CH₄biogas BlueSens system](image-url)
The substrate used was kiwi residue, collected at a food distribution unit in the city of Bragança, Portugal. The kiwi residue was triturated and transformed into a pasty material. This material was stored in a refrigerator at 3-4 °C until use. All experiments performed in this study used the same initially prepared residue and the respective volume varied as desired. The analyzed parameters are shown in Table 1.

Table 1. Parameters analysed in the experiments

| Parameters                  | Methods     |
|-----------------------------|-------------|
| pH                          | 4500 H⁺ B [12] |
| Alkalinity                  | 2330 B [12]  |
| Volatile fatty acids (VFA)  | [13]        |
| Volatile solids (VS)        | 2540 E [12]  |
| Chemical oxygen demand (COD)| 5220 C [12]  |

The inoculum was introduced into the reactor to start up the process because it provides microorganisms that facilitate the transformation of organic matter (substrate) by anaerobic digestion. The inoculum chosen to feed the system was anaerobic slurry from the anaerobic digesters of the WWTP of Bragança, Portugal, and the WWTP of Ave, Portugal, and from a septic tank. The volume of inoculum introduced varied according to the conditions previously defined for each assay (Table 2).

Table 2. Assays performed and initial operating conditions

| #  | Experiment | Substrate (g) | Inoculum (mL) | NaHCO₃ (mg) | KNO₃ (mg) | Inoculum                                      |
|----|------------|---------------|---------------|-------------|-----------|-----------------------------------------------|
| 1  | 1.1        | 1             | 99            | 150         | -         | Slurry from anaerobic digesters of the WWTP of Bragança in 03/11/2015 |
|    | 1.2        | 2             | 98            | 150         | -         | Bragança in 03/11/2015                          |
|    | 1.3        | 3             | 97            | 150         | -         | Bragança in 03/11/2015                          |
|    | 1.4        | 4             | 96            | 150         | -         | Bragança in 03/11/2015                          |
|    | 2.1        | 2             | 198           | 300         | -         | Slurry from anaerobic digesters of the WWTP of Bragança in 03/11/2015 |
|    | 2.2        | 4             | 196           | 300         | -         | Bragança in 03/11/2015                          |
|    | 2.3        | 6             | 194           | 300         | -         | Bragança in 03/11/2015                          |
|    | 2.4        | 8             | 192           | 300         | -         | Bragança in 03/11/2015                          |
|    | 3.1        | 2             | 198           | 300         | -         | Slurry from anaerobic digesters of the WWTP of Bragança in 03/11/2015 |
|    | 3.2        | 4             | 196           | 300         | -         | Bragança in 03/11/2015                          |
|    | 3.3        | 6             | 194           | 300         | -         | Bragança in 03/11/2015                          |
|    | 3.4        | 8             | 192           | 300         | -         | Bragança in 03/11/2015                          |
|    | 4.1        | 2             | 198           | 300         | -         | Slurry from anaerobic digesters of the WWTP of Bragança in 03/11/2015 |
|    | 4.2        | 4             | 196           | 300         | -         | Bragança in 03/11/2015                          |
|    | 4.3        | 6             | 194           | 300         | -         | Bragança in 03/11/2015                          |
|    | 4.4        | 8             | 192           | 300         | -         | Bragança in 03/11/2015                          |
|    | 5.1        | 4             | 96            | 150         | 166.51    | Slurry from anaerobic digesters of the WWTP of Bragança in 07/03/2016 |
|    | 5.2        | 4             | 96            | 150         | 66.57     | Bragança in 07/03/2016                          |
|    | 5.3        | 4             | 96            | 150         | 33.36     | Bragança in 07/03/2016                          |
|    | 5.4        | 4             | 96            | 150         | 16.61     | Bragança in 07/03/2016                          |
|    | 6.1        | 4             | 96            | 150         | 166.51    | Slurry from anaerobic digesters of the WWTP of Bragança in 02/04/2016 |
|    | 6.2        | 4             | 96            | 150         | 66.57     | Bragança in 02/04/2016                          |
|    | 6.3        | 4             | 96            | 150         | 33.36     | Bragança in 02/04/2016                          |
|    | 6.4        | 4             | 96            | 150         | 16.61     | Bragança in 02/04/2016                          |
|    | 7.1        | 2             | 198           | 300         | -         | Slurry from anaerobic digesters of the WWTP of Bragança in 07/04/2016 |
|    | 7.2        | 4             | 196           | 300         | -         | Bragança in 07/04/2016                          |
|    | 7.3        | 6             | 194           | 300         | -         | Bragança in 07/04/2016                          |
|    | 7.4        | 8             | 192           | 300         | -         | Bragança in 07/04/2016                          |
### Experiment Substrate (g) Inoculum (mL) NaHCO3 (mg) KNO3 (mg) Inoculum

| # | Experiment | Substrate (g) | Inoculum (mL) | NaHCO3 (mg) | KNO3 (mg) | Inoculum |
|---|------------|---------------|---------------|-------------|-----------|-----------|
| 8.2 | 4 | 196 | 300 | - |
| 8.3 | 6 | 194 | 300 | - |
| 8.4 | 8 | 192 | 300 | - |
| 9.1 | 12 | 388 | 600 | - |
| 9.2 | 16 | 384 | 600 | - |
| 9.3 | 20 | 380 | 600 | - |
| 9.4 | 24 | 376 | 600 | - |
| 9.5 | 16 | 384 | 400 | 666.04 |
| 10.1 | 12 | 388 | 600 | - |
| 10.2 | 16 | 384 | 600 | - |
| 10.3 | 20 | 380 | 600 | - |
| 10.4 | 24 | 376 | 600 | - |
| 10.5 | 12 | 384 | 600 | 666.04 |

### Results and discussion

At the beginning of the experiment, the pH of the mixture in the reactor was set to 7, by adding sodium bicarbonate, 150 mg.L⁻¹, which also provided the alkalinity adequate to the anaerobic digestion process as described in the literature [14]. When the process was interrupted, approximately after 360 hours, the pH was between 7 and 7.6 for all the tests, being in accordance with the values considered satisfactory for the AD process, evidencing that the added alkalinity was enough to maintain the pH within the reactor in a suitable range.

The alkalinity of the medium was adjusted to 1500 mg of CaCO₃.L⁻¹, which was found to be adequate, to maintain an endless VFA concentration between 400-600 mg.L⁻¹, which does not inhibit the process. It was found that the addition of nitrogen as potassium nitrate, to evaluate the effect of the C:N ratio, caused the inhibition of microbial activity. Moreover, the inoculum collected in the winter season showed less microbial activity, due to the low ambient temperature and consequently into the anaerobic digester.

Comparing the biogas (L biogas.kg⁻¹ COD) and methane (L CH₄.kg⁻¹ COD) production, it is possible to obtain the best conditions in relation to the added amounts of substrate, inoculum, KNO₃ and NaHCO₃. Substrate values of less than 5 g and between 5 and 10 g led to higher yields of both biogas and methane (Figure 2). The same happened with the use of 200 to 250 mL of inoculum. Values of KNO₃ greater than 100 mg inhibit the process and the best results were obtained for an alkalinity corresponding to the addition of NaHCO₃ between 300 and 400 mg (Figure 2).

In relation to the volume of biogas produced, the best result (1628 L biogas.kg⁻¹ VS) corresponds to the assay (2.1) (1% the substrate), with 57% CH₄ (Figure 3). However, as regards the biogas quality expressed as percentage of methane, the best result was obtained in the test (10.3) (5% the substrate), where a value of 85% was recorded (Figure 4), whereas a production of 464 L biogas.kg⁻¹ VS was achieved. Pellera and Gidarakos [15] reported a methane production of 259 L CH₄.kg⁻¹ VS for olive residues; Fabbri et al. [16] indicated an average of 169 L CH₄.kg⁻¹ VS for grape marc and Dinuccio et al. [17] presented values of 218, 229 and 195 L CH₄.kg⁻¹ VS for tomato, barley and rice residues, respectively. In this study values higher than those obtained in similar studies were achieved using other agroindustry residues. Proving that the kiwi residue has adequate characteristics for the anaerobic digestion process, the energy recovery is of extreme interest.
Figure 2. Biogas production as a function of the initial conditions.

Figure 3. Production of biogas and methane.
Based on the results from Eriksson [18], the volume of biogas generated in the process was converted into the corresponding volume of natural gas, taking into account the calorific value of methane (5.7 kWh.Nm⁻³). For this purpose, the highest biogas volume generated (assay 2.1) was used, which means a methane production of 928 L.kg⁻¹ VS (1628 L biogas.kg⁻¹ VS, 57% CH₄). For natural gas, the energy content is 11 kWh.Nm⁻³ [18]; considering the value 0.0688 € of kWh in the domestic market, this corresponds to a value of 0.76 € per Nm³ of natural gas. Considering the energy content of the biogas with 57% CH₄ (1 Nm³ biogas with 97% CH₄ = 9.67 kWh, [18]), in comparison with natural gas, one obtains a value of 0.39 € Nm⁻³ of biogas. Considering the VS content of kiwi (16% by mass), a monetary income of 102 € is obtained per ton of residue.

**Table 3.** Production and quality values of CH₄ for different residues.

| Substrate Type          | L CH₄.kg⁻¹ VS | % CH₄ in biogas | Reference |
|-------------------------|--------------|----------------|-----------|
| Grape marc              | 169          | 51             | [16]      |
| Barley                  | 229          | 60             | [17]      |
| Citrus fruit            | 176          | 57             | [19]      |
| Grass clippings         | 226          | 61             | [20]      |
| Cattle manure           | 68           | 44             | [20]      |
| Fruits and vegetables   | 430          | 61             |           |
| Orange residue          | 658          | 62             | [1]       |
| Corn residue            | 317          | 68             | [17]      |
| Olive residue           | 259          | 81             | [15]      |
| Urban solid residues    | 350          | 64             | [21]      |
| Cotton stalks           | 242          | 55             | [22]      |
| Tomato residue          | 218          | 70             | [17]      |
| Kiwi residue            | 928          | 57             | This study|
| Kiwi residue            | 464          | 85             | This study|

**Figure 4.** Volume of biogas and percentage of methane.
Several authors have directed their research towards the recovery of waste either focused on energy production, or aiming at solving the environmental problems caused by wastes of different types and origins. In Table 3 are presented values of methane production and biogas quality for different types of waste, including the most favourable results obtained in this study. As can be seen, the range of methane volume generated in the anaerobic digestion process is wide, and the value obtained in this study is very satisfactory (931 L CH₄.kg⁻¹ VS). Some authors reported methane percentages above 50%, a value considered as a starting point to make energy recovery economically interesting. In this study, one of the trials (10.3) provided a very significant value, around 85%.

4. Conclusions
Out of the 10 experiments carried out, two of them led to very interesting results in relation to the available data in literature; the test with 1% of substrate (experiment 2) yielded a biogas production of 1628 L.kg⁻¹ VS with 57% CH₄ and the highest quality of the biogas (85% CH₄) was obtained using 5% of kiwi residue (experiment 10.3). The experiments designed to evaluate the effect of the C: N ratio were the least fruitful, possibly due to the inhibition of the activity of the microbial population by KNO₃. The quality of the inoculum proved to be determinant in a set of tests, namely when collected in winter, when the digester operates at lower temperature. According to the most favourable conditions for the production of biogas, a gross monetary income of 102 € can be obtained per tonne of kiwi residue, solving the problem posed by the elimination of this residue while recovering energy.

Acknowledgment
This work was financially supported by: Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia.

References
[1] A. P. Sanjaya, M. N. Cahyanto, and R. Millati, “Mesophilic batch anaerobic digestion from fruit fragments”. Renewable Energy, vol. 98, pp. 135–141, 2016.
[2] S. Nanda, J. Isen, A. K. & L Dalai, and J. A.Kozinski, “Gasification of fruit wastes and agro-food residues in supercritical water”. Energy Conversion and Management, vol. 110, pp. 296–30, 2016.
[3] S. Kumar, N. Nimchuk, R. Kumar, J. Zietsman, T. Ramani, C. Spiegelman, and M. Kenney, “Specific model for the estimation of methane emission from municipal solid waste landfills in India”. Bioresource Technology, vol. 216, pp. 981–987, 2016.
[4] X. Fonoll, S. Astals, J. Dosta, and J. Mata-Alvarez, “Anaerobic co-digestion of sewage sludge and fruit wastes: Evaluation of the transitory states when the co-substrate is changed”. Chemical Engineering Journal, vol. 262, pp. 1268-1274, 2015.
[5] Y. Wu, C. Wang, X. Liu, H. Ma, J. Wu, J. Zuo, and K. Wang, “A new method of two-phase anaerobic digestion for fruit and vegetable waste treatment”. Bioresource Technology, 211, 16-23. 2016.
[6] M. Piatek, A. Lisowski, A. Kasprycka, and B. Lisowska, “The dynamics of an anaerobic digestion of crop substrates with an unfavourable carbon to nitrogen ratio”. Bioresource Technology, vol. 216, pp. 607–612, 2016.
[7] X. Fonoll, S. Astals, J. Dosta, and J. Mata-Alvarez, “Anaerobic co-digestion of sewage sludge and fruit wastes: Evaluation of the transitory states when the co-substrate is changed”. Chemical Engineering Journal, vol. 262, pp. 1268-1274, 2015.
[8] C. Zhao, H. Yan, H. Liu, R. Zhang, C. Chen, and G. Liu, “Bio-energy conversion performance, biodegradability, and kinetic analysis of different fruit residues during discontinuous anaerobic digestion”. Waste Management, vol. 52, pp. 295-301, 2016.
[9] E. A. Scano, C. Asquer, A. Pistis, L. Ortu, V. Demontis, and D. Cocco, “Biogas from anaerobic
digestion of fruit and vegetable wastes: Experimental results on pilot-scale and preliminary performance evaluation of a full-scale power plant”. *Energy Conversion and Management*, vol. 77, pp. 22-30, 2014.

[10] L. Zhang, Y. Lee, and D. Jahng, “Anaerobic co-digestion of food waste and piggery wastewater: Focusing on the role of trace elements”. *Bioresource Technology*, vol. 102, pp. 5048-5059, 2011.

[11] V. N. Gunaseelan, “Biochemical methane potential of fruits and vegetable solid waste feedstocks”. *Biomass and Bioenergy*, vol. 26, pp. 389-399, 2004.

[12] APHA. Standard Methods for the examination of water and wastewater. American Public Health Association, American Water Works Association, *Water Environmental Federation*, 20th Edition, Washington, 2012.

[13] K. Buchauer, “A comparison of two simple titration procedures to determine volatile fatty acids in influents to wastewater and sludge treatment processes”. *Water S. A*, vol. 24 (1), pp. 49-56, 1998.

[14] S. Fiore, B. Ruffino, G. Campo, C. Roati, and M. C. Zanetti, “Scale-up evaluation of the anaerobic digestion of food-processing industrial wastes”. *Renewable Energy*, vol. 96, pp. 949-959, 2016.

[15] F. Pellera, and E. Gidarakos, “Effect of substrate to inoculum ratio and inoculum type on the biochemical methane potential of solid agroindustry waste”. *Journal of Environmental Chemical Engineering*, vol. 4(3), pp. 3217–3229, 2016.

[16] A. Fabbri, G. Bonifazi, and S. Serranti, “Micro-scale energy valorization of grape marc in winery production plants”. *Waste Management*, vol. 36, pp. 156–165, 2015.

[17] E. Dinuccio, P. Balsari, F. Gioelli, and S. Menardo, “Evaluation of the biogas productivity potential of some Italian agro-industrial biomasses”. *Bioresource Technology*, vol. 101, pp. 3780-3873, 2010.

[18] O. Eriksson, “Environmental technology assessment of natural gas compared to biogas”. *Natural Gas*, Primož Potocnik (Ed.), pp. 127-146, 2010.

[19] H. Su, F. Tan, and Y. Xu, “Enhancement of biogas and methanization of citrus waste via biodegradation pretreatment and subsequent optimized fermentation”. *Fuel*, vol. 181, pp. 843-851, 2016.

[20] T. G. Poulsen, and L. Adelard, “Improving biogas quality and methane yield via co-digestion of agricultural and urban biomass wastes”. *Waste Management*, vol. 54, pp. 118-125, 2016.

[21] L. Martin-Gonzalez, L. F. Colturato, X. Font, and T. Vicent, “Anaerobic codigestion of the organic fraction of municipal solid waste with FOG waste from a sewage treatment plant: Recovering a wasted methane potential and enhancing the biogas yield”. *Waste Management*, vol. 30, pp. 1854-1859, 2010.

[22] M. Adl, K. Sheng, and A. Gharibi, “Technical assessment of bioenergy recovery from cotton stalks through anaerobic digestion process and the effects of inexpensive pre-treatments”. *Applied Energy*, vol. 93, pp. 251-260, 2012.