## Influence of cavitation, pelleting, extrusion and torrefaction petreatments on anaerobic biodegradability of barley straw and vine shoots

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Out of all bioconversion technologies for production of biofuels, anaerobic digestion (AD) is one of the most profitable and this is the reason why it has been implemented worldwide for the commercial production of electricity, heat and compressed natural gas (CNG) from all kind of organic materials, including waste. On the other hand, large quantities of lignocellulosic biomass that accumulate from agricultural, forestry and other activities are available for the sustainable production of biofuels. However, the use of lignocellulosic biomass for the production of biogas through anaerobic digestion has not been widely adopted because the inherent structure and chemical properties of the plant cell wall makes it resistant to microbial attack.

Lignocellulosic biomass is mainly composed of three components: cellulose, hemicellulose and lignin. Cellulose and hemicellulose are the main carbohydrate components of the biomass structure, while lignin is a highly cross-linked polyphenolic macromolecule that provides rigidity to the cell wall of the material. Therefore, to recover the monomeric sugars present in the carbohydrate fractions for later use in bioprocesses, a pretreatment stage is required to open the structure of the material, facilitating its degradation by enzymes and microbes. Numerous methods have been developed to pretreat lignocellulosic biomass. Four of them: cavitation, pelleting, extrusion and torrefaction have been evaluated in this paper to improve the production of methane by anaerobic digestion of barley straw and vine shoot.

Hydrodynamic cavitation (HC) is a technology with application potential in different areas, including the production of biofuels. Although HC is an undesirable phenomenon for hydraulic equipment, the net energy released during this process is sufficient to accelerate certain chemical reactions. The application of cavitation energy to improve the efficiency of pretreatment of lignocellulosic biomass is an interesting strategy. The beneficial effects of HC are attributed to the release of large amounts of energy in a very small location ("hot spots") during the collapse of the cavities, resulting in very high energy densities due to the generation of local conditions of very high temperature and pressure.

Biomass densification, as pelleting or extrusion, can be employed to reduce biomass volume and facilitate logistic in biomass management activities. Pelleting of biomass involves size reduction and conditioning of the ground biomass by applying heat and/or pressure. These operations may hydrolize the hemicellulose and lignin into lower molecular carbohydrates, sugar polymers and other derivatives. On the other hand, extrusion is a process that combines multiple operations in one unit. The raw materials are fed into the extruder and as the material moves along the equipment, it is subjected to heat by friction, mixing and vigorous shear by releasing the pressure at the end. Extrusion can significantly reduce the particle size, increasing the specific surface area of the biomass and causing depolymerization of cellulose, hemicellulose, lignin and proteins, and can also cause thermal degradation of sugars and amino acids, depending on the stress intensity of the extrusion screw.

Finally, torrefaction is a thermo-chemical pretreatment method taking place at temperatures ranging between 200 and 300 °C. At these temperatures the skeleton of lignin and hemicellulose can be broken down partly, which is an interesting effect that can favour AD process.

Prior to each of these pretreatments, the barley straw and the vine shoot were mechanically milled so that they reached an adequate particle size. The equipment used was a blade mill for the straw and a hammer mill for the vine shoot, both with light of 2 mm. In addition, prior to cavitation, a refining was done with diameter reductions to 0.25 mm.

The ability of the different pretreatments to create structural damages on the biomass morphology was analysed by SEM. In order to study the biodegradability of the pretreated biomass, batch experiments were run in glass serum bottles with a liquid volume of 500 mL (1000 mL of total volume). All the experiments were carried out at  $34\pm1$  °C in a thermostatic room. Digestate from an anaerobic reactor operating in a municipal wastewater treatment plant, with a VS concentration of  $7,1\pm0,5$  g L-1, was used as inoculum for the anaerobic test. Final inoculum concentration in the tests medium was  $5.0\pm0.5$  g L-1. The substrate/inoculum (S/X) ratio was maintained for all samples at  $0.50\pm0.05$  gSVsubstrate / gSVinoculum. Biogas production was automatically measured by using pressure transmitters (Desin Instruments, TPR-14 / N, range 0-1 bar) connected in the upper space of each reactor. The biogas composition was measured using a Varian CP-4900 Micro-GC chromatograph with a Thermal Conductivity Detector. The individual Volatile Fatty Acids (i.e., acetic, propionic, isobutyric, butyric, isovaleric, valeric acids and others) were quantified using GC equipped with flame ionization detector (GC-FID) (GC2014, Shimadzu, Japan).

The SEM images of the untreated biomass under various magnifications clearly showed the robust structure and relatively smooth surface in straw and vine shoot fibers. The SEM images of biomass pretreated by the technologies under clearly show that the pretreatments led to breakdown of the robust structure of the materials and the structure became loose and disordered after the pretreatments (Figure 1).

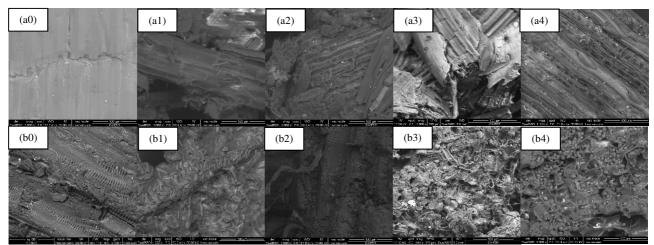


Figure 1. SEM images (x|1000) of barley straw (a) and vine shoots (b) particles untreated (0) and pretreated by cavitation (1), pelleting (2), extrusion (3) and torrefaction (4).

The distribution of individual VFA is strongly depended on the type of biomass and also on the type of pretreatment used. During the anaerobic digestion of untreated barley straw or vine hoots, propionic acid, followed by acetic and butyric acids dominated the VFAs profile. These profiles change drastically when a pretreatment is applied. In the case of cavitation, acetic acid becomes the major individual VFA, however, during the digestion of pelletized biomass, the presence of butyric acid increases and even becomes the dominant VFA when pelletized vine shoots is the biomass anaerobically digested.

The pretreatments assayed showed a different degree of effectiveness on methane production when applied to barley straw or to vine shoots. In all the cases, the application of the pretreatments revealed to affect positively the methane yield and lag phase of the digestion process, although the effects were more marked on straw.

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