

# Valorization of industrial orange waste towards biofuel production

D. Tsipiras, A. Christofi, E.M. Barampouti, S. Mai, D. Malamis

National Technical University of Athens, School of Chemical Engineering, Unit of Environmental Science & Technology, 9 Iroon Polytechniou Str., Zographou Campus, GR-15780 Athens, Greece

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## Introduction

According to Food and Agriculture Organisation, the total production of orange fruits in 2019 was 78.7 million metric tonnes following an increasing trend over the last decade. A large proportion up to 36% (Meneguzzo *et al*, 2019) is processed by industry. During orange industrial processing, half of the initial fruit mass ends up as waste (De la Torre *et al*, 2019). The largest proportion of this waste is the orange peels that correspond approximately to 44% of the fruit's mass while the rest consists of pulp, seeds, as well as, unprocessed fruits that do not match the quality criteria (Rezzadori *et al*, 2012). Common utilisation pathways of orange peel waste include animal feeding and burning. These methods can be described either as inefficient or uneconomical because valuable material is lost. The aim of the current study is the valorization of industrial orange waste towards biofuels such as bioethanol and biogas.

## Materials and Methods

### Raw materials

Orange industrial waste utilized in the present study was provided by the industrial facility of Aspis Hellenic Juice Industries, Argos, Greece. The orange waste was transferred to the Unit of Environmental Science and Technology (UEST), School of Chemical Engineering, National Technical University of Athens. Two different waste streams were examined; orange peel and pulp. These were dried and milled by a rotary drum dryer GAIA GC-100 and stored at room temperature conditions in sealed containers until use. The average particle size of the dried material used in the experiments was 1.4 mm.

Orange peel waste had the following composition (%w/w dry base): Volatile solids  $96.80 \pm 0.10$ , water soluble solids  $38.34 \pm 0.04$ , cellulose  $13.87 \pm 0.76$ , hemicellulose  $31.70 \pm 1.12$ , starch  $1.02 \pm 0.26$ , acid soluble lignin  $1.72 \pm 0.18$ , acid insoluble residue  $17.12 \pm 0.21$ , free sugars  $4.70 \pm 0.10$ .

Orange pulp waste had the following composition (%w/w dry base): Volatile solids  $97.15 \pm 0.05$ , water soluble solids  $22.41 \pm 0.10$ , cellulose  $24.86 \pm 2.07$ , hemicellulose  $33.76 \pm 1.33$ , starch  $3.16 \pm 0.46$ , acid soluble lignin  $3.55 \pm 0.12$ , acid insoluble residue  $19.90 \pm 0.17$ , free sugars  $1.69 \pm 0.05$ .

### Physicochemical Characterisation

Cellulose, hemicellulose, acid-soluble lignin, acid-insoluble residue, ash and moisture were measured following the analytical procedures of NREL laboratory analytical protocols (Sluiter *et al*, 2012). For the acid hydrolysis of starch, the technique 996.11 of the Association of Official Analytical Chemists (AOAC, 1995) was used. Glucose was estimated following the Glucose Oxidase–Peroxidase method via a commercial kit (Biosis SA). The concentration of ethanol in the liquor was estimated by the 2019.11 technique (AOAC, 1995).

### Enzymatic Hydrolysis

Enzymatic hydrolysis of each orange waste was performed in 250 mL autoclavable bottles. NaOH (2M) solution was used to correct the pH to the optimum pH range of 5.0-5.5. Enzymatic saccharification of cellulose was performed at 50°C by the addition of a cellulolytic formulation; Cellic CTec2 (Novozymes, Denmark) for 24h in an Incubator Shaker (IKA-KS 3000i). Dosages of 50, 150, 300 and 450  $\mu\text{L}_{\text{enzyme}}/\text{g}_{\text{cellulose}}$  were adopted.

### Alcoholic Fermentation

Bioconversion of the glucose produced to bioethanol via ethanolic fermentation was achieved by the addition of *Saccharomyces cerevisiae* (2% w/w) in the same autoclavable bottles, at 30°C for 24h. After the 24-hour fermentation period, the solid and liquid phases were separated by centrifugation (3500rpm for 10min) and were physicochemically characterized.

### Anaerobic Digestion

In line with Angelidaki *et al* (2009), biomethane potential tests (BMP) were executed in 250 mL autoclavable bottles aiming to assess the anaerobic digestibility of the raw and stillage orange peel/pulp. The bottles were inoculated with 50 mL inoculum and 50 mL nutrients medium. The inoculum was delivered from a full-scale anaerobic digester (Metamorfosis Wastewater Treatment Plant, Attica) treating municipal wastewater (5% TS). Furthermore, one positive sample containing inoculum, medium and 0.1 mL acetic acid, as well as, a blank sample containing only inoculum and medium were set as control samples. The bottles were put in a horizontal shaking water bath at 60 rpm and 36.6 °C. The biogas production was measured daily following the procedure proposed by Esposito (2012).

## Results and discussion

Two simplified flow diagrams (Fig.1, Fig.2) of the alternative valorization routes that summarise the results of the work, are presented for each orange waste.

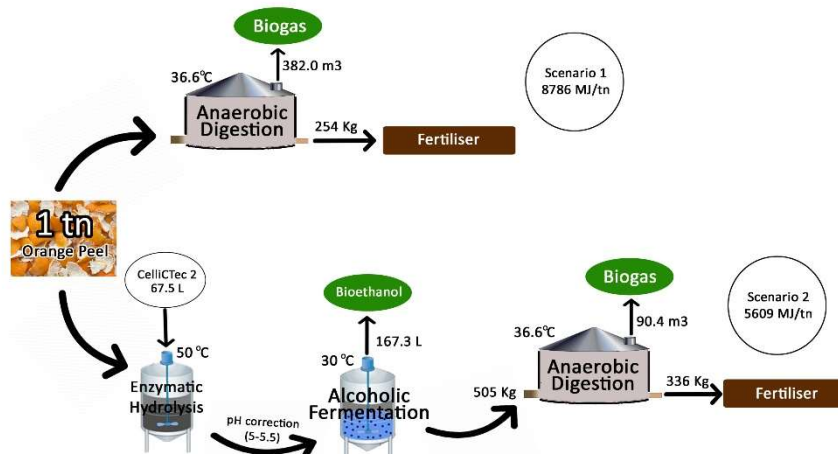


Fig. 1: Simplified flow diagram of the two alternative valorization routes of orange peel waste

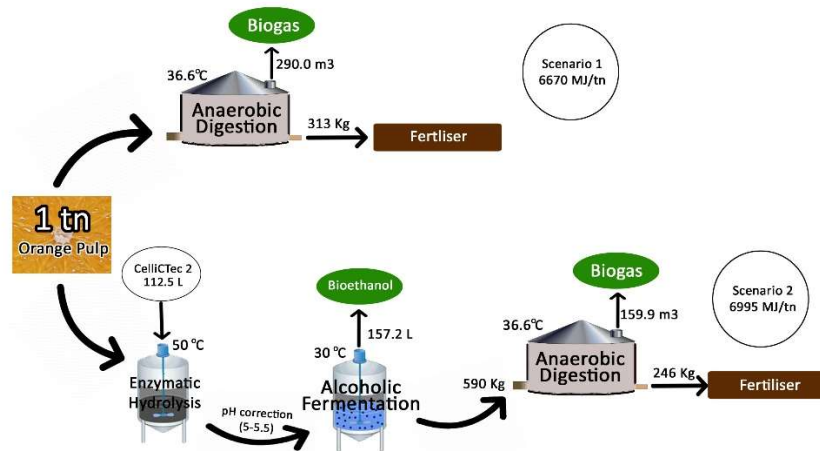


Fig. 2: Simplified flow diagram of the two alternative valorization routes of orange pulp waste

As presented in Fig.1, the best scenario regarding the maximisation of energy production and the minimisation of the final residue for the valorisation of orange peels is anaerobic digestion as a stand-alone procedure. One metric tonne of orange peels (Scenario 1) could produce 8786 MJ/tn of energy and 254 kg as a final residue.

Regarding orange pulp waste, the combination of the procedures is considered as the optimum solution both in terms of energy production, but also regarding the minimization of the final residue. Scenario 2 may result in 6996 MJ/tn total energy production and 246kg of residue.

### Conclusions

Conclusively, orange waste can be a promising feedstock in a biorefinery with great abundance across the globe. The different utilization pathways highlight the potential of orange peel and pulp waste to produce a variety of biofuels. Yet, there still exist numerous issues that should be addressed before the valorization of orange waste could reach full scale.

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