

---

**Programa de Doctorado en Ingeniería Química****Chain elongation of volatile fatty acids from sewage sludge HTC process water**

**L. Martinez-Sanchez<sup>1\*</sup>, G. Langa<sup>1</sup>, J.F. Hernández<sup>1</sup>, C. Diaz-Padilla<sup>1</sup>,  
E. Diaz<sup>1,2</sup>, A.F. Mohedano<sup>1,2</sup>, M. Tobajas<sup>1,2</sup>, M.A. de la Rubia<sup>1,2</sup>**

<sup>1</sup>Department of Chemical Engineering, Universidad Autonoma de Madrid, Spain

<sup>2</sup>Institute for Advanced Research in Chemistry, Universidad Autonoma de Madrid, Spain

Acidogenic fermentation is an anaerobic biological process that converts organic-rich substrates into valuable products such as hydrogen and volatile fatty acids (VFA). In this study, process water (PW) obtained from the hydrothermal carbonization (HTC) of sewage sludge, particularly rich in acetic acid, was evaluated as a substrate for VFA production. A thermally pretreated inoculum sourced from a mesophilic anaerobic digester was employed. Ethanol, lactic acid, wine lees, and cheese whey were evaluated as electron donors to promote VFA chain elongation.

Batch experiments were carried out in 80 mL working-volume reactors under mesophilic conditions (35 °C). The time-evolution of solids, pH, soluble and total chemical oxygen demand (COD) was monitored until VFA stabilization. Individual VFA concentrations and ethanol were quantified by gas chromatography (GC-FID), while lactic acid and lactose were determined by liquid chromatography (HPLC).

Initially, PW was used as the sole substrate to identify optimal pH conditions and the effect of solid content on acidogenic fermentation. Experiments were conducted using the native PW pH (7.2), as well as adjusted pH of 5.5 and 9.0. Additionally, PW was filtered through a 0.5 mm mesh to remove coarse solids, and further filtration using 0.45 µm filters was evaluated. The highest VFA production was obtained at unmodified pH, with a slight increase when PW was filtered at 0.45 µm, reaching 7.9 g COD/L. However, the VFA profile was strongly dominated by acetic acid, accounting for 54% of the total.

The addition of electron donors (ethanol, lactic acid, wine lees, and cheese whey) at concentrations ranging from 5 to 15 g/L significantly enhanced both VFA production and chain elongation. Maximum VFA concentrations 33.5 and 32.0 g COD/L were reached with the addition of 15 g/L of ethanol and lactic acid, respectively. Ethanol favored the formation of butyric and caproic acids, which are valuable intermediates for polyhydroxyalkanoates synthesis. In contrast, wine lees led to lower VFA production than pure ethanol at equivalent dosages and did not promote chain elongation. Conversely, cheese whey significantly increased total VFA production to 25.7 g COD/L respect to the control without electron donor, and substantially enriched the VFA profile in butyric acid, which represented 67.8% of the total.

Overall, PW derived from the hydrothermal carbonization of sewage sludge proved to be a promising substrate for VFA production through acidogenic fermentation. The combination of process water valorization with the addition of suitable electron donors effectively promoted VFA chain elongation, enabling the generation of biopolymer precursors. This integrated approach contributes to the valorization of multiple waste streams and aligns with circular economy principles.

---