



***Enhancement of bioenergy production ( $H_2 + CH_4$ ) from organic waste in anaerobic fermentation processes***

Outline of the Thesis:

The question about energy security is increasingly urgent, especially due to the ever-growing societal energy consumption patterns. Therefore, it is necessary to evaluate the different options and/or alternatives that are framed under the precepts of sustainability and which can compete with traditional energy sources, aiming not only to guarantee the needs of the current population, but also considering future scenarios. One of the most promising alternatives, which is widely spread, is Anaerobic Digestion (AD). AD exploits different biogeochemical cycles for the transformation of organic material (i.e. different organic waste and wastewaters) into products of interest, such as bioenergy carriers ( $H_2$  and  $CH_4$ ) and the solid digestate.

This thesis consists of a compendium of experimental works that are framed in different areas of interest of the Chemical Engineering field regarding the production of bioenergy through anaerobic fermentation process, which can potentially allow an enhanced energy-recovery: the use of *Process Analytical Tools* (PAT), *Microbial Communities Engineering* (MCE) and *Energy Sustainability Analysis* (ESA), in detail:

**Chapter I** is introductory and presents a brief background and the major milestones that allowed the technical and scientific development of Anaerobic Digestion. In addition, the current panorama of energy production at a European level from biogas is presented, highlighting the different quotas of primary energy, as well as the correspondent power and heat production figures of the major players at regional level.

**Chapter II** presents a brief theoretical review of the hydrolysis process and the difficulties associated with the modelling of this phase of the AD. The experimental part includes the effect of comminution pre-treatments (i.e. ultrasonication, bead milling and rotor-stator degradation) on the Particle Size Distribution, using a PAT probe (i.e. single mode fiber in-situ laser back reflection) along with Image Analysis to determine the effect on the different phases of interest: biotic phase, using model microorganisms (*Clostridium acetobutylicum* and *Bacillus subtilis*) and complex feedstocks (mixture of grass silage, soil and water). The effects of the different parameters for each pre-treatment were assessed in terms of specific cuts of interest (D0-D50, D50-D90) as well as specific energy consumption.

In **Chapter III**, two experimental techniques that are the state-of-the-art in the field of Microbial Communities (i.e. Frequency-Dependent Polarizability Anisotropy measurements and Flow Cytometry) for bioenergy production are tested to monitor the activity of the microorganisms involved in the process of biohydrogen production through Dark Fermentation, giving attention to cellular viability, metabolic products, the physiological state of fermentative bacteria and about the dynamics of the involved microbial groups.



**Chapter IV** examines the synergistic interactions between Anaerobic Corrosion (AC) of  $\text{Fe}^\circ$  particles and Dark Fermentation (DF) systems, using a Hydrogen Producing Bacteria (HPB) consortium and different  $\text{Fe}^\circ$  doses. An increased bio- $\text{H}_2$  production for the  $\text{Fe}^\circ$  dosed samples coupled to a significant  $\text{CO}_2$ -sink was observed. Moreover, the dynamics of  $\text{H}_2$  production for supplemented and non-supplemented samples were examined; while  $\text{Fe}^\circ$  supplemented samples exhibit a longer lag phase, which suggests that the biological phase requires a longer time for the adaptation to the presence of  $\text{Fe}^\circ$ , the achieved biohydrogen production rates and yields increased significantly. Additionally, a literature review is provided with the possible mechanisms of the synergistic interactions.

**Chapter V** provides insights into the continuous operation of Two-Stage Anaerobic Digestion (TSAD) systems, in order to physically segregate the microbial community into Hydrogen Producing Bacteria (HPB) and Hydrogen Consuming Bacteria (HCB), under optimized environments for the production of each bioenergy carrier (i.e. bio- $\text{H}_2$  and bio- $\text{CH}_4$ ). The energetic performance resulted in an enhanced energy-recovery in TSAD compared to classical one-stage processes, due to the energy produced as hydrogen, the higher methane production and the role of the first stage as biological pre-treatment. A reliable energy-recovery is assured through operational parameters, in each stage, such as pH, temperature, mixing rate, Organic Loading Rate (OLR), Red-Ox potential, Hydraulic Retention Time (HRT) and kinetic selection of the microorganisms.

Lastly, in **Chapter VI**, an Energy Sustainability Analysis (ESA) methodology was developed and applied to evaluate the convenience of distributed  $\text{H}_2$  production. This methodology serves to rationalize the main energy flows which cross the technological boundaries, considering the diverted energy from other societal purposes to run a facility, for the construction of the plant, for the production of the required chemicals among other indirect energy flows. Three technologies are analysed: Steam Methane Reforming (SMR), Solar-Powered Water Electrolysis (SPWE) and TSAD. The results of the ESA are expressed through dedicated indicators: Energy Sustainability Index (ESI), Energy Return on Investment (EROI) and Energy Payback-Time (EPT), which reflect the intrinsic performance of a given technology based on the required energy flows.