Syngas upgrading to biomethane via co-digestion with brewery wastewater

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The path towards decarbonization implies the maximization of industrial symbiosis and a transition from linear to circular waste management concepts (Branca *et al*, 2021). This contribution deals specifically with the integration of gasification and anaerobic digestion as it proposes a biological route for syngas upgrading to methane valorizing brewery wastewater (BWW). Syngas is the gaseous product of the biomass gasification process and is mainly composed of CO, H_2, CO_2, N_2, CH_4, and tars, in variable amounts depending on the gasification technology used, biomass type, and operating conditions applied (Lepage e*t al*, 2021). Currently, syngas is mainly used for heat and power production, but a strong focus in research is devoted to diversifying the product range and advancing towards an economically feasible production of biofuels (Lepage *et al*, 2021; Lozano & Lozano, 2018; Patuzzi *et al*, 2021). Catalytic reforming is an established pathway for the conversion of syngas to methane. However, the high processing costs and the vulnerability of metallic catalysts to gas impurities are driving the advancement of alternative processes like biological methanation of syngas (Grimalt-Alemany *et al*, 2018). Recently, Asimakopoulos *et al* (2021) operated a semi-pilot system consisting of a fluidized bed gasifier for wood pellets connected to a trickle-bed reactor for syngas biomethanation achieving almost 100 % H_2 and CO conversion efficiency. This achievement developed from a series of fundamental investigations on the enrichment of methanogenic bacteria from mixed microbial consortia and the use of these enriched cultures as inoculums for lab-scale syngas biomethanation in a trickle-bed reactor feeding on a synthetic growth medium (Asimakopoulos *et al*, 2020; Grimalt-Alemany, Asimakopoulos, *et al*, 2020; Grimalt-Alemany, Łężyk, *et al*, 2020). Besides, the co-digestion of syngas and organic waste materials has been also actively investigated. Yang *et al* (2020) were able to convert syngas stoichiometrically by simultaneously halving the initial Chemical Oxygen Demand (COD) content of co-digested food waste in a continuously stirred lab-scale tank reactor. Furthermore, Andreides *et al* (2021) achieved the production of highly concentrated methane (94.7 vol.%) in a lab-scale two-staged reactor system for co-digestion of syngas, sewage sludge, and hydrogen, in a Power-to-Gas perspective. Within this framework, exploring further process pathways involving syngas biomethanation integrated with the treatment of secondary raw materials represents a research priority under the perspective of circular economy models. The brewing industry is a large waste generator as beer is one of the most consumed beverages in the world. For each liter of beer, three to ten liters of organics-rich wastewater are produced, with residual sugars, suspended solids, soluble starch, ethanol, and volatile fatty acids as the main components. Anaerobic digestion of BWW has been demonstrated as a feasible in-plant energy recovery concept (Chen *et al*, 2016; Simate *et al*, 2011). However, the feasibility of syngas co-digestion with BWW remains unexplored, although the integration of biomass gasification for biomethane production into the brewing process could represent a powerful carbon-neutral, polygenerative system.

This study investigates experimentally the co-digestion of syngas and BWW. The study is divided into two phases: (1) enrichment of methanogenic microbial populations in batch bottles; (2) methane production in continuously stirred tank reactors (CSTRs). Digestate collected from a local anaerobic digestion plant treating the organic fraction of municipal waste is used as inoculum while BWW (with an average COD content of 2 g/L) collected from a local large-scale brewery is used as co-substrate. The enrichment phase consists of the following steps: (a) placing 100 ml of a liquid volume containing 15 vol.% digestate and 85 vol.% BWW in 300 ml DURAN® glass bottles, (b) flushing and pressurizing the headspace to 0.4 bar with synthetic syngas (32 vol.% CO, 68 vol.% H_2) (c) shaking the glass bottles for 10 days in a rotary incubator at 37 °C and 100 rpm, (d) repeating steps (a)-(c) by transferring an aliquot of the residual liquid phase as inoculum in step (a). In the second phase of the study, a CSTR with an active volume of 1 L is inoculated with the enriched culture and operated for 90 days in continuous mode at a hydraulic retention time (HRT) of 20 d, mesophilic conditions (37 °C), neutral pH and 300 rpm stirring speed. Syngas is constantly injected into the reactors' liquid phase under increasing flow rates from 0.1 ml/min to 1 ml/min. A second CSTR is used as the control reactor operated at the same conditions but under an N_2 flow. Gas and liquid phases compositions are analyzed by means of a Micro Gas Chromatograph (μGC) and a Gas Chromatograph-Mass Spectrometer (GC-MS), respectively. Additionally, the liquid phase is analyzed in terms of COD, and the composition of the mixed microbial consortia is investigated by 16S rRNA gene amplicon analysis.

During the enrichment phase, the presence of methane gas is detected in the gas atmosphere of the glass bottles after 4 days since inoculation. The observed methane fraction consists of up to 30 vol.% of the total gas

composition, hinting at the adaptation ability of the initial mixed microbial consortium within the syngas environment as well as to an evolution of the microbial species characterized by the selection of methanogenic species. The GC-MS analysis reveals a peak of the acetate concentration in the liquid phase within the first four days after inoculation suggesting an initial shift of the microbial community to the prevalence of acetogenic species, which are later substituted by methanogenic species. By operating the CSTR inoculated with the enriched cultures a significant portion of the electron equivalents of the syngas is depleted with a simultaneous reduction of the COD content of BWW. The resulting methane production rate reaches an average value (over the whole operation time) of 0.5 ml/min for the syngas-fed CSTR, slightly higher with respect to the control N_2-fed CSTR. Furthermore, 16S rRNA gene amplicon analysis reveals the prevalence of CO-tolerant microbial species within the syngas-fed CSTR as opposed to the control N_2-fed CSTR.

In conclusion, this study demonstrates the possibility to enrich mixed microbial consortia to produce methane via co-digestion of syngas and BWW. Additionally, syngas and BWW co-digestion to methane is proven to be feasible in a lab-scale CSTR. In future work, the syngas inflow rate, the hydraulic retention time, as well as the reactor configuration (e.g., shift towards operation in a trickle-bed reactor) should be optimized to increase the methane production rate and consequently advance towards the pilot-scale operation.

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