

# Hydrogen and Methane Production from Food Residue Biomass Product (FORBI)

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## Abstract

This study concerns the production of Hydrogen and Methane from a Food Residue Biomass (FORBI) product, generated from pre-sorted fermentable household waste in a (CSTR) and in a Periodic Anaerobic Baffled Reactor (PABR) respectively. FORBI is generated by drying and shredding the fermentable fraction of household food waste collected door-to-door in the Municipality of Halandri, Greece.

Hydrogen production from FORBI through anaerobic fermentation under acidogenic mesophilic conditions was carried out using a 4L CSTR, operated at 12 hrs HRT with an organic loading of 15 g TS/L. Volatile fatty acids, TSS, VSS, COD, dCOD, total and dissolved carbohydrates, pH and hydrogen content were evaluated. The H<sub>2</sub>-CSTR was operated for 40 days. During the operation of H<sub>2</sub>-CSTR the production of biogas reached up to 0.1026L<sub>biogas</sub>/g<sub>FORBI</sub> and the percentage of hydrogen in the gas up to 48.2 %.

The conversion of FORBI into methane was carried out through the operation of a 77L PABR operated under mesophilic methanogenic conditions at 10 days HRT and an organic loading of 10 g tCOD/L. TSS, VSS, COD, dissolved COD, pH, VFAs and methane were measured. The mean biogas production rate was 0.158L<sub>biogas</sub>/g<sub>FORBI</sub> and the mean methane percentage in the biogas was 70.34%.

**Keywords:** Methane, Hydrogen, Volatile Fatty Acids, Food Residue Biomass (FORBI) product, Anaerobic Fermentation.

## 1. Introduction

The generation and disposal of Municipal Solid Waste (MSW) is dramatically increasing in the recent years due to the rapid industrialization and modernization throughout the world. It is expected to reach 9.5 billion by 2050 (FAO, 2009). 30-50% of the MSW is food waste, 95% of which is ultimately landfilled. Fermentable food waste has a high carbon and nutrient content and is the major contributor to landfill methane emissions, but also presents a source for energy

recovery and biofuel production. In Europe, 88 million tons of food are wasted, with an overall cost estimated at 143 billion euros (FUSION, 2016; Breunig *et al.* 2017). Nevertheless, fermentable household waste is comprised of materials rich in sugars, minerals, and proteins that could be used for other processes as substrates or raw materials (FUSION, 2016; Pham *et al.* 2015). Anaerobic digestion and fermentation of food waste have been extensively studied in lab-scale bioreactors under mesophilic and thermophilic conditions (Ismail *et al.* 2009; Li *et al.* 2008; Pan *et al.* 2008; Zhan *et al.* 2016; Zhang 2007). However, little is known about the effectiveness of anaerobic digestion for methane (CH<sub>4</sub>) production and anaerobic fermentation for hydrogen (H<sub>2</sub>) production from previously dried and shredded food waste, .

The present work is in the framework of Waste4Think, a Horizon 2020 project, which proposes source separation and separate collection of the Fermentable Household Waste (FHW) in the Municipality of Halandri, followed by drying and shredding at the Municipality level, aiming to evaluate the generated product, called FORBI (Food Residue Biomass) as a potential feedstock for the production of biofuels, among various valorization alternatives. FORBI is a high quality homogenized and dry biomass product with a weight approximately 25% of the original food waste, which may be stored for prolonged periods of time without deterioration.

## 2. Materials and Methods

The measurements of dissolved and total chemical oxygen demand (COD), total (TS) and volatile (VS) solids, total alkalinity and temperature were carried out according to Standard Methods (APHA, 1995). Total carbohydrates were measured according to (Josefsson, 1983). The pH and conductivity were measured using a digital pH-meter (WTW INOLAB PH720) and conductivity meter (WTW INOLAB), respectively. The methane content of biogas was quantified indirectly using an experimental set-up in which CO<sub>2</sub> was absorbed by NaOH. The biogas production rate was measured using an oil displacement technique (Skiadas, and Lyberatos 1998).

### 2.1. Hydrogen production experimental procedure

In order to investigate the use of FORBI as feedstock for the production of biohydrogen through dark fermentation a Continuous Stirred Tank Reactor (CSTR) was used. The CSTR had a working volume of 4L and operated under anaerobic and mesophilic conditions (35°C).

During start-up, the CSTR was inoculated with 1 L of thermally treated (95°C for 15 minutes) activated sludge and was fed with an aquatic suspension of FORBI (15g FORBI/L). The bioreactor was started up in batch mode for 48 hrs (data not shown). It was then operated in a continuous mode with an HRT (hydraulic retention time) of 12 hours using the same aquatic suspension of FORBI. The CSTR operated without pH regulation.

During the experiment, liquid samples were taken at regular intervals for determination of pH, Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), and Volatile Fatty Acids (VFAs). The production of biogas was also measured.

### 2.2. Methane production experimental procedure

For the production of methane from FORBI a Periodic Anaerobic Baffled Reactor (PABR) was used.

The PABR is a high-rate anaerobic bioreactor, similar to the ABR (anaerobic baffled reactor), but it has the option of switching the feeding compartment (and consequently, the effluent compartment) periodically. In this way, the PABR flexibly adapts its dynamic behavior from full compartmentalization (zero switching frequency; the feed enters the bioreactor in a single compartment and the PABR behaves as an ABR) to single compartment behavior for high switching frequencies. This flexibility in adapting the

level of compartmentalization of the bioreactor allows the biomass to withstand fluctuations of the feed concentration and therefore culture adaptation is easier under varying conditions (Skiadas, and Lyberatos 1998; Reicher, 1998; Skiadas et al, 2000; Stamatelatou et al, 2009; Michalopoulos et al., 2016).

The PABR was initially operated with an HRT of 12.2d and a switching period (T) of 2d, with an influent tCOD of 7,250mg/L for an operation period of 86d (phase #1). After a steady periodic state was reached, the HRT was decreased to 10d and the mean influent tCOD was increased to 11,690mg/L for an operation period of 43d (phase #2). A solids/liquid separation step was used as pretreatment during phases #1 and #2, so as to keep the solids content of the feed low, a general requirement for high-rate bioreactors. Initially, FORBI was suspended in water and was vigorously stirred for 30 minutes. Then the slurry was filtered under pressure using a cloth filter. The liquid phase (filtrate) retained 36.4% of the organic content of the waste during phase #1 and 29.3% during phase #2. The solid phase collected was valorized for the production of compost (not shown here).

After a steady periodic state was reached, the HRT was decreased to 8.7d and the PABR was fed with a mean influent tCOD of 10,760mg/L (phase #3). During phase #3, the solids/liquid separation step was not used, in order to see if FORBI hydrolysis is fast enough to sustain a high-rate anaerobic digestion without solids separation.

During the experiment, gas and liquid samples were taken at regular intervals and biogas production, Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), pH, alkalinity, soluble and total COD were determined.

**Table 1.** Operating parameters for methane production

	Phase #1	Phase #2	Phase #3
Separation step	✓	✓	×
TSS <sub>feedstock</sub> (g/L)	1	1	10
HRT (d)	12.2	10	8.7
Switching period (d)	2	2	2
Influent tCOD (g/L)	7.25	11.69	10.76
Organic Loading Rate (g <sub>COD</sub> /L <sub>reactor</sub> /d)	0.59	1.17	1.23

## 3. Results and Discussion

### 3.1. Hydrogen production

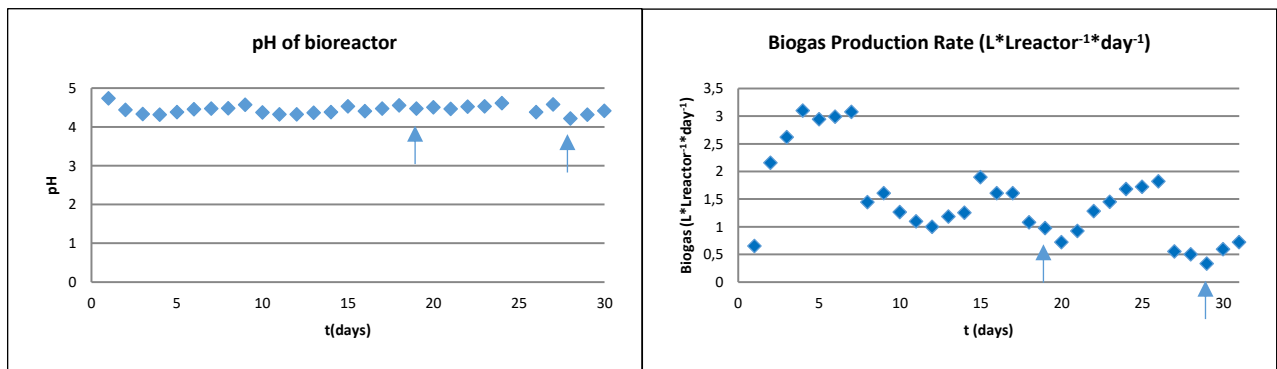
The CSTR was operated for 30 days. During the operation the production of biogas reached

0.1026L<sub>biogas</sub>/g<sub>FORBI</sub> and the percentage of hydrogen up to 48.2 %.

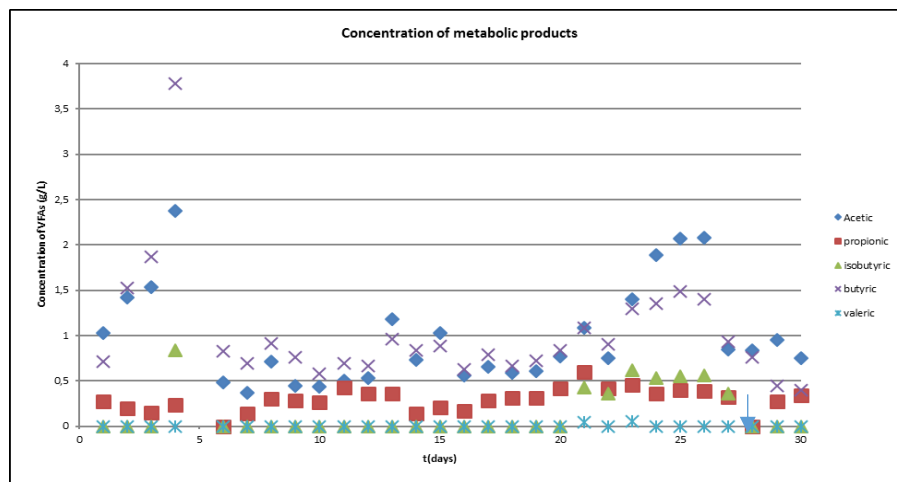
During the operation of bioreactor, the biogas production rate was not stable (Fig. 1b), despite the fact that the pH of the bioreactor remained 4.2-4.6 throughout the period (Fig. 1a). During the first 7 days the production rate of biogas increased from 0.65 L\*L<sub>bioreactor</sub><sup>-1</sup>\*d<sup>-1</sup> to 3.07 L\*L<sub>bioreactor</sub><sup>-1</sup>\*d<sup>-1</sup>. Afterwards,

it decreased significantly and was  $1.37 \text{ L} \cdot \text{L}_{\text{bioreactor}}^{-1} \cdot \text{d}^{-1}$  on the average for the rest of the period. The concentrations of the main metabolic products measured during the operation of the hydrogen producing reactor are presented in Fig.2. The dominant metabolic products were acetic and butyric acids, which are common for biohydrogen producing bioreactors (Alexandropoulou *et al.* 2016). The low concentrations of propionic acid indicate an efficient hydrogen production process, as the formation of propionate consumes hydrogen (Sivagurunathan *et al.* 2015; Guo *et al.* 2010).

The decrease of the biogas production rate after the 7<sup>th</sup> day of operation could be attributed to the consumption of hydrogen by hydrogen consuming microorganisms, such as homoacetogenic bacteria (Alexandropoulou *et al.* 2016). In order to eliminate these hydrogen consuming microorganisms, the bioreactor was purged with air for one hour using an air pump (arrows in figures 1a and 1b). After each purging, the biogas production rate increased significantly but not to the level observed in the beginning of the operation.



**Figure 1.** (a). pH of CSTR vs time, (b). Biogas production rate of CSTR vs time.



**Figure 2.** Concentration of metabolic products of H<sub>2</sub>-CSTR vs time.

### 3.2. Methane production

The PABR exhibited great stability during all three phases of the process. During the steady periodic state of phase#1 the mean tCOD removal rate was 89% (Fig.1b) with a mean effluent tCOD concentration of 872mg/L. The Volatile Solids remained below 0.5g/L in all four compartments of the PABR during the whole phase #1. The mean biogas production rate was

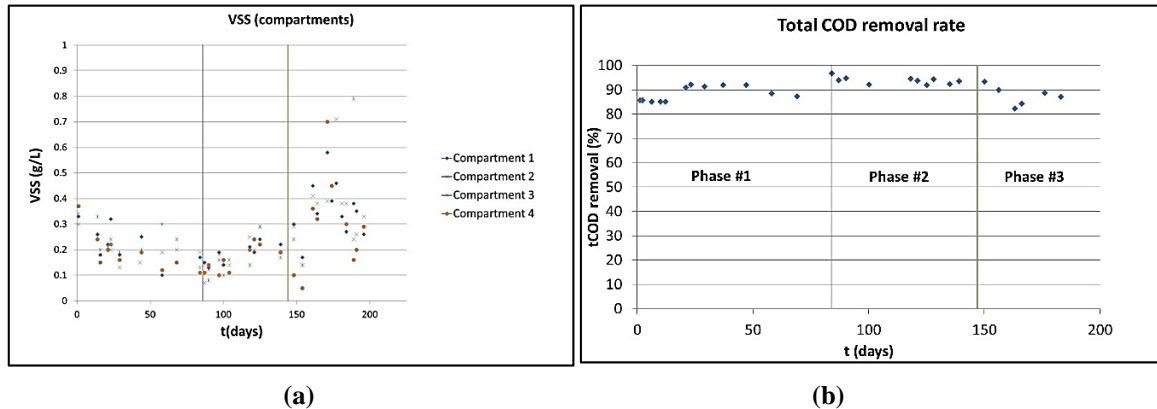
$0.158 \text{ L}_{\text{biogas}}/\text{g}_{\text{FORBI}}$  and the mean methane composition of the biogas was 70%.

During phase #2, the OLR almost doubled from  $0.59 \text{ g}_{\text{COD}}/\text{L}_{\text{reactor}} \cdot \text{d}^{-1}$  to  $1.17 \text{ g}_{\text{COD}}/\text{L}_{\text{reactor}} \cdot \text{d}^{-1}$ , by decreasing the HRT from 12.2d to 10d and by increasing the mean influent tCOD from 7.25mgO<sub>2</sub>/L to 11.69mgO<sub>2</sub>/L. The mean tCOD removal rate was 93.5% (Fig.1b) and the mean biogas production rate was  $0.11 \text{ L}_{\text{biogas}}/\text{g}_{\text{FORBI}}$ . The pH remained at optimum levels for methane

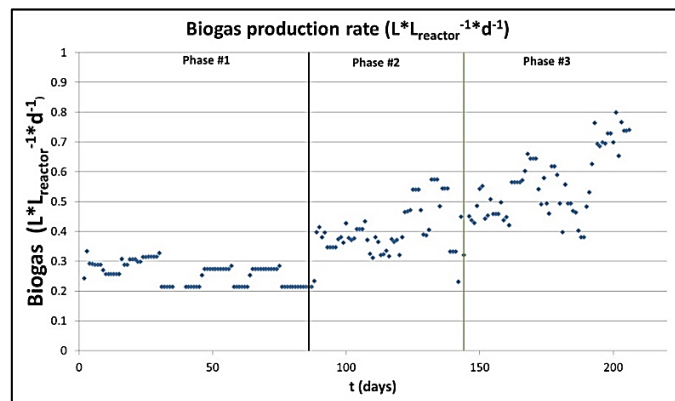
production in all four compartments of the reactor during phases #1 and #2. The mean methane composition of the biogas was 79%.

Subsequently, the HRT was decreased to 8.7d and the feedstock TSS concentration was increased to 10g/L (phase#3). During the steady periodic state of phase#3, the PABR responded effectively to the increase of the

organic loading rate and the TSS concentration (separation step not used) while no problems were observed by the high solids content. The mean tCOD removal rate was 85%. The exclusion of the solids/liquid separation step resulted in the increase of the mean biogas production rate to  $0.47L_{\text{biogas}}/g_{\text{FORBI}}$ . The mean methane composition of the biogas was 67.4%.



**Figure 3.** (a). Volatile Solids concentration vs time, (b). Total COD removal rate of PABR reactor vs time.



**Figure 4.** Biogas production rate of PABR reactor vs time.

#### 4. Conclusion

The present work concerns the production of Hydrogen and Methane from a Food Residue Biomass (FORBI) product, generated from pre-sorted fermentable household waste in a (CSTR) and in a Periodic Anaerobic Baffled Reactor (PABR) respectively. FORBI is generated by drying and shredding the fermentable fraction of household food waste collected door-to-door in the Municipality of Halandri.

The conversion of FORBI into hydrogen production reached up to  $0.1026L_{\text{biogas}}/g_{\text{FORBI}}$  and the

concentration of Hydrogen up to 48.2%. Respectively, for methane the mean biogas production rate was  $0.158L_{\text{biogas}}/g_{\text{FORBI}}$  and the mean methane composition of the biogas was 70.34%.

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