Seasonal variation of the biochemical methane potential of fruit and vegetable wastes produced in the Mediterranean area.

A. Kalogiannis[1], I.A. Vasiliadou[1], K. Stamatelatou[1]*

[1]Department of Environmental Engineering, Democritus University of Thrace, Xanthi, Greece

*corresponding author: K. Stamatelatou

e-mail: astamat@env.duth.gr

Abstract Fruit and vegetable wastes produced massively in open markets are a suitable feedstock for biogas production and digestate of high fertilizing value. A first step of designing anaerobic digestion systems for treating these wastes efficiently is to study the impact of the seasonal variation on the biochemical methane potential. Moreover, during mechanical pretreatment applied to reduce the size of the waste mixtures, several fractions derive which affect the rate of the methane production as well as the ultimate methane yield. Fractionation of the chopped wastes through sieving resulted in fractions of different parts of wastes and size, affecting the initial rate and the ultimate methane yield. It was found that the smaller fraction yielded methane at an initial higher rate but at lower ultimate value than the larger fraction. These results were consistent in all waste mixtures chosen to represent the typical composition of the organic fraction of wastes generated in open market in autumn/winter, spring and summer. In all cases examined the BMP of these wastes varied between 360 and 527 NmL CH_4 g VS^{-1} with an average value of 436±51 NmL CH_4 g VS^{-1}.

Keywords: biogas, fruit and vegetable wastes, Mediterranean, open markets

1. Introduction

The open markets (also known as farmer or public markets) are a popular form of trading among farmers or traders and customers, especially in the Mediterranean area (Ochoa et al 2020). This type of Food Supply Chain is characterized as Short (SFSC) and shows increasing trend (Pensado-Leglise and Smolski, 2017). The wastes generated from this activity contain leaves and whole vegetables and fruits unused or spoiled (Food and Vegetable Wastes; FVW). Open markets generate several tonnes per day of such wastes which are perfect feedstocks for biogas production through anaerobic digestion (AD). The digestate, as a by-product of the AD, is ideal for its fertilizing value due to the absence of pathogens (found mostly in manures or food wastes containing meat and fish residues) and pharmaceuticals. Therefore, exploring schemes for the valorization of FVW from open markets where they are massively produced could be important for promoting the circular economy locally. The first step of this effort is to evaluate the Biochemical Methane Potential (BMP) of FVW and the effect of the seasonal variation as well as the size of the waste particles.

There are few studies focusing on the effect of the seasonal variation on BMP of FVW (Edwiges et al, 2018), and moreover, they do not take into account the size these wastes are chopped to, which may be critical to determine the rate of methane production. The present study is part of a concerted effort to assess the BMP of FWW mixtures produced in the open markets of Tunisia and Jordan as typical Mediterranean countries in the framework of CEOMED project (Papirio et al 2021).

2. Materials and methods

2.1. Waste's collection and characterization

The composition of FVW was determined based on the wastes produced from the municipal open markets in Jordan and Tunisia (Papirio et al 2021) and was classified in three mixtures (Figure 1) to represent the seasonal variation, namely Autumn/winter season (S1), Spring season (S2) and Summer season (S3). The FVW were simulated via fruits and vegetables purchased from local markets, located in Xanthi city (Greece) and mixed together, in order to maintain the composition depicted in Figure 1.

Initially, FVW of each season were chopped and sieved through 10 mm and 4 mm sieves successively. It was necessary to used 400 mL of water facilitate the process. This procedure was also repeated using only the 10 mm sieve. For this study, the two fractions obtained from the successive sieving (4-10 mm and <4 mm) were used and compared with the larger fraction (<10 mm) obtained from the one step sieving. The size distribution on a dry weight basis of each mixture after the sieving process, is shown in Figure 2.

2.2. BMP test preparation

In order to evaluate the Biochemical Methane Potential (BMP) of the three seasonal waste mixtures, samples of the fractions 4-10 mm and <4mm, as well as of the larger (0-10 mm), were separately digested in batch anaerobic reactors. The reactors were borosilicate glass bottles of different volumes: i) total volume 595 mL and working volume 420 mL for the 4-10 and 0-10 mm fractions and ii) total volume 295 mL and working volume 226 mL for the <4 mm fraction. All BMP tests were performed in triplicate at 37°C. The larger and smaller reactors were inoculated with 400 and 200 mL of sewage sludge each. The inoculum was taken from a wastewater treatment plant, located in the wider area of Alexandroupoli city (Greece) and contained 6-9 gVS L^{-1}. The inoculum had been kept for about 5 days before the inoculation at 37°C for degassing. The waste fractions were mixed with the inoculum to achieve a loading of 0.5 gVS_{waste} g^{-1} $VS_{inoculum}$. Blank tests, containing only the inoculum and water to reach the same final volume, were also set up. There was no addition of macro elements or trace elements during BMP tests. Degasification of the reactors with N_2/CO_2 mixture (80/20) was carried out for 1 min to obtain anaerobic conditions and the reactors were sealed with rubber stoppers. The headspace of each reactor was connected with a NaOH (6N) displacement apparatus to trap CO_2. Methane production was monitored via the volume displacement method and was expressed at Standard Temperature (0°C) and Pressure (1 atm) conditions (STP). In all cases, the methane volume produced from the blank tests was subtracted to exclude the interference of the inoculum in each BMP test.

2.3. Analytical methods

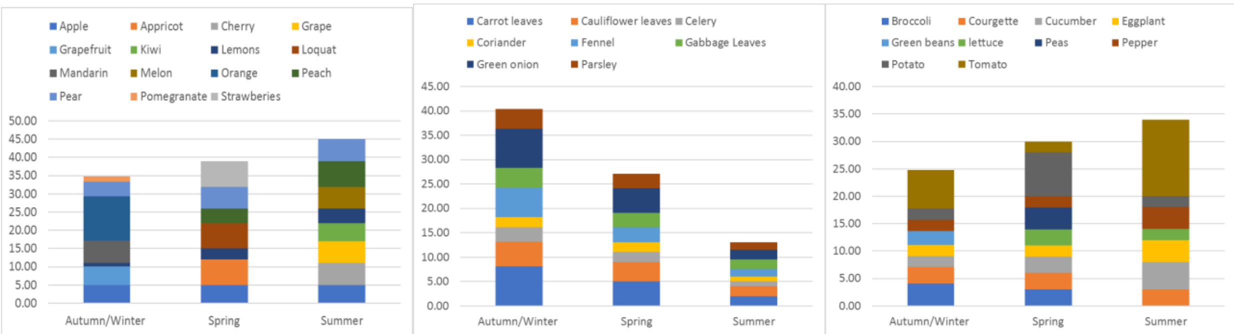
Samples of all fractions were dried (105ºC) and milled to analyze the total Chemical oxygen demand (COD), Total Kjeldahl nitrogen (TKN) and total carbohydrates. Total solids (TS), Volatile solids (VS), COD and TKN were measured according to standard methods (APHA 1999), while carbohydrates were determined following the anthrone method as developed by Hansen and Møller (1975) and Juranović et al. (2011). Analysis was performed in triplicate.

2.4 Calculations

The averages and standard variations were determined on a three-sample basis for each measurement (including the BMP). The methane yield expressed per COD mass added was calculated by dividing the BMP (expressed per g VS) with the COD content (expressed per g VS). Regarding the calculation of the standard deviation, the error propagation was taken into account by applying the following equation (Bevington and Robinson 1992):

$$\mathrm{SD_{BMP/COD}} = \mathrm{AV_{BMP/COD}}\sqrt{\left(\frac{SD_{BMP}}{AV_{BMP}}\right)^2 + \left(\frac{SD_{COD}}{AV_{COD}}\right)^2}$$

where SD: standard deviation and AV: average



(a) (b) (c)

Figure 1. Percentage variation of (a) fruit and (b-c) vegetable mixtures representing the typical wastes from the open markets of the Mediterranean area.

(a) (b) (c)

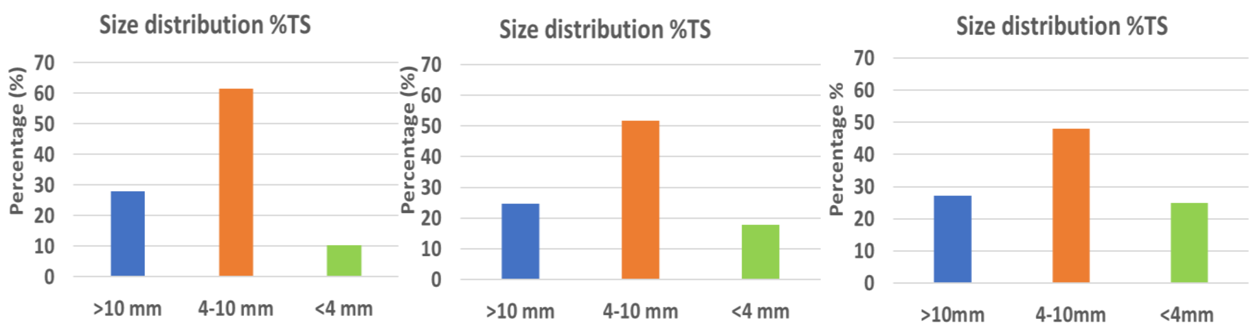
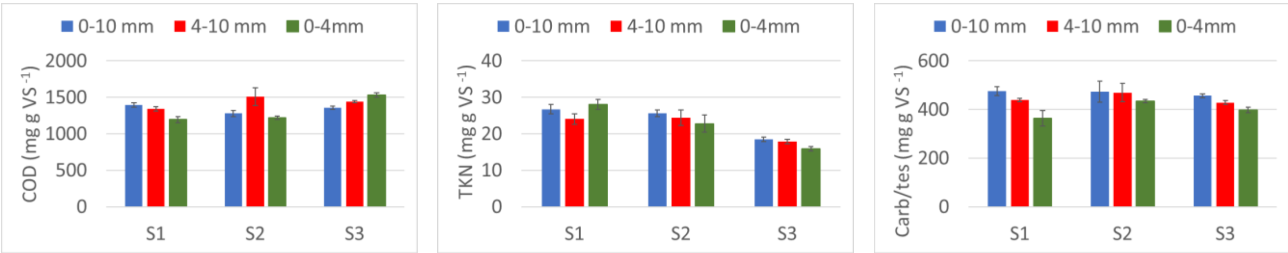


Figure 2. Size distribution considering dry weight of each mixture after sieving process for (a) Autumn/winter season (S1), (b) Spring season (S2) and (c) Summer season (S3).

3. Results and discussion

The composition variation as depicted in Figure 1 shows that fruits and vegetables are dominant in summer (Figure 1a and 1c), while the leafy vegetables prevail in the autumn/winter seasons (Figure 1b). This differentiation seems to affect the TKN content but not the total COD or carbohydrates (Figure 2). However, Papirio et al (2021) showed that the extractable carbohydrates are higher in the summer waste mixtures which is probably attributed to the higher proportion of fruits during this season. Reducing the size of wastes does not result in a mixture of uniform size. On the contrary, different size fractions are generated through chopping which have different characteristics. Regarding the fraction size effect, it seems that the smaller fraction (0-4 mm) contains less TKN and total carbohydrates than the larger one (4-10 mm). This indicates that fractionation of the waste material does not only result in the separation of the waste into different particle sizes but also into different types of wastes; indeed, visual observation of the two fractions proved that the smaller fraction contained mostly small leaves, seeds from the fruits and juice from cutting the FVW. On the other hand, the larger fraction consisted of pieces of the FVW. In most cases the characteristics of the whole fraction (0-10 mm) resembles the characteristics of the larger fraction (4-10 mm). This can be correlated with the fact that the fraction of 4-10 mm constitutes the largest part after chopping (Figure 2) for all three waste mixtures. However, it should be stressed that there was an extra degree of uncertainty due to the chopping and sieving procedures which was not taken into account, since all triplicates came from the same chopping/sieving process.



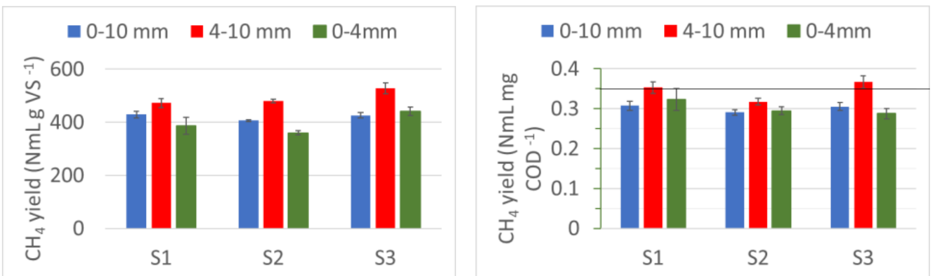
(a) (b) (c)

Figure 3. (a) COD, (b) TKN and (c) carbohydrate content of various fractions of FVW collected during Autumn/winter (S1), Spring (S2) and Summer (S3) from the open markets of the Mediterranean area.

There was no appreciable difference in the BMP of the wastes at each season, but it is obvious that the larger fraction (4-10 mm) exhibited higher yield (493±14.6 NmL CH_4 g VS^{-1}) than the smaller fraction (0-4 mm) in all three seasons (395±19.0 NmL CH_4 g VS^{-1}) (Figure 4a). On the other hand, the BMP of the 0-10 fractions was at similar level regardless the season (420±8.9 NmL CH_4 g VS^{-1}). It should be noted that the values of BMP determined in the present study are in good agreement with the ones measured by Edwiges et al. (2018) ranging from 288 and 516 NmL CH_4 g VS^{-1}.

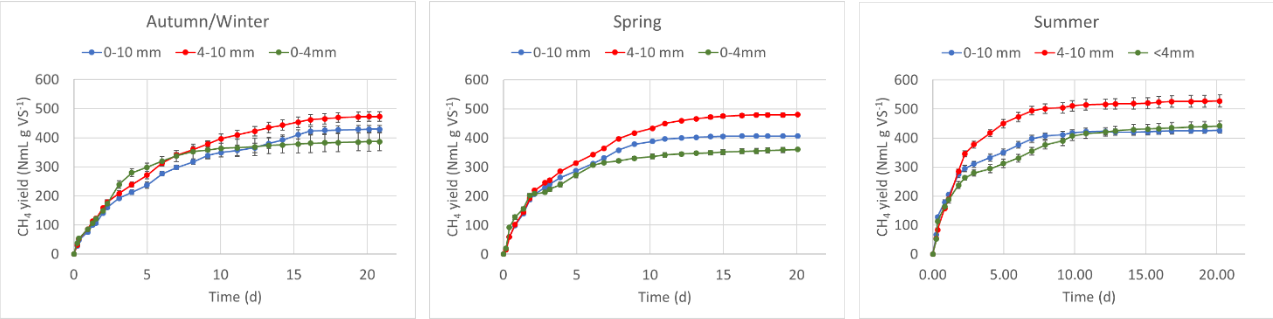
The BMP was normalized to the COD added (Figure 4b) and it was compared to the maximum yield (0.35 NmL CH_4 mg COD^{-1}). It can be seen that all fractions were close to the maximum theoretical yield (meaning that there are highly biodegradable) and the highest yield was obtained from the fraction 4-10 mm. Specifically, the yields of the 0-10mm, 4-10 mm and 0-4 mm fractions were 0.301±0.01, 0.346±0.013, 0.302±0.017 NmL CH_4 mg COD^{-1} respectively).

Focusing on the BMP profiles (Figure 5), the 0-4 fraction exhibited a higher rate during the first 3 days (probably due to the smaller particulates and the soluble organic matter abundant in this fraction). However, in the course of the methane evolution during the tests, the rate was decreasing until it stabilized at a lower level compared to the 4-10 mm fraction). It seems that the smaller fractions contain component of the waste mixtures (such as leaves or seeds) which are less biodegradable or even inhibitory and counteract the initially higher rate of the methane production. These results were consistent in all waste mixtures studied. The 0-10 mm fraction which included both 0-4 and 4-10 fractions showed intermediate rates and ultimate yields, representing the average BMP profiles of the FVW after chopping to 10 mm.



(a) (b)

Figure 4. Methane yield in terms of (a) VS and (b) COD added of various fractions of FVW collected during Autumn/winter (S1), Spring (S2) and (c) Summer (S3) from the open markets of the Mediterranean area.



(a) (b) (c)

Figure 5. Methane yield of various fractions of FVW collected during (a) Autumn/winter (S1), (b) Spring (S2) and (c) Summer (S3) from the open markets of the Mediterranean area.

4. Conclusions

The reduction of the size of wastes does not result in a uniform size. It seems that when reducing the size of FVW, leaves, seeds and the aqueous phase end up in smaller size fraction which exhibits higher initial methane rates, but smaller ultimate yields, probably due to the lower biodegradability or inhibitory properties of some of its components. On the other hand, the larger fraction is more biodegradable. As a whole, the FVW ranging from 0 to 10 mm seem to be highly biodegradable reaching 420±8.9 NmL CH_4 g VS^{-1} or 0.301±0.01 NmL CH_4 mg COD^{-1}. The standard deviation expresses the seasonal variation due to the different composition of the FVW during the year. The average methane yield of the FVW regardless of the size or the seasonal mixture was estimated to be 436±51 NmL CH_4 g VS^{-1}.

Acknowledgements: The CEOMED project (ref.: A_B.4.2_0058) is co-financed by EU ENI CBC Mediterranean Sea Basin Programme, under the Priority B.4.2 - Reduce municipal waste generation and promote the source-separated collection and the optimal exploitation of its organic component of the Thematic Objective B.4 - Environmental protection, climate change adaptation and mitigation (Address common challenges in the environment).

References

Abudi, Z. N., Hu, Z., Sun, N., Xiao, B., Rajaa, N., Liu, C., et al. (2016). *Batch anaerobic co-digestion of OFMSW (organic fraction of municipal solid waste), TWAS (thickened waste activated sludge) and RS (rice straw): influence of TWAS and RS pretreatment and mixing ratio*. Energy 107, 131-140. doi: 10.1016/j.energy.2016.03.141

APHA, AWWA, WEF, 1999. *Standard Methods for the Examination of Water and Wastewater*, twentieth ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Bevington, P. R. and D.K. Robinson, D. K. (1992) Data Reduction and Error Analysis for the Physical Sciences, WCB/McGraw-Hill Boston USA, p.328.

Edwiges T., Frare L. Mayer B. Lins L., Triolo J.M. Flotats X. Costa M.S. (2018). *Influence of chemical composition on biochemical methane potential of fruit and vegetable waste*. Waste Management, 71 618–625.

Filer, J., Ding, H.H., Chang, S., (2016) Biochemical Methane Potential (BMP) Assay Method for Anaerobic Digestion Research. Water 11, 921; doi:10.3390/w11050921

Hansen J, Møller IB, (1975). *Percolation of starch and soluble carbohydrates from plant tissue for quantitative determination with anthrone.* Anal Biochem 68: 87-94.

Juranović Cindrić I., Kunštić M., Zeiner M., Stingeder G., Rusak G., (2011). *Sample Preparation Methods for the Determination of the Antioxidative Capacity of Apple Juices.* Croatica Chemica Acta 84(3):435-438

Ma, J., Duong, T. H., Smits, M., Vestraete,W., and Carballa, M. (2011). *Enhanced biomethanation of kitchen waste by different pretreatments.* Bioresour. Technol. 102, 592-599. doi: 10.1016/j.biortech.2010.07.122

Owen, W.F., Stuckey, D.C., Healy, J.B., Young, L.Y., McCarty, P.L. (1979) *Bioassay for Monitoring Biochemical Methane Potential and Anaerobic Toxicity.* Water Res. 13, 485-492.

Papirio S., Esposito G., Fermoso F.G., Frunzo L, Kalogiannis A., Kassab G., Khoufi S., Scotto di Perta E., Sayadi S., Stamatelatou K., Trujillo Reyes A. (2021). Exploring the biochemical methane potential of open market waste from Jordan and Tunisia for a future scale-up of anaerobic digestion in Amman and Sfax. 8th ınternatıonal conference on sustaınable solıd waste management. 23-26 june 2021, Thessalonıkı, Greece