ORANGE PEEL: ORGANIC WASTE OR ENERGETIC RESOURCE?

Martín M.A.[1*], Siles J.A.[1], El Bari H.[2], Chica A. F.[1], Martín A.[1]
[1] Chemical Engineering Department, University of Cordoba. Campus de Rabanales, Ctra. N-IV, km 396, edificio Marie Curie (C-3), planta baja. CP/ 14071. Cordoba, Spain.
[2] LABEG. Université Ibn Tofail. Faculté dos Sciences. Kenitra (Maroc).
*Corresponding autor: Tel: +34 957218586. Fax: +34 957 218625. Email: iq2masam@uco.es

1 INTRODUCTION

Orange juice is one of the most widely-consumed beverages today. Consequently, the cultivation of oranges has become a major industry and an important economic sector in the United States and most Mediterranean countries. A high percentage of orange production (70%) is used to manufacture derivative products and approximately 50–60% of the processed fruit is transformed into citrus peel waste (peel, seeds and membrane residues) (Wilkins et al., 2007a). In order to prevent problems related to the disposal of this product and environmental concerns, this waste must be properly processed. Until relatively recently orange peel has just been utilized as raw material in the manufacture of cattle feed or simply burnt (Higher caloric power: 4545 kcal/kg dry matter). However, these processes generate highly polluted wastewater given that the previous pressing stage requires the addition of binder. Anaerobic digestion, in which both pollution control and energy recovery can be achieved, is an interesting way to treat and revalorize abundant orange peel waste. This process is defined as the biological conversion of organic material to a variety of end products including ‘biogas’ whose main constituents are methane (65-70%) and carbon dioxide (Wheatley, 1990). Nevertheless, citrus peel contains essential oils (90% D-Limonene) which are well-known antimicrobial agents that may cause upset or failure of anaerobic digesters. In addition, essential oils are employed in the manufacture of food and medicines as flavoring agents, cosmetics and domestic household products (Braddock et al., 1986). The aim of this study was to determine the most suitable conditions to carry out anaerobic digestion of orange peel waste after a pre-treatment to extract D-Limonene. The methane yield coefficient ($Y_{CH4/S}$), organic loading rate (OLR) and biodegradability were determined at pilot scale using a continuous stirred-tank reactor (CSTR) operating in semi-continuous mode and under thermophilic conditions.

2 MATERIALS AND METHODS

2.1 Experimental set-up and procedure

The experimental set-up used at laboratory scale consisted of two 3.5-liter CSTR connected to a thermostatic jacket containing glycerol which allowed maintaining the reactors temperature (35ºC for mesophilic experiments and 55ºC for thermophilic assays). All of the experiments were carried out in batch mode. The volume of methane produced during the process was measured after removing the CO_2 contained in the biogas. At pilot scale, a 3200-liter CSTR working in semi-continuous mode was utilized. The temperature was maintained at 55ºC by means of an electrical thermostatic jacket. Biogas was transported to a condenser to remove the moisture and it was then quantified by using a flow meter.

The orange peel used as substrate derived from the orange juice manufacturing processes carried out at the Companies Cítricos del Andévalo (Spain) and CITRUMA (Morocco), showing similar characteristics in both cases. The peel was chopped until obtaining a final particle size of < 2 mm and it was then steam distilled at laboratory scale to reduce the concentration of D-Limonene and to ensure the stability of the anaerobic process. Distillation time varied from 0 to 6 hours and the ratio of water to chopped orange peel waste was fixed at 6:1 (w/w). Table 1 shows the chemical composition of orange peel before and after steam distillation.

The innoculum were selected on the basis of their high methanogenic activity, showing values ranging from 0.87 to 0.99 g COD/g volatile suspended solid (VSS)·d for mesophilic bacteria and 0.98-1.09 g COD/g VSS·d for thermophilic microorganisms. The experiments at laboratory scale were carried out using an innoculum concentration of 12 g VSS/L, while it was fixed at 80 g volatile solids (VS)/L (8%) at pilot scale. The start-up was developed by adding a synthetic solution composed of glucose (50 g/L), sodium acetate (25 g/L) and lactic acid

(20.8 mL/L), over a 14-day period. Subsequently, the acclimatization was carried out by increasing the added load with pretreated orange peel waste to 2 g VS/L over a 16-day period at laboratory scale. Once this preliminary acclimatization step was completed, a series of batch mesophilic and thermophilic experiments were carried out using the pre-treated orange peel at a concentration of 2 g VS/L. Each assay lasted a maximum of 120 hours; the time interval required to completely biomethanize each load. The volume of methane was measured as a function of time and samples were taken and analyzed before and after feeding. At pilot scale, biomass acclimatization was carried out over a 30-day period by increasing the organic loading rate (OLR) from 0.44 to 1.20 kg COD/m^3·d. The reactor was fed in semi-continuous mode three times per day and the hydraulic retention time was fixed at 25 days. Each load was carried out at least in duplicate and the results expressed as means.

All analyses were carried out in accordance with the Standard Methods of the American Public Health Association (APHA, 1989). D-Limonene concentration was determined according to the method suggested by Scott and Veldhuis (1966).

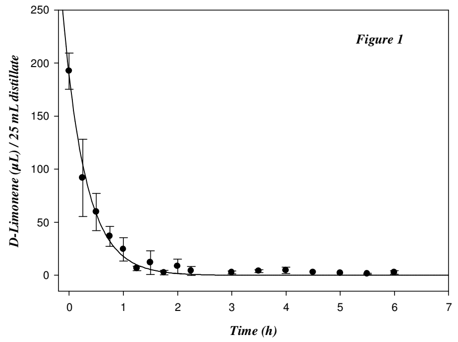
TABLE 1 **Chemical composition of orange peel waste before and after steam distillation.**

	Parameter	**Orange peel waste**	**Pre-treated orange peel waste**
Wet basis	pH	3.42 ± 0.02	3.41 ± 0.03
	VA (mg acetic acid/kg aqueous suspension)	1950 ± 27	220 ± 12
	Alkalinity (mg $CaCO_3$/kg aqueous suspension)	Under range (pH < 4.5)	Under range (pH < 4.5)
	Moisture (%)	79.83 ± 0.08	91.15 ± 0.01
	Total Solids (TS) (%)	20.17 ± 0.08	8.85 ± 0.01
	Mineral Solids (MS) (%)	0.87 ± 0.03	0.26 ± 0.05
	Volatile Solids (VS) (%)	19.31 ± 0.11	8.58 ± 0.05
Dry basis	COD (mg O_2/g)	1085 ± 55	1177 ± 46
	Total N (mg N/g)	12.24 ± 0.56	11.14 ± 0.04
	Kjeldahl N (mg N/g)	11.67 ± 0.24	9.66 ± 0.56
	Ammonia N (mg N/g)	1.68 ± 0.19	1.88 ± 0.20
	Total P (mg P/g)	1.18 ± 0.03	2.37 ± 0.03
	Cu (mg/kg)	Under range	13.3 ± 1.4
	Cr (mg/kg)	1.6 ± 0.7	3.0 ± 0.1
	Ni (mg/kg)	6.1 ± 1.3	6.2 ± 0.3
	Cd (mg/kg)	4.9 ± 0.8	5.8 ± 1.0
	Pb (mg/kg)	Under range	8.7 ± 1.3
	Zn (mg/kg)	4.5 ± 0.4	12.4 ± 1.1

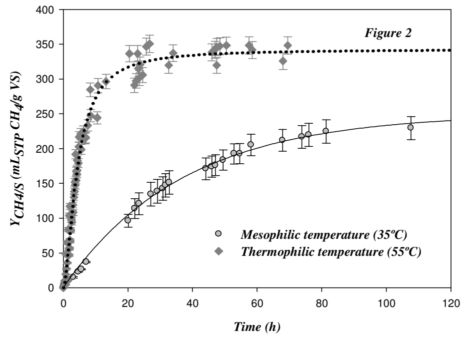
3 RESULTS AND DISCUSSION

3.1 D-Limonene extraction and anaerobic digestion viability

Figure 1a) shows the variation of the D-Limonene concentration in the distillate samples taken during the distillation time. As can be observed, the D-Limonene concentration in the distillate became stable after one hour, thus suggesting that, from the economical point of view, this is the most appropriate distillation time for reducing the concentration of D-Limonene in orange peel waste. Consequently, this time was fixed for the experiments at pilot scale. On the other hand, the D-Limonene removal yield achieved with this pretreatment for one hour was found to be 70%. Concretely, around 12.5% of the water initially added was necessary to achieve this yield, which is equivalent to an energy requirement of 1.7 kJ/g wet orange peel waste. These results are in line with those obtained by Wilkins et al. (2007b), who found that pre-treatment by steam explosion removed 90% of D-limonene in the orange peel. Figure 1b) shows the variation of methane yield coefficient from pre-treated orange peel waste under mesophilic and thermophilic conditions in batch mode and at laboratory scale. The methane yield coefficient at standard temperature and pressure conditions (STP) was found to be higher under thermophilic conditions (332 ± 17 mL_{STP} CH_4/g VS added) than at mesophilic temperature (230 ± 16 mL_{STP} CH_4/g VS added). Additionally, the mean rate was considerably different in both cases, being higher under thermophilic conditions (13.28 mL_{STP} CH_4/g VS added·h) than at the lowest temperature (1.92 mL_{STP} CH_4/g VS added·h). This justifies the election of thermophilic temperature as being the most suitable temperature for the anaerobic treatment of orange peel waste at pilot scale.



a)



b)

FIGURE 1 **a) Variation of D-Limonene concentration in the distillate versus time; b) Evolution of the methane yield coefficient from pre-treated orange peel under mesophilic and thermophilic temperature.**

3.2 Stability, organic loading rate (OLR) and biodegradability. Thermophilic conditions

The stability of the process at pilot scale was evaluated based on the evolution of the pH, alkalinity, volatile acidity (mg C_2/L) and volatile acidity/alkalinity ratio (VA/Alk). Table 2 shows the variation of OLR, biodegradability, pH, VA/Alk ratio and methane yield coefficient ($Y_{CH4/S}$) during the thermophilic anaerobic process. In summary, the OLR obtained values in the range of 1.20-3.67 kg COD/m^3·d under stable conditions and with a COD removal of 84-90 %, with 4 kg COD/m^3·d being the highest value that may be reached without acidification risk and the inhibition of methane production.

TABLE 2 **Variation of OLR, biodegradability, pH, VA/Alk ratio and $Y_{CH4/S}$ at pilot scale.**

	OLR (kg COD/m^3·d)	Biodegradability (%)	pH	VA/Alk (eq C_2/eq $CaCO_3$)	$Y_{CH4/S}$ (L_{STP} CH4/g COD)
Acclimatization	0.44-1.20	Nd	8.08 ± 0.19	0.38 ± 0.07	Nd
Set conditions	1.20-3.67	84-90	7.40 ± 0.20	0.22 ± 0.06	0.27-0.29
Acidification	3.67-5.1	63	6.80 ± 0.12	0.45 ± 0.07	0.09

3.4 Methane yield coefficient ($YCH_{4/S}$)

The generation of methane is of special interest as methane is a useful compound due to its caloric power (Lower Caloric Power): 35,793 kJ/m^3, equivalent to 9.96 kWh/m^3. Figure 2 shows the evolution of the methane yield coefficient with the organic loading rate during the thermophilic experiments at pilot scale. For OLR ranging from 1.20 to 3.67 kg COD/m^3·d, the yield remained relatively stable (around 0.27-0.29 L_{STP} CH_4/g COD added) (Table 2). On the other hand, for OLR in the range of 3.67-5.10 kg COD/m^3·d this variable decreased to 0.09 L_{STP} CH_4/g COD added as a consequence of the acidification process and the inhibition of the methanogenic bacteria.

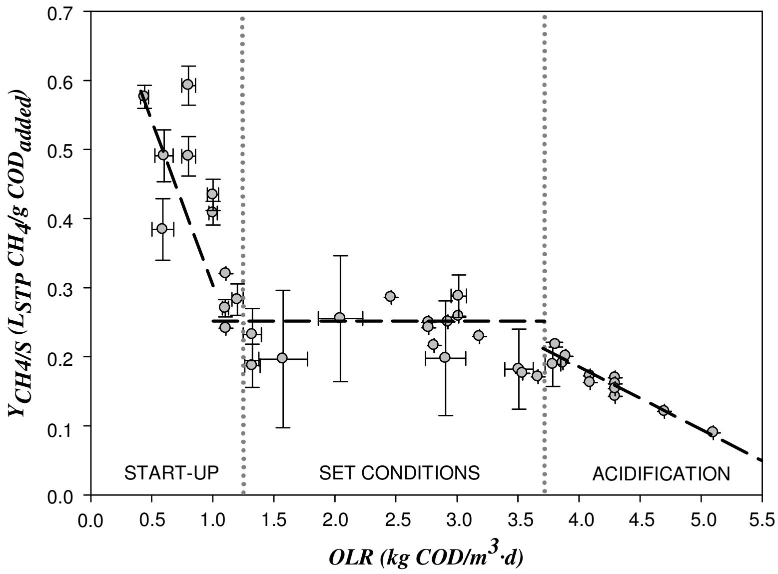


FIGURE 2 **Variation of the methane yield coefficient with the organic loading rate (OLR) during the thermophilic experiments at pilot scale.**

4 CONCLUSIONS

The results obtained through this research study reveal that, after a pre-treatment, orange peel waste derived from orange juice manufacturing has a high level of anaerobic biodegradability and that a substantial quantity of methane can be obtained this way. Additionally, the digestate may be use as a quality fertilizer. This technique provides an excellent opportunity for harnessing the economic benefits of this agri-industrial waste and for developing more efficient and sustainable systems.

ACKNOWLEDGEMENTS

The authors are very grateful to the Companies Cítricos del Andévalo S.A. (Huelva, Spain) and CITRUMA (Morocco) for funding this research. We also wish to express our gratitude to the Spanish Ministry of Science and Innovation for funding José Ángel Siles López through Project CTM2005-01293 and Grant BES-2006-14074. This study was co-financed by the European Social Fund.

REFERENCES

APHA (American Public Health Association) 1989. Standard Methods for the Examination of Water and Wastewater, 17th ed. Washington, DC, USA.

Braddock R J, Temelli F, Cadwallader K R 1986. Citrus essential oils - A dossier for material safety data sheets. Food Technol. 40 (11), 114-116.

Scott W C, Veldhuis M K 1966. Rapid estimation of recoverable oil in citrus juices by bromate titration. J. Assoc. Ofic. Anal. Chem. 49 (3), 628-633.

Wheatley A 1990. Anaerobic Digestion: A Waste Treatment Technology. Elsevier (ed.). London (UK).

Wilkins M R, Suryawati L, Maness N O, Chrz D 2007a. Ethanol production by *Saccharomyces cerevisiae* and *Kluyveromyces marxianus* in the presence of orange-peel oil. World J. Microbiol. Biotechnol. 23, 1161-1168.

Wilkins M R, Widmer W W, Grohmann K 2007b. Simultaneous saccharification and fermentation of citrus peel waste by Saccharomyces cerevisiae to produce ethanol. Proc. Biochem. 42 (12), 1614-1619.