RHODES 2024
11th International Conference on Sustainable Solid Waste Management

Comparison of GC methods for VFAs analysis: the role of plasma detection

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INTRODUCTION

The island of Lesvos supports its economic development in the agricultural industry. The large number of food industries such as olive mills, wineries, distilleries and dairy processing facilities are the main source of the largest volume of wastewater on the island. One of the most widespread methods of wastewater treatment, and more specifically food waste, is anaerobic digestion. Anaerobic digestion is a biochemical process through which moisture and solid waste residues are significantly reduced and biogas and chemical products such as Volatile Fatty Acids (VFAs) are produced. Therefore, biogas produced from food industry wastewater can be an important source of energy and through anaerobic digestion can produce VFAs. In this particular research, food waste more specifically wine sludge and anise underwent hydrothermal carbonization and hydrochar was added to BMP experiments. Cocoa biochar was also added. With the introduction of hydrochar and biochar in BMP experiments the goal was to increase the production of VFAs in the process of anaerobic digestion. In addition, hydrothermal treatment experiments were conducted with anaerobic sludge as the basic material for the production of VFAs by a thermochemical process too. This study investigated the production of VFAs through two different wastewater treatment technologies and simultaneously investigated the concentrations of VFAs through two different gas chromatographs and three different columns.

METHODS

HT treatment reactor experiments: This research begins with the experiments of hydrothermal treatment. The experiments took place in a Parr 4570A hydrothermal reactor with a capacity of 1L. The main material used was Anaerobic Digested Sewage Sludge (ADSS). Into the reactor 500 ml of ADSS was added and hydrothermal treatment was carried out at 200 ℃, the pressure developed was 14.2 bar and the residence time was 2 hours. With the end of hydrothermal treatment, analyses such as measurement of pH, conductivity, determination of COD concentration, phenols and concentration of VFAs were performed. VFAs were measured on a Shimadzu Nexis 2030 GC-BID.

BMP experiment: The anaerobic digestion experiment was carried out in 15 Wheaton bottles with a volume of 25 ml and septum seals were used to measure biogas. The experiment involved 5 triplets containing the same substrate with a different kind of hydrochar and biochar in each triplet. In all experiments underwent anaerobic digestion of 10 ml of sludge with a substrate of 5 ml of cheese whey (ratio 2: 1 respectively) and added quantities of hydrochar anise, wine sludge and biochar cacao, specifically 100 mg. Anaerobic digestion took place in mesophilic conditions. The production of the biogas was evaluated by BMP tests, while the VFAs from the final digestate were analyzed by two gas chromatographs and three different columns. More specifically a Shimadzu Nexis 2030 GC-BID gas chromatograph and an Agilent 6891 GC-FID.

GC analysis: The one measuring column of VFAs was an Agilent J&W HP-FFAP and was held on Shimadzu Nexis 2030 GC-BID. The parameters of the method included 1 μL sample injection volume, an injection temperature of 160 °C, an oven temperature program ranging from 80°C to 230 °C, a flow rate of 59 ml/min and BID detector temperature at 280 °C. The other column was an Agilent J&W DB-FFAP and the measurement took place on an Agilent 6891 GC-FID. The parameters of the method included 1 μL sample injection volume, an injection temperature of 250 °C, an oven temperature program ranging from 140°C to 170 °C, a flow rate of 45 ml/min and FID detector temperature at 250 °C. The last column waw a DB-WAXETR and the measurement waw held on Agilent 6891 GC-FID too. The parameters of the method included 1 μL sample injection volume, an injection temperature of 220 °C, an oven temperature program ranging from 158°C to 200 °C, a flow rate of 30 ml/min and FID detector temperature at 240 °C.

BMP tests	Sample Content and Quantity of Ingredients
Sludge	10 ml sludge
S/CW	10 ml sludge + 5 ml Cheese whey Wastewater (CW)
S/CW-C	10 ml sludge + 5 ml whey cheese + 100 mg Cacao BC (C)
S/CW-W	10 ml sludge + 5 ml whey cheese + 100 mg Wine sludge HC (W)
S/CW-A	10 ml sludge + 5 ml whey cheese + 100 mg Anise HC (A)

Table 1. Experimental conditions - AD

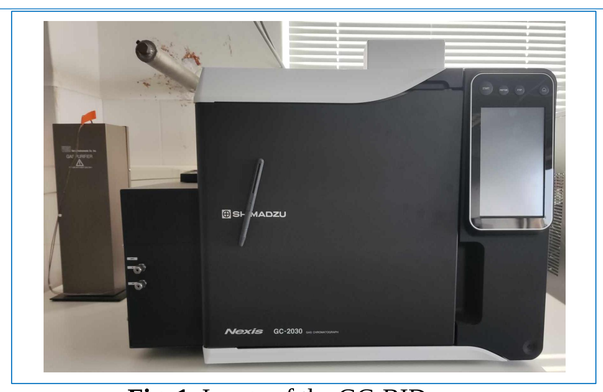

Fig. 1. Image of the GC-BID

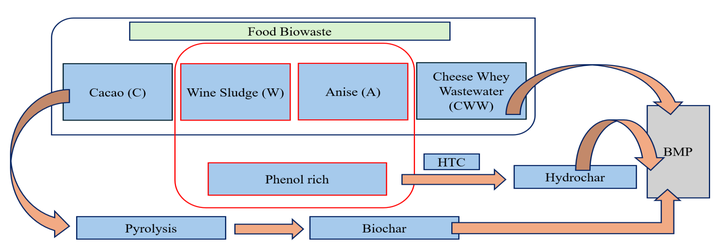

Fig. 2. Experimental scheme of HTC and AD

RESULTS AND DISCUSSION

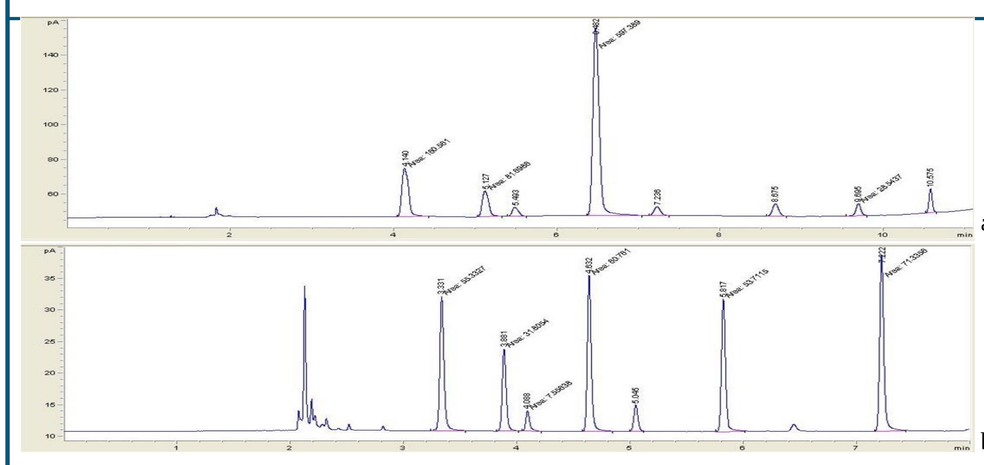

Fig. 3. GC-graphs. Up: GC graph of VFAs from sample S/CW-W with DB-WAXETR column on Agilent 3891 GC-FID/ Down: GC graph of VFAs from sample S/CW-W with Agilent J&W DB-FFAP column on Agilent 3891 GC-FID.

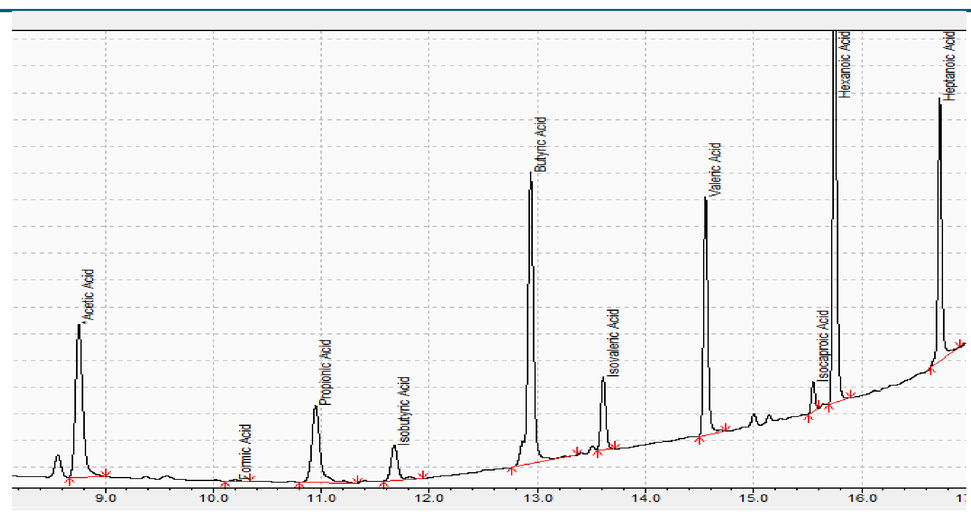

Fig. 5. GC-graph of VFAs from sample S/CW-W with Agilent J&W HP-FFAP on Shimadzu Nexis 2030 GC-BID

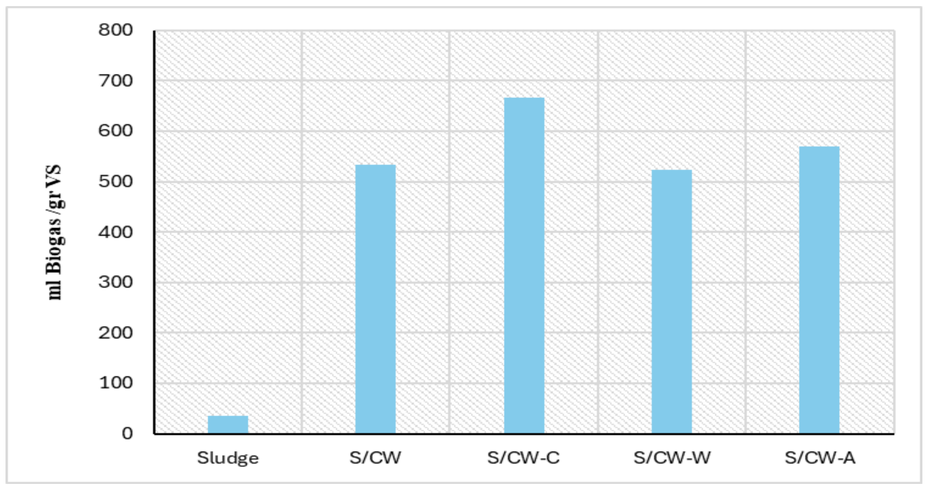

Fig. 4. BMP results about Biogas

- The highest concentrations of VFAs appear to occur in Acetic acid, Propionic acid, Butyric acid, Valeric acid, Hexanoic acid and Heptanoic acid.
- The measurement carried out in Shimadzu Nexis 2030 GC-BID with the Agilent J&W HP-FFAP column shows a higher number of VFAs compared to the other two columns.
- The measurement carried out in Shimadzu Nexis 2030 GC-BID shows formic acid with a concentration of 28.5 mg/l, while in the other two chromatograms after acetic acid, propionic acid appears.
- At the same gas chromatograph also shows high concentrations of hexanoic acid and Heptanoic acid amounting to 114.1 mg/L and 100.3 mg/l.
- It is observed that in anaerobic digestion the presence of biochar and hydrochar, specifically hydrochar of anise, enhanced the production of biogas.
- The largest quantities of biogas amount to 666.9 ml/gr VS and 569.2 ml/gr VS and belong to the samples S/CW-C and S/CW-A respectively.

CONCLUSIONS

- The plasma gas chromatograph and Agilent column J&W HP-FFAP show a very good result by detecting concentrations of 10 VFAs.
- The same chromatograph shows the ability to detect Formic acid even at low concentrations.
- The gas chromatograph Agilent 3891 GC-FID and the columns DB-WAXETR, Agilent J&W DB-FFAP seemed to be able to detect only 6 VFAs.
- It is important that Formic acid cannot be detected from the two columns in Agilent 3891 GC-FID, with a high probability that its concentration is incorporated and displayed along with the curve of Propionic acid.
- Along with the enhanced production of VFAs, there is also a large production of biogas.
- The presence of hydrochar and biochar was noticeable in biogas production mainly of hydrochar of anise.

References:

Huezo, L., Vasco-Correa, J., & Shah, A. (2021). Hydrothermal carbonization of anaerobically digested sewage sludge for hydrochar production. *Bioresource Technology Reports*, *15*, 100795.

Nguyen, V. K., Chaudhary, D. K., Dahal, R. H., Trinh, N. H., Kim, J., Chang, S. W., ... & Nguyen, D. D. (2021). Review on pretreatment techniques to improve anaerobic digestion of sewage sludge. *Fuel*, *285*, 119105.