Volatile fatty acids (VFA) such as acetate or butyrate are intermediates of the biogas production process. Therefore, they can be produced from waste streams and have a higher economic value as they can be used as industrial precursors and bulk chemicals. Several specific organisms present in mixed cultures have the capacity to elongate short VFA to caproate or others with a higher value using ethanol as a reducing agent. In this study we explored different operational conditions to enhance VFA production from thin stillage of a bio-ethanol biorefinery.

**Low pH rather than HRT to produce long-chain VFA**

Two continuous stirred tank reactors (CSTR) were fed with distilled thin stillage and operated at 35°C and pH 5.5 or pH 6.5. They ran for 300 days at different HRT.

![Figure 2. CSTRs with stillage.](image)

**Figure 3.** VFA concentration and composition at different pH and HRT.

- HRT decrease improved VFA production rate from 2.7 to 8.8 g COD L⁻¹d⁻¹.
- Concentration and composition remained similar even when varying the HRT within the same pH set-point.
- Lower pH inhibited methane production by VFA present in the acid form.
- Lower pH decreased the maximum VFA concentration by product (VFA in the acid form) inhibition.
- pH reduction induced ethanol production (more ethanol in the effluent) and, therefore, a higher presence of longer carboxylates.

**Conclusions**

Low pH induces ethanol generation in stillage fermentation and the introduction of small portions of beer can enhance the generation of ethanol and elongate carboxylates.

![BIOREFINERY existing route](image)

**INTEGRATED BIOREFINERY new route**

Batch tests with inoculum from the reactor controlled at pH 5.5 were performed with different proportions of beer and stillage to determine maximum VFA and ethanol inhibition.

- Active yeast from beer induces ethanol production.
- Chain elongation improves with higher ethanol concentration.
- High ethanol (> 40 g L⁻¹) inhibits VFA production and chain elongation.

![Figure 4.](image)

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