

STUDY OF PRE-TREATMENTS FOR AN ENHANCED BIO-ETHANOL PRODUCTION FROM THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTES

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ABSTRACT

This study investigates the effect of different pre-treatments on the bio-ethanol production from the soluble compounds of the organic fraction of the municipal solid wastes (OFMSW). The experimental evaluation was performed on leachate samples obtained after mixing OFMSW with water during 10 d. The most relevant result was that the acid and organosolv, using sulphuric acid as catalysts, pre-treatments yielded the best results. After the acid pre-treatment, the bio-ethanol production was 2.4 times higher than that obtained without pre-treatments. The main conclusion is that the pre-treatment significantly enhance the bio-ethanol production.

Keywords: OFMSW, Bio-energy, pre-treatments

1. Introduction

Energy consumption has increased during the last century due to the world population development and growth (Sun *et al.*, 2002). Nowadays, the increasing problem of the CO₂ emissions due to energy consumption, besides to the future petroleum scarcity, has strengthened the interest in alternative, nonpetroleum-based sources of energy.

One of the potential options to solve the environmental and energetic problems is the use of bio-ethanol (Hamelinck *et al.*, 2005). This is a renewable fuel, which avoids the negative environmental impacts generated by petroleum-based fuels.

The bio-ethanol can be produced by using different technologies. One of the most important technology, the fermentation, produce the bio-ethanol by means of biological transformation of natural starch and sugars resources such as energy-rich crops, (first-generation biofuels) and lignocellulosic biomass (second-generation biofuels). Nowadays, most of the bio-ethanol production is mainly based on sugarcane and corn (Sarkar *et al.*, 2012) but there has been considerable debate about its sustainability and ethics implications. Because of that, other organic substrates should be used to produce the bio-ethanol. In this context, bio-ethanol produced from wastes seems to be a very interesting option.

Parallel, the European Landfill Directive, 1999 strongly advice to minimize the use of landfills in European countries. Being the objective to reduce the amount of biodegradable municipal solid wastes

(MSW) discarded into landfills to 75% of 1995 levels by 16 July 2006, to 50% by 16 July 2009 and to 35% by 16 July 2016 (Fernandez *et al.*, 2008). The major components of the MSW are organics (37,4% \pm 11.1) and paper (32,3% \pm 10,6), accounting for more than 60% of the total mass weight (Milke *et al.*, 2008).

The bio-wastes contained in the organic fraction of the municipal solid wastes (OFMSW) seem to be a very interesting option for bio-ethanol production because green energy can be extracted from the waste at the same time that the waste is stabilized, reducing the landfill disposal requirements.

The biological conversion of OFMSW to ethanol offers numerous benefits but its development is still hampered by economic and technical obstacles (Li *et al.*, 2007). Some of the most important factors are: the efficient utilization of the raw material to obtain high ethanol yields and productivity. Ethanol production from MSW comprises the following main steps: hydrolysis, fermentation, separation of residue and, finally, recovery and purifying the ethanol to meet fuel specifications. The task of hydrolyzing OFMSW to fermentable monosaccharides is still technically problematic because the digestibility of complex organic substrates contained in the OFMSW is hindered by many physico-chemical, structural and compositional factors. Owing to these structural characteristics, pre-treatment is an essential step for obtaining potentially fermentable sugars in the hydrolysis step (Ballesteros *et al.*, 2010). The aim of the pre-treatment is to break down the complex substrates.

In this context, the aim of this work was to study the effect of different pre-treatments on the bio-ethanol production from a leachate from the OFMSW. The soluble part was studied in order to isolate its behaviour when it is pre-treated. The results obtained working in this way could be very interesting for a possible bio-ethanol production from landfill leachates. The pre-treatments studied were based on chemical techniques: acid pre-treatment, alkaline pre-treatment and organosolv pre-treatment.

In order to evaluate the effect of the pre-treatment on the bio-ethanol production from OFMSW not only stoichiometric but also kinetic determinations were carried out. Kinetic parameters are of paramount importance in the design of the fermentation stages and are also very important to control these systems (Cekmecelioglu *et al.*, 2012).

2. Materials and methods

2.1 Raw material

The OFMSW was produced synthetically in the laboratory according to constituents and compositions indicated on Table 1. The foodstuff used to synthesize the OFMSW was fresh, raw and unpeeled, before its use it was chopped using a mechanical mixer. The characteristic of the OFMSW used in this study was similar to others reported in literature (Martín *et al.*, 1997; Kim *et al.*, 2008).

Table 1. Composition of the synthetic OFMSW

Constituent	% w/w	Constituent	% w/w	Constituent	% w/w
Potato	6,20	Cabbage	5,30	Minced beef	2,2
Carrot	2,80	Onion	2,80	Boiled pasta	2,3
Peas	1,30	Cauliflower	0,90	Boiled rice	2,3
Apple	4,90	Orange	4,9	Bread	3,5
Banana	3,50	Tomato	1,3	Paper	55,8

Usually, the pre-treatments are performed with the whole OFMSW. However, in this work the focus has been pointed out on the evaluation of the effects of the pre-treatments on the soluble fractions. Therefore a leachate from the OFMSW was used in the experiments. In order to obtain the leachate, 500 g of the synthetic OFMSW was mixed with 1.5 l of demineralised water in a glass reactor (see Figure 1). The mixture was homogenized by means of a recycle and a rotating stirrer, 150 r.p.m., during 10 d at 20 °C. Afterwards, the solids were removed from the liquid phase by means of centrifugation and subsequent filtration through a glass fibre filter (0.45 μ m), obtaining a leachate containing the main

soluble substrates contained in the OFMSW. During the lixiviation of the substrates the gas production was monitored. The reactor was sparged with nitrogen gas at a flow rate of 30 ml min^{-1} to ensure anaerobic conditions. The nitrogen gas was also used as carrier, and the effluent gas was analyzed using a multi-component gas analyzer (Emerson).

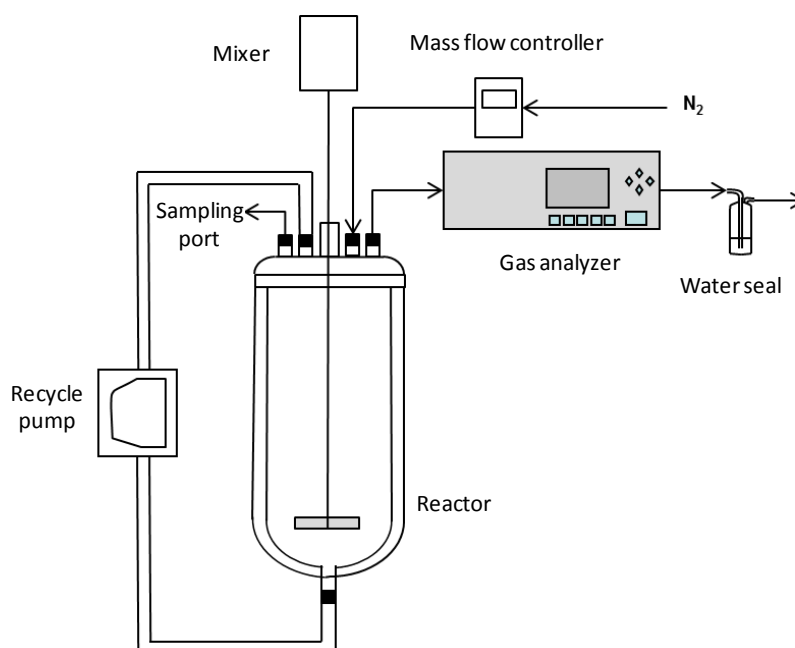


Figure 1. Reaction system used to extract the leachate from the OFMSW.

2.2 Pre-treatments methods

The OFMSW leachate was subjected to acid, alkaline and organosolv pre-treatments. Pre-treatments were performed in a 500 ml vessel. For the acid pre-treatment, dilute sulphuric acid at 0.75% v/v was added, then the mixture was digested at $121 \text{ }^\circ\text{C}$ for 1h according to literature (Saha *et al.*, 2005). The alkaline pre-treatment consist on the addition of an excess of calcium hydroxide ($0.5 \text{ g Ca(OH)}_2 \text{ g}^{-1}$ waste) in oxidative, aerobic, conditions in accordance with Kim and Koltzaple (2005). Then the mixture was digested at $121 \text{ }^\circ\text{C}$ during 1 h. The organosolv pre-treatment consists on the addition of a aqueous ethanol solution, 50% v/v, containing H_2SO_4 , 1.25 % w/w, at 160°C for 45 min. Then, a rotary evaporator was used to remove the dissolvent used; the operating conditions were temperature $65 \text{ }^\circ\text{C}$ during 25 minutes (Zhao *et al.*, 2009). After the pre-treatment the pH values were corrected to the original one by adding acid or alkali. In order to compare the effect of the pre-treatments, a control experiment without any pre-treatment, was performed.

2.3 Fermentation

The leachate previously obtained was fermented to obtain bio-ethanol. Fermentation experiments were conducted using a glass SBR with a working volume of 3 liters. The top of the bioreactor had inlets and outlets used to house a pH probe, a mechanism for NaOH or HCl addition (used to control pH), a nitrogen gas input (to ensure anaerobic conditions), a purge gas output, and sample and feed pipes. The reactor was surrounded by a constant-temperature ($35 \text{ }^\circ\text{C}$) jacket maintained by a flow of temperature-controlled water. Mixing was performed using a magnetic bar rotating at 400 rpm. To prevent excessive foaming during fermentation, a solution with a 2.5/100 ratio of antifoam silicone 426 R (Prolabo) to water was added to the reactor at a flow rate of $25 \text{ } \mu\text{l min}^{-1}$. Each fermentation experiment was conducted by adding leachate of OFMSW to reach a COD concentration in the fermentation reactor of 1000 mg l^{-1} . More information about the set-up can be found elsewhere (Infantes *et al.*, 2011). The biomass used for the fermentation was 0.8 g l^{-1} of the yeast *Saccharomyces cerevisiae* (Prasad *et al.*, 2007). Along the experiments the fermentation reactor was flushed with oxygen free nitrogen gas, at 30

ml min⁻¹ measured by a Mass Flow controller (Aalborg), in order to ensure anaerobic condition and to carry the gas produced to the multi-component analyser. A scheme of this set up can be seen in Figure 2.

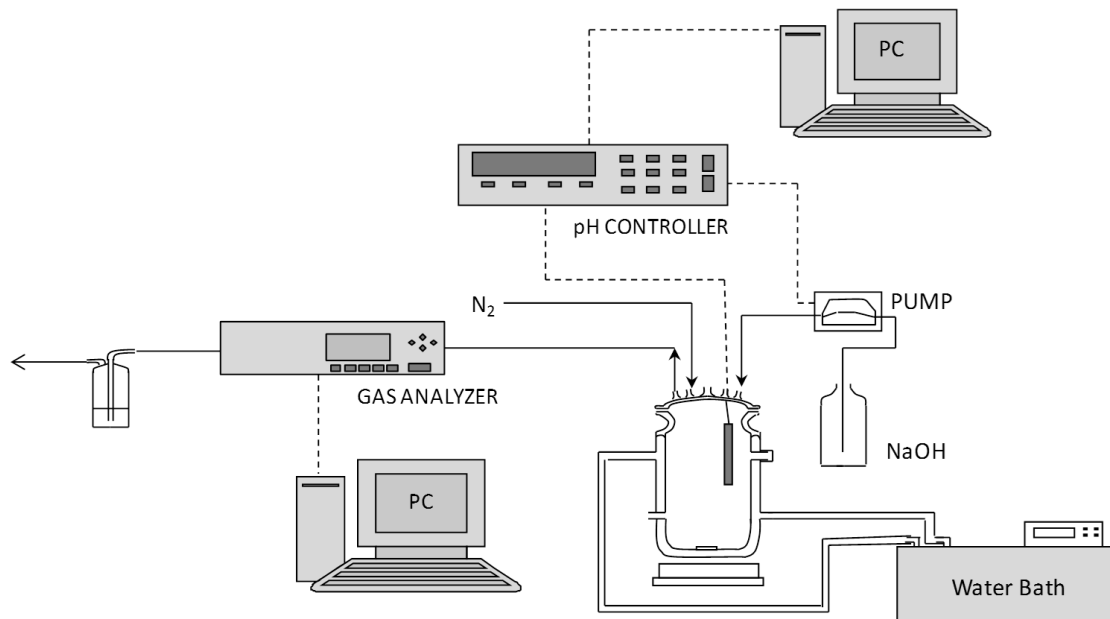


Figure 2. Reaction system used for the fermentation experiments

2.4 Analytical Methods

A variety of analyses were carried out to determine the composition of the aqueous and the gas phases during the fermentation. To measure the substrate and products, the samples were immediately centrifuged at 12000 rpm (approximately 9000 x g), filtered through a 0.45 µm membrane filter and frozen at -4 °C until they were analysed. Substrate concentration was measured by means of COD analysis according to (APHA, 1998). Volatile fatty acids (acetic, propionic and butyric acids) and ethanol were determined from centrifuged and filtered samples by gas chromatography (Perkin Elmer) with a flame ionisation detector (FID) using a Crossbond Carbowax Column (15 m x 0.32 mmID, 0.25 mm df). The oven temperature was set at 140 °C for 1.5 min and subsequently increased at a rate of 25 °C min⁻¹ until it reached 190 °C, where it was maintained for 2 min. The injector and detector temperatures were 200 and 230 °C, respectively. Lactic acid concentration was measured in centrifuged and filtered samples using an HPLC (Agilent) equipped with an ultra violet diode array detection (UV-DAD) detector and a Zorbax SB-Aq column (4.6 x 150 mm 5 µm). The mobile phase used here was a buffer with pH 2 (0.05 M phosphate) composed of 99% water and 1% acetonitrile (Fernández *et al.*, 2011). pH was measured and controlled using BioXpert software and a Biocontroller ADI 1030 (Applikon). The composition of the gas generated during the fermentation process was analyzed by a multi-component gas analyzer (Emerson-NGA 2000) that use IR, UV and Thermal Conductivity detectors.

3. Results/findings

3.1 OFMSW solubilisation

In order to solubilisation the OFMSW, 1.5 l of demineralised water was mixed with 500 g of the synthetic OFMSW. After 10 the solubilisation was stopped and the solids were removed by centrifugation and filtration. The COD concentration of the leachate obtained was 16.100 mg l⁻¹. During the solubilisation the gas produced was analyzed, this gas contained both CH₄ and CO₂, which indicates that not only a solubilisation but also an anaerobic transformation took place in the system.

Then the leachate obtained was fermented with and without pre-treatments. In order to quantify the performance of the process in terms of bio-ethanol and gas production, the experimental results were fitted to the Boltzmann equation. The equation is expressed as:

$$Y = \frac{A_1 - A_2}{1 + e^{(x-x_0)/dx}} + A_2$$

where A_1 represents the bottom value, A_2 the top value, x_0 is the center value and dx is the slope, also known as rate in.

3.2 Reference experiment

In order to establish a reference value for the effect of the pre-treatments on the soluble fractions of the OFMSW, a fermentation experiment of the raw OFMSW leachate was carried out by using *Saccharomyces cerevisiae*. The bio-ethanol production as well as the gas generation are presented on Figure 3.

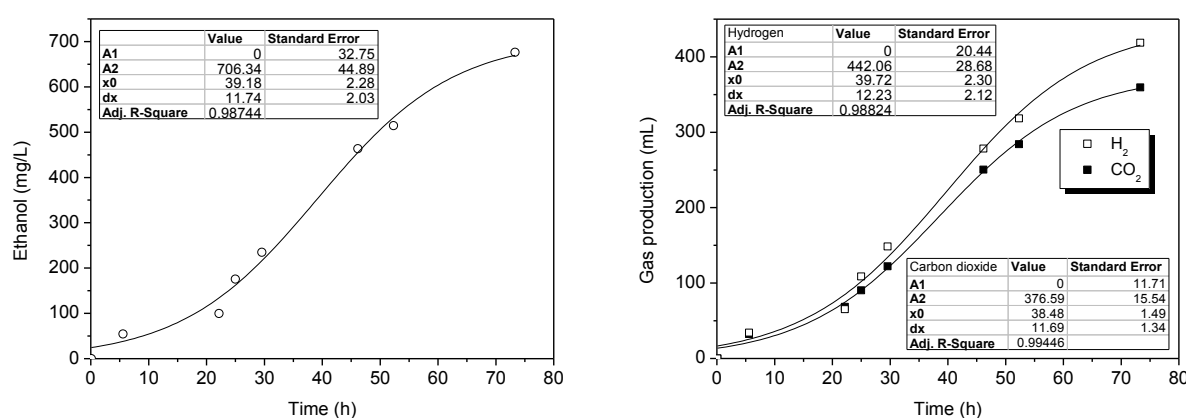


Figure 3. Plots of bio-ethanol (left plot) and gas production (right plot) during the fermentation experiments of raw OFMSW leachate

As can be seen from the values of the R-square parameter the sigmoidal trend fit accurately the experimental data. From the obtained results it can be observed that a lag phase exists during the fermentation experiments. The length of this phase was about 15 h. This lag phase could be explained because of the necessity of a previous transformation of the substrates contained in the leachate for its subsequent transformation (Infantes *et al.*, 2012). The final bio-ethanol concentration reached was 706 mg l^{-1} which means a total bio-ethanol production of about 2.1 g. Taking into account the amount of OFMSW used to obtain the leachate and the COD concentration obtained (16.100 mg l^{-1}), the bio-ethanol yield, when fermenting raw OFMSW, was about 22.4 mg of bio-ethanol per gram of OFMSW. Regarding to the gas production it must be remarked the appearance of hydrogen in the gas phase. The ethanol fermentation only produces carbon dioxide, therefore the existence of hydrogen in the gas phase indicates the existence of an acidogenic transformation (Fernandez-Morales *et al.*, 2010) to volatile fatty acids (VFA). This was verified determining the existence of VFA in the liquid phase, being the main VFA identified lactic, formic and butyric acids. In literature these VFA have been described as enhancers of the biological nutrient removal process (Rodriguez *et al.*, 2007).

In order to avoid the lag phase and to enhance the bio-ethanol yield, the performance of different pre-treatments was studied. These pre-treatments were based on acid, organosolv and alkaline digestions.

3.3 Acid Pre-treatment

The acid pre-treatment consisted on the acid digestion with sulphuric acid at 121 °C during 1 h. Once digested the leachate, it was fermented with *Saccharomyces cerevisiae*. The experimental results obtained are presented on Figure 4.

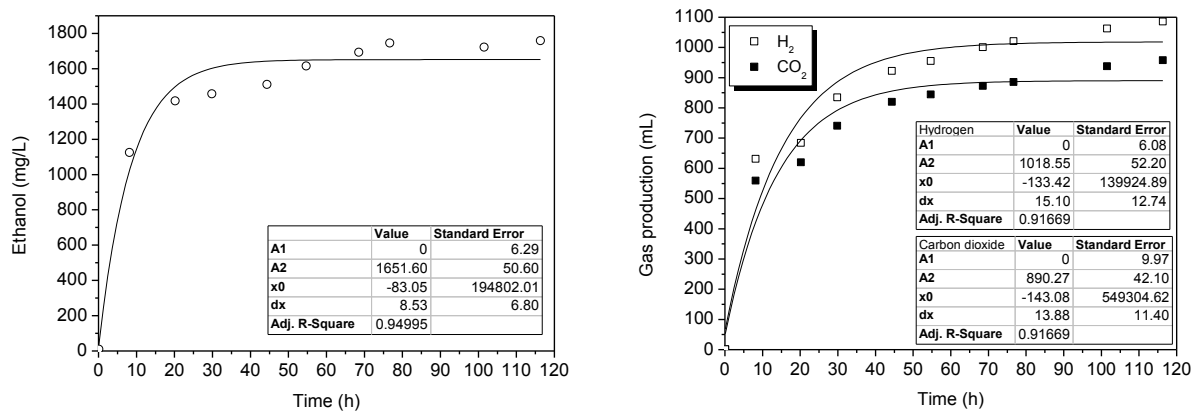


Figure 4. Plots of bio-ethanol (left plot) and gas production (right plot) during the fermentation experiments of acid pre-treated OFMSW leachate

As can be seen in this figure any lag phase appeared, this could be explained because of the transformation of the pollutants contained in the leachate to a more simple ones which can be easily processed by the yeast (Saha *et al.*, 2005). The absence of lag phase, when the leachate was acid pre-treated, drastically reduced the time required for the fermentation of the substrates contained in the leachate from about 75 h, without pre-treatment, to about 25 h. It is also noticeable the higher bio-ethanol production compared with the test carried out without any pre-treatment. This indicates that, after the acid pre-treatment, not only the substrates were more easily fermented but also that the amount of substrates that potentially can be fermented was higher. This could be explained because the acid medium attacks the polysaccharides such as hemicellulose (Cardona *et al.*, 2009) increasing the concentration of fermentable substrates. When the acid pre-treatment was performed the yield obtained was about 52.8 mg of bio-ethanol per gram of OFMSW, which means a yield about 2,4 times higher than that obtained with the raw leachate. Regarding to the gas composition, the distribution of the hydrogen and carbon dioxide indicates that similar metabolic routes were used when fermenting the raw and the acid pre-treated OFMSW leachate. It is important to remark that after the pre-treatment the hydrogen and carbon dioxide productions were significantly improved which indicates a higher extension of the acidogenic and ethanol fermentations.

3.4 Organosolv Pre-treatment

The organosolv pre-treatment consist on the addition of a solvent, in this case ethanol and a catalysts, in this case sulphuric acid. Then the mixture was digested at 160 °C during 70 min. Finally the dissolvent was removed by means of a rotary evaporator working at 65 °C. Once removed the dissolvent, the acidic pH was corrected and the leachate was fermented with *Saccharomyces cerevisiae*. The main results obtained are presented on Figure 5.

As can be seen from Figure 5, when using the organosolv pre-treatment the bio-ethanol yield obtained was lower than that obtained after the acid pre-treatment. The lower bio-ethanol yield obtained could be explained because of the stronger oxidant conditions used in the organosolv pre-treatment process: high acid concentration, high temperature and long digestion time. These more oxidant conditions could not only hydrolyze, but also mineralize some of the substrates contained in the leachate, leading to a

lower content of substrates that potentially could be oxidized. Also growth inhibitors such as furfural and 5 hydroxymethylfurfural could be produced during this severe oxidation stage (Mosier *et al.*, 2005).

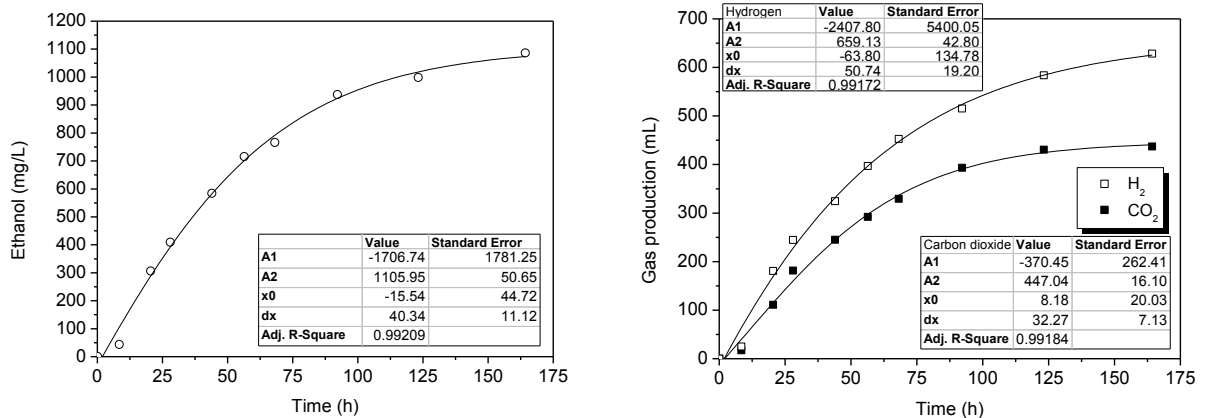


Figure 5. Plots of bio-ethanol (left plot) and gas production (right plot) during the fermentation experiments of organosolv pre-treated OFMSW leachate

3.5 Alkaline Pre-treatment

The alkaline pre-treatment consist on the digestion with Ca(OH)₂ at 121 °C during 1 h. Then, the digested leachate was fermented with *Saccharomyces cerevisiae*. The main results obtained are presented on Figure 6.

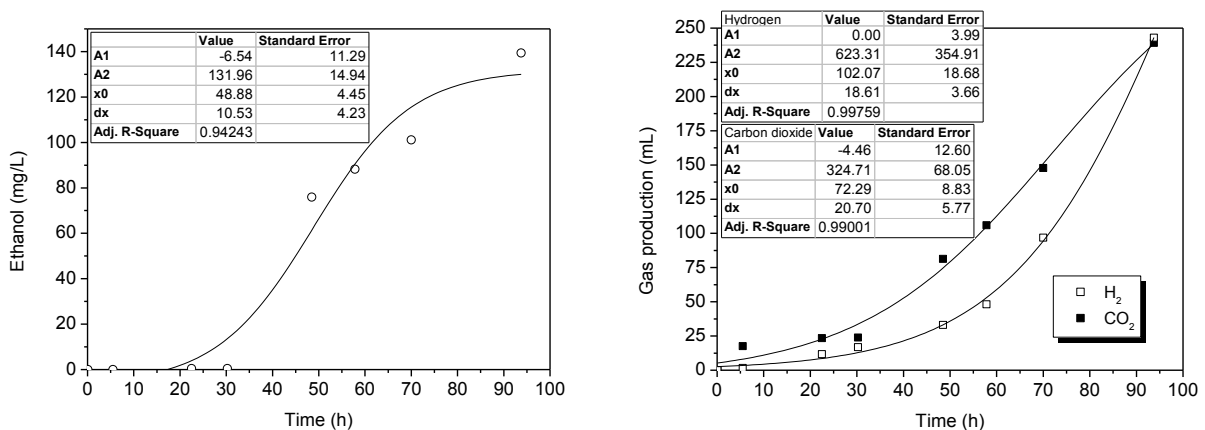


Figure 6. Plots of bio-ethanol (left plot) and gas production (right plot) during the fermentation experiments of alkaline pre-treated OFMSW leachate

In this figure it can be seen that, when the alkaline pre-treatment was performed, the bio-ethanol production got worse comparing with the raw OFMSW fermentation. This deterioration can be appreciated in the reduction of the bio-ethanol yield, which was about a 25% of that obtained with the raw OFMSW, and in the increase of the lag phase length from 15 h to 30 h. This behaviour could be explained because alkaline-based methods exhibit only minor cellulose and hemicellulose transformation (Carvalho *et al.*, 2008).

It is also important to remark that in this case the hydrogen production was higher than that of the carbon dioxide, which is just opposite to that previously obtained. The lower hydrogen production is

caused by a lower acidogenic activity, which indicates that this pre-treatment affects in a more severe way to the acidogenic organisms. Moreover the gas production was significantly lower, which can be explained because of the low conversion obtained

4. Conclusions

For the results obtained in this work the following conclusions can be extracted:

The alkaline pre-treatment used in this work was not useful to enhance neither the yield nor the kinetic of the fermentation stage. The acid and organosolv pre-treatments clearly enhanced the kinetics and stoichiometry of the bio-ethanol fermentation of the OFMSW.

The best results were obtained when using the acid pre-treatment. When this pre-treatment, based on sulphuric acid digestion, was applied the bio-ethanol production was 2,4 timer higher than that obtained without pre-treatments.

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