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Electromethanogenesis for the conversion of hydrothermal carbonization exhaust gases into methane

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ABSTRACT

Hydrothermal carbonization (HTC) is a biomass conversion process that generates a CO_2-rich gaseous phase that is commonly released directly into the atmosphere. Microbial electromethanogeneis (EM) can potentially use this off-gas to convert the residual CO_2 into CH_4, thus avoiding GHG emissions while adding extra value to the overall bioprocess. In the present work, the HTC gas phase was fed to two mixed-culture biocathodes (replicates) polarized at −1.0V vs. Ag/AgCl. Compared to pure CO_2, HTC gas had a marked negative effect on the process, decreasing current density by 61%, while maximum CH_4 yield contracted up to 50%. HTC also had an unequal impact on the cathodic microbial communities, with the methanogenic hydrogenotrophic archaea *Methanobacteriaceae* experiencing the largest decline. Despite that, the present study demonstrates that HTC can be used in EM as a raw material to produce a biogas with a methane content of up to 70%.

1. Introduction

Depletion of fossil fuels and the contribution of carbon dioxide emissions to climate change are stimulating the transition from traditional petrochemical refineries to biorefineries [1]. These facilities can contribute to meet the ambitious goals set by the European Union on the reduction greenhouse gases emissions and the implementation of a circular economy, especially when using wastes (instead of crops) as feedstock [2,3]. The list of industrial processes that produce CO_2-rich waste streams is certainly large, and the ability of some living microorganisms to assimilate CO_2 opens the way for using these wastes as chemical raw materials [4].

Within this context, hydrothermal carbonization (HTC) represents a very attractive process [5]. HTC is a thermochemical technology that offers a sustainable and cost-effective solution for waste management while pursuing the concept of a carbon-neutral society [6]. This process, that occurs under autogenous pressure and at moderate temperatures (150 °C–300 °C) compared to conventional pyrolysis (400 °C–600 °C), can convert organic wastes into three different products [7,8]. The main product is the solid phase, commonly known as hydrochar, which can find applications as solid biofuel, low-cost adsorbents or soil amendment among others [9]. There is also a liquid phase that usually contains a wide spectrum of valuable chemicals for biorefineries [10,11], and a gaseous phase that is composed mainly of CO_2 (ca. 85–95%) with minor proportions of other gases such as CO, CH_4 or H_2 [8] and small traces of hydrocarbons [12]. Because of its large CO_2 content, the gaseous phase is commonly seen as a waste. However, as previously demonstrated [13], the valorisation of this side product could improve the overall economy of HTC, while avoiding CO_2 emissions to the atmosphere. Despite that, and to the best of our knowledge, only a few works have explored the possibilities of HTC off-gas conversion and valorisation [14,15]. One example is the work of González-Castaño and colleagues [15], who showed how the Reverse Water Gas Shift reaction pathway can be implemented after the HTC process to obtain syngas.

HTC off-gas also represents an ideal feedstock for methane production through electromethanogenesis (EM) [16,17]. EM is a biologically mediated process that results in the conversion of CO_2 to methane on the cathode side of a bioelectrochemcial systems (BES). For more details on BES and EM the reader is referred to Ref. [18]. EM has aroused significant interest among scientists and engineers because of its environmental and economic potential. It can proceed at room temperatures and pressures and involves bacteria as catalysts, all of which suggest that EM can become a more cost-effective and environmentally friendly method of methane production compared to conventional technologies [17]. Despite that, technical and economic limitations still remain, and the scaling up of this technology represents a major challenge [19].

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Previous studies have shown that methanogenic biocathodes can be successfully fed with synthetic mixtures of CO_2 and other gases [20–22], and it has been even demonstrated that the CO_2 present in a real biogas is a suitable substrate for EM [23,24]. However, the use of real CO_2-rich waste streams (such as the HTC off-gas) as feedstock has not been yet explored. Thus, in this paper we aim at exploring the technical feasibility of using real HTC off-gas as a raw material for EM. We pay special attention to the impact that this gas has on process performance and on the cathodophilic microbial communities.

2. Materials and methods

2.1. Reactors

The experiments were conducted using two standard H-type reactors (referred to as R1 and R2 throughout the paper) with an internal volume of 500 mL per chamber. The biocathodes (working electrodes) used in these experiments were inoculated with the biofilm scratched from the biocathodes used in a previous experiment [20]. Each of the electrodes consisted of two pieces (2 × 8 cm) of carbon felt (SGL Group, Germany) attached by titanium wire and suspended inside the cathodic chamber with a graphite rod. Prior to inoculation, the electrodes were pretreated by subsequent immersion in nitric acid 1 M, acetone 1 M and ethanol 1 M during 24 h each to avoid hydrophobicity and impurities [25]. The counter electrodes (CE) were made of a 2 × 2 cm platinum mesh (Goodfellow, UK) suspended inside the anodic chamber with titanium wire. A cation exchange membrane (CMI7000, Membranes International, USA) was used to separate the anodic and cathodic compartments (Fig. 1). Before utilization in the EM reactors, the membrane was pre-treated by immersion in a 5% NaCl solution for 24h.

Both reactors were operated on a three-electrode configuration using a Biologic VSP potentiostat (Biologic, France) and EC-Lab® software (ver. 11.31). An Ag/AgCl commercial reference electrode (Sigma-Aldrich, USA) (0.20 vs. SHE; the stability of the reference electrode was checked prior to every batch cycle) was used as reference electrode.

Appropriate connections and sealing were designed for sampling ports and substrate supply as illustrated in Fig. 1. Gas was collected using a 1 L gas bag (Ritter, Germany). Reactors were placed inside a phytotron (Fitotron, Sanyo, Osaka, Japan) that maintained temperature constant at 30 ± 1 °C. The catholyte was continuously stirred (200 rpm) using a magnetic stirrer (RO15, IKA. Staufen, Germany) in order to prevent mass transfer limitations [26].

2.2. Electrolytes

The anolyte contained 0.1 M potassium phosphate buffer in deionised water, and the catholyte consisted of 20 mM potassium phosphate buffer, macronutrients (280 mg L^{-1} NH_4Cl, 5.7 mg L^{-1} $CaCl_2$, 10 mg L^{-1} $MgSO_4{\cdot}7H_2O$, and 90 mg L^{-1} $MgCl_2{\cdot}6H_2O$), 1 mL L^{-1} of a micronutrients solution, and 1 mL L^{-1} of a vitamin solution as described in Ref. [27].

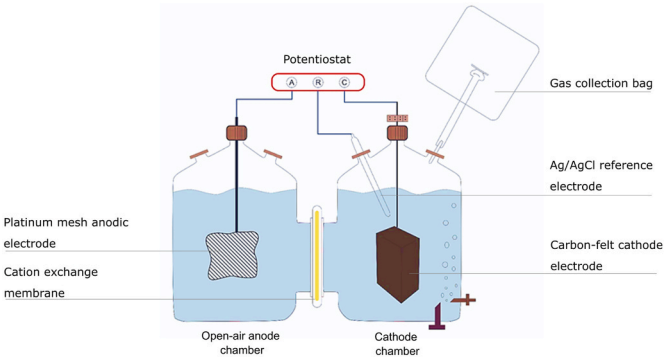

Fig. 1. Reactor diagram.

300 mL of CO_2 were added as a carbon source during the start-up period and then its gas was gradually replaced by HTC gas. Catholyte and anolyte were renewed at the beginning of each cycle. Prior to catholyte replacement, the fresh catholyte was purged with nitrogen gas for 30 min. In addition, the cathode chamber was continuously fluxed with nitrogen during the emptying/refilling operation to displace any oxygen (the biocathode remained inside the cathode chamber during the whole process).

2.3. HTC off-gas

The feedstock used for the production HTC off-gas consisted of the pruning of arboreal biomass collected form a nearby poplar farm. 50 g of biomass were mixed with 1000 mL of deionised water at a 1/20 biomass/water ratio in a 2 L stirred pressured reactor (APP Parr reactor, Parr instrument company, Moline, IL, USA) operated at 250 °C during 1 h (the reaction parameters are based on previous experiences [28]). The off-gas was collected in a 1 L Tedlar gas bag, and consisted of a mixture of: CO_2 90.10% ± 1.72; CO 9.19% ± 1.68; H_2 0.14 ± 0.04; CH_4 0.13% ± 0.01; and traces of N_2.

2.4. Operation

Reactors were operated in batch-mode in cycles of 7 days. During the start-up, the cathode chambers were fed with 300 mL of CO_2 gas (with the aid of the gas-bag) as sole carbon source and were allowed a stabilization period of 15 batch cycles, after which current density profiles were fairly repeatable between cycles and the experimental phase itself began (see SI Fig S1). The biocathodes (working electrodes) were polarized at −1.0V against the Ag/AgCl reference electrode along the start-up and normal operation.

During the experimental period the cathode chambers were batch-fed with 400 mL of a mixture of HTC off-gas and pure CO_2 (with the aid of the gas-bag). The proportion of HTC off-gas was progressively increased until the feed was exclusively HTC off-gas (Tests 1 to 5 in Table 1). In the final test (Test 6), pure CO_2 was fed again to evaluate the eventual reversibility of the process as well as to infer possible toxic effects from the HTC.

2.5. Analytical techniques

Liquid samples were analysed for total organic carbon (TOC), total inorganic carbon (IC), total nitrogen (TN; Multi N/C 3100, Analytikjena) and volatile fatty acids (VFAs) from C_2 to C_6 (Bruker 450-GC with a flame ionisation detector (FID)). Dissolved oxygen (Hach, HQ40d two-channel digital multimeter), redox (pH Meter, pH 91; Wissenschaftlich Technische Werkstätten, WTW), pH (pH Meter BASIC 20+, Crison) and ammonium (781 pH/Ion Meter, Metrohm) were measured following standard methodologies [25].

At the end of each batch cycle, the gas bag was disconnected from the reactor and the amount of gas in the bag (V_g) was measured with the aid of a gastight syringe (50 mL, Hamilton SampleLock syringe). Gas composition, i.e., hydrogen (H_2), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2) and methane (CH_4), were determined by means of a gas chromatograph (Varian CP3800 GC) equipped with a thermal conductivity detector (TCD) [25]. The volume of hydrogen and methane produced in each cycle was calculated from V_g and was corrected to the standard temperature and pressure (STP) conditions.

The electrochemical performance of the biocathodes was

Table 1
Proportions of pure CO_2 and HTC in the fed-gas during the experimental phase.

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
% CO_2	100	80	50	25	0	100
% HTC	0	20	50	75	100	0

characterised by means of cyclic voltammetry (CV) tests using a Biologic VSP potentiostat. CV tests were performed in turnover and non-turnover conditions (i.e., in the presence and absence of CO_2 respectively) between −1.0 and 0.1 V vs. Ag/AgCl and at a scan rate of 1 mVs^{-1} and a temperature of 30 °C.

2.6. Molecular biology techniques

At the end of test 6 (Table 1), the cathode was cut into samples of about 300 mg of electrode. These samples were used to characterise the microorganisms that had developed at the methane-producing biocathode.

Microbial communities were analysed and followed at the end of the experimental period by high throughput sequencing of massive 16S rRNA gene libraries. Total Bacteria and Archaea were analysed. Genomic DNA was extracted with a DNeasy PowerSoil Kit (Qiagen) according to manufacturer's instructions. All PCR reactions were carried out in a Mastercycler (Eppendorf, Hamburg, Germany), and PCR samples were checked for size of the product on a 1% agarose gel and quantified by NanoDrop 1000 (Thermo Scientific). The entire DNA extract was used for high-throughput sequencing of 16S rRNA gene-based massive libraries with 16S rRNA gene-based primers for Bacteria and Archaea 515F to 806R. The Novogene Company (Cambridge, UK) carried Illumina sequencing out using a HiSeq 2500 PE250 platform.

The obtained DNA reads were compiled in FASTq files for further bioinformatics processing carried out using QIIME software version 1.7.0 [29]. Sequence analyses were performed by Uparse software (v7.0.1001) using all the effective tags. Sequences with ≥97% similarity were assigned to the same OTUs. Representative sequence for each OTU was screened for further annotation. For each representative sequence, Mothur software was performed against the SSUrRNA database of SILVA Database [30] for species annotation at each taxonomic rank (Threshold:0.8–1).

The quantitative analysis of all samples was carried out by means of quantitative-PCR (qPCR) using PowerUp SYBR Green Master Mix (Applied Biosystems) in a StepOnePlus Real-Time PCR System (Applied Biosystems) as described previously [31]. The qPCR amplification was performed for the 16S-rRNA gene in order to quantify the entire eubacterial community and for the mcrA gene to quantify the total methanogen community. The primer sets 314F qPCR (5′-CCTACGGGAGGCAGCAG-3) and 518R qPCR (5′-ATTACCGCGGCTGCTGG-3′) at an annealing temperature of 60 °C for 30 s was used for Bacteria and Arc 349F (5′-GYGCASCAGKCGMGAAW-3′) and Arc 806R (5′-GGACTACVSGGGTATCTAAT-3′) for Archaea quantification.

3. Results and discussion

Before the experimental phase began, the biocathodes were allowed a stabilization period of 15 batch cycles (7-day duration of each cycle) during which the reactors were fed with pure CO_2 as the sole carbon source. By the end of this period, the current density profiles tended to be repeatable between cycles (see Figure S1), indicating that the biocathodes were mature enough to initiate the experiments.

3.1. The impact of gradually increasing the amount of HTC off-gas in the feeding

During the experimental phase, the reactors were batch-fed (7-day duration of each cycle) with 300 mL of a gas mixture consisting of CO_2 and increasing amounts of HTC gas (Table 1). Fig. 2a shows how current density declines steadily with the HTC, falling from about 1.5 A m^{-2} when no HTC is present to 0.6 A m^{-2} when only HTC is fed to the reactors, which reveals a negative impact on the microorganisms that are directly involved in current production (see Fig. 2S). Methane production was also affected by the presence of HTC in the fed-gas (Fig. 2b),

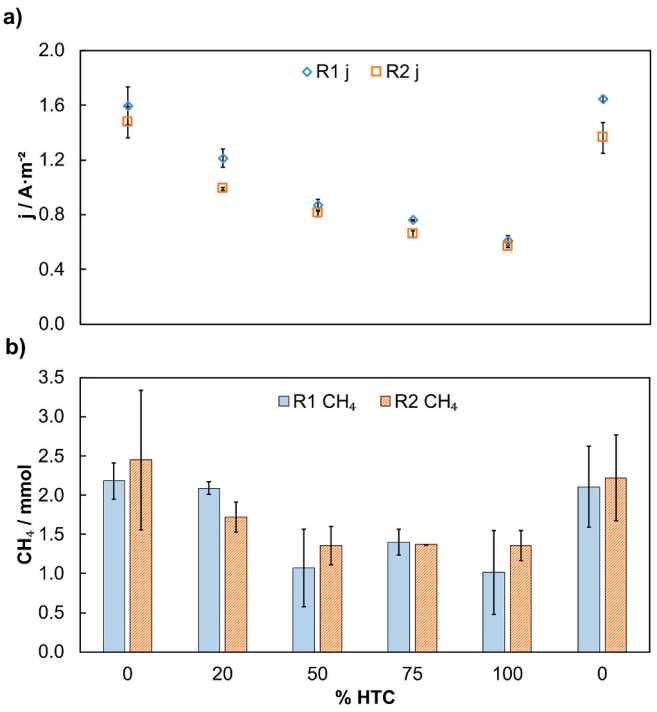

Fig. 2. Average current density (top) and methane production (bottom) as a function of the proportion of HTC feed to the reactors. The last condition represents the return to a feeding with pure CO_2.

decaying form about 2.3 mmol per cycle (0% HTC) to 1.2 mmol per cycle (100% HTC). This decline in both, current density and methane production, might be connected to the presence of carbon monoxide (CO) in the HTC (Fig. 3), as CO can inhibit the activity of metal-containing hydrogenases that catalyse the reversible conversion of protons and electrons to hydrogen [32,33]. Nevertheless, when pure CO_2 was fed again to the reactors at the end of the experimental phase, current density and methane production returned to values similar to those observed before HTC gas was fed, which suggests that the changes induced by HTC were reversible.

It is interesting to note that, in contrast to current density and methane production, the coulombic efficiency improved with HTC (Fig. 4), which apparently means that HTC promotes a more efficient use of current, probably because less electrons are being diverted to biomass.

This hypothesis is coherent with the loss of biomass detected by qPCR analyses as it will be discussed below. However, it does not explain why HTC concentrations above 75% resulted in coulombic efficiencies greater than 100% (Fig. 4). Under these circumstances, a more plausible

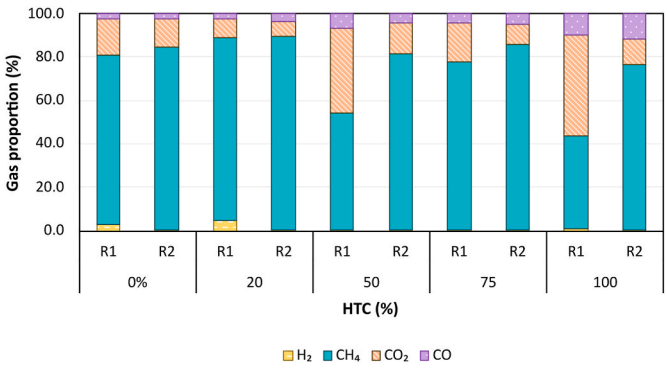

Fig. 3. Gas content as a function of the amount of HTC off-gas fed to the reactors.

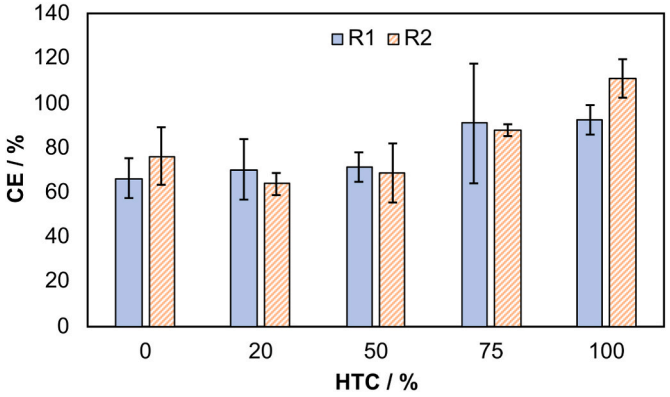

Fig. 4. Average values of coulombic efficiency (CE) as a function of the proportion of HTC off-gas fed to each reactor.

explanation can be traced to the potential role of CO as an electron donor (alternative to the cathode) that "artificially" increases the CE. Indeed, previous studies on CO fermentation have found that carboxydotrophic bacteria can use CO to produce acetate, H_2, and CH_4 [34,35]. To make sure whether this might be happening in our reactors, we operated them for two cycles with 300 mL of HTC and in the absence of any applied voltage. This resulted in the production of significant amounts of CH_4 that can only be attributed to CO fermentation (Fig. 5). Moreover, the amount of methane measured in these tests is stoichiometrically coherent with the amount of CO in the HTC.

CO conversion to methane in the presence of hydrogen (according to Equation (1) [35]) can also explain the increase in the CE. This route requires only 6 mol of electrons per mole of methane —instead of the 8 mol of electrons for CO_2 route—, which represents a 25% reduction in current usage, and therefore an increase in the CE.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \text{Equation 1}$$

As the catholyte is replace by a fresh nutrient solution at the beginning of each cycle, the accumulation of reducing power between cycles via extracellular matrix or through the loss of biomass can be ruled out as significant source of reducing power for methane production.

To deepen the understanding of the impact of the HTC gas on the bioelectrochemistry of the methanogenic biocathode, electrochemical and microbiology analyses were performed.

3.2. Electrochemical analyses

Fig. 6 represents the voltammograms recorded at the beginning of each batch cycle for the different HTC fractions. Both reactors showed a large reduction peak at potentials below −0.9 V vs. Ag/AgCl that has been usually associated to H_2 evolution [36]. As our reactors were operated at −1.0V vs. Ag/AgCl, this peak confirms that methanogenesis is occurring through the H_2-mediated indirect electron transfer (IET) mechanism [37]. In addition, the size of the hydrogen peak decreased with the fraction of HTC in the fed-gas, which is consistent with the averaged current densities presented in Fig. 2. The impact of HTC was more apparent on R2 (37% decrease in peak current) that on R1(27% decrease), so it seems that R1 might have developed a more robust and resilient electrotrophic biofilm. However, the microbiology analysis (see Figs. 7 and 8 in the next section) did not provide a clear support to this hypothesis.

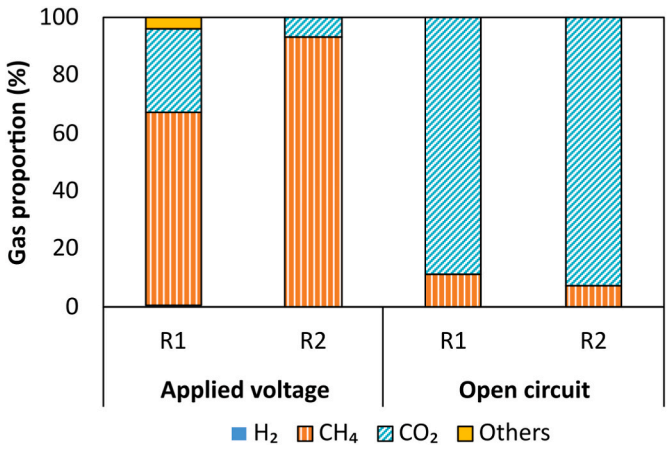

Fig. 5. Gas composition under applied voltage and open circuit conditions using 100% HTC off-gas as substrate.

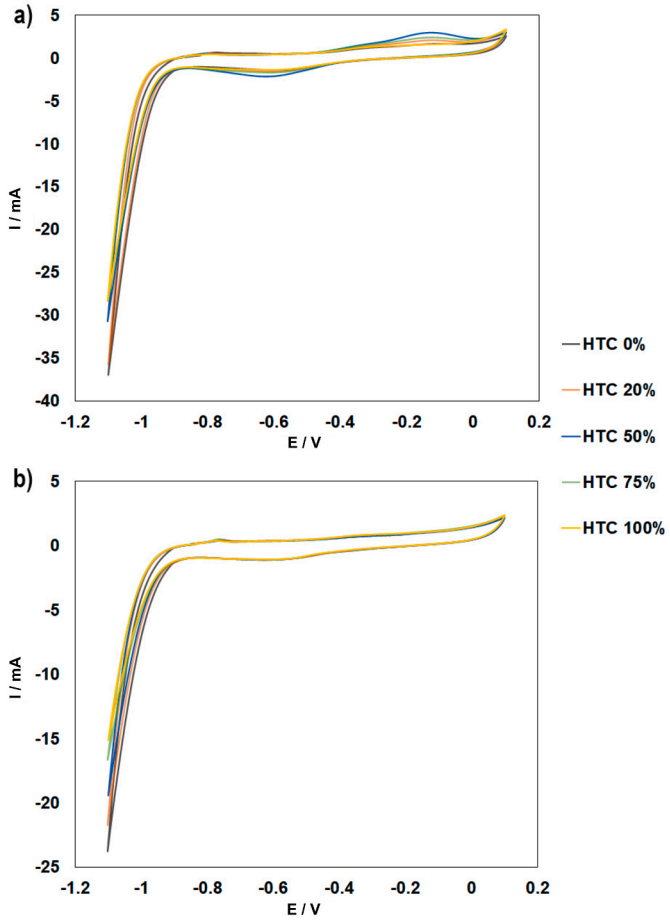

Fig. 6. CVs for R1 (top) and R2 (bottom) at the different HTC proportions in the fed-gas. Electrode potential is referred to the Ag/AgCl reference electrode.

CVs showed another reduction peak —much smaller than that associated to hydrogen evolution— at about −0.6 V vs. Ag/AgCl. As the onset potential of the hydrogen evolution reaction on a biocathode is around −0.8 V [38], this peak could most probably be attributed to electromethanogenesis via the direct electron transfer (DET) mechanisms [36], or even to acetate production [39] that would eventually be converted to methane (the concentration of acetate and other volatile fatty acids was below the detention limit of the chromatograph). In any event, their contribution to electromethanogenesis would be marginal compared to the IET mechanism [20,37]. In addition, the size of the DET peak in R1 varied with the amount of HTC, although no apparent trend was visible. An oxidation peak appeared only in R1, with no apparent trend either. These two peaks, that seem to be inter-related, disappeared almost completely when HTC proportion was 100%, which might be indicating an adaptation process.

3.3. Microbiology analyses

qPCR analysis revealed that both, bacteria and archaea were seriously damaged by the presence of HTC off-gas in the fed (Fig. 7). However, the impact —measured in terms of the decrease in the number of gene copies— was unequal for both groups; while for bacteria the introduction of HTC meant a loss of 85% and 66% (R1 and R2, respectively) of their communities, for archaea it meant 96% and 97% (R1 and R2, respectively). This loss in biomass would explain the poor performance, but also —at least partially— the better CE values observed with HTC off-gas as discussed above. Previous studies have pointed out the ability of CO to inhibit methanogenic organisms, which could explain the greater decrease in archaea [40].

Relative abundance analyses (Fig. 8) indicated that *Methanobacteriaceae* dominated archaea in both reactors, although its proportion experienced a notable decay with HTC off-gas: from 56.6% to 44.6% in R1 and from 56.8% to 30.1% in R2. Nevertheless, its relatively large presence is consistent with the hypothesis that H_2 acts as an intermediary in the electron transfer [36,41,42], as most members of this family are hydrogenotrophic methanogens. Moreover, some species of this family have been reported to grow on CO as the sole carbon source while producing methane, although they appear to be not very metabolically efficient [33].

The *Methanosacetaceae* family, all of its members use acetate as their sole source of energy [43], completely disappeared after HTC off-gas was fed, which can be related to the total absence of *Clostridiaceae* (Fig. 7). Indeed, many species within the later are well known acetogenic bacteria [44], so there might be a syntrophic link between this two families that was broken with the presence of HTC, causing them both to disappear. This result contrasts with [45], where the authors proved that the electroactive bacteria of a CO-fed microbial electrosynthesis biocathode not only tolerated CO, but they were able to convert it into acetate (and other volatile fatty acids).

Regarding bacteria, their diversity was greater than that of archaea. The *Desulfomicrobiaceae* family, capable of electrotrophic hydrogen production [46], occupied a preeminent position in terms of relative abundance regardless of the gas fed. Interestingly *Rhodocyclaceae*, *Sphingobacteriaceae* and *Anaerolineaceae* families —all of them microorganisms also capable of using the electrons arriving at the cathode to catalyse reductive process such as H_2 formation [22,25,47–50]— increased its proportion in the presence of HTC off-gas. In addition, other microorganisms with a less clear role in methane production such as *Moraxellaceae* (previously described as electrotrophic bacteria in cathodic environments [51,52]), *Neisseriaceae*, *Pseudomonadacea* (electrotrophic denitrifier [53] and oxygen scavenger in biocathodes [54]) and *Synthrophaceae* also increased their relative proportion in the presence of HTC. This observation might be revealing that CO is inducing a shift in the bacterial communities that results in the selection of those families directly involved in electrotrophic reductive processes. As these bacteria need to be in close contact with the electrode, it can be hypothesised that archaea —that relay on the hydrogen generated by bacteria— might be forming a protective biofilm above them that alleviate the potential impact of CO.

4. Conclusions

The present study demonstrates the technical feasibility of converting HTC off-gas into methane through EM. Results reveal that although this gas severely affects both current density and methane production, it allows the production of biogas with up to 70% of methane content. HTC off-gas also had a negative impact on the cathodic microbial communities, especially on the archaeal family *Methanomicrobiaceae* that uses hydrogen to produce methane. Although feeding HTC off-gas also resulted in a decrease in the total number of gene copies of bacteria, the impact was less pronounced, probably because the archaea form a protective biofilm. Finally, it was hypothesised that the CO present in the HTC could be responsible for this biological inhibition, although its eventual conversion to methane could also lead to higher coulombic efficiencies.

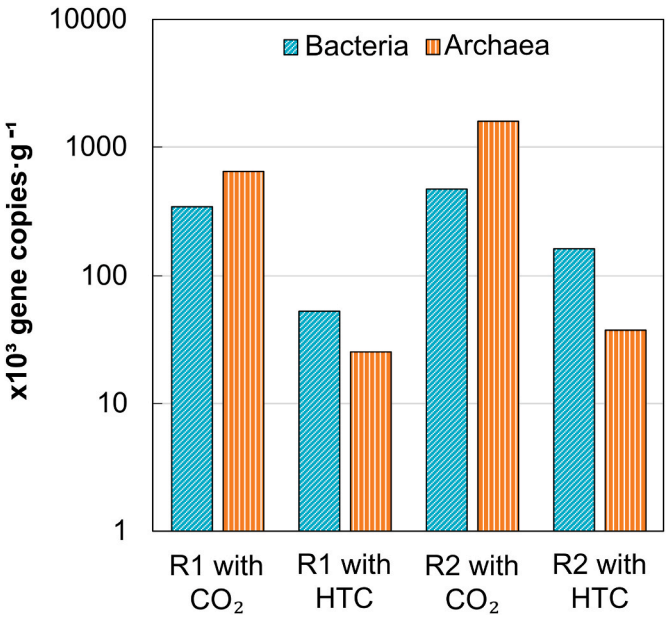

Fig. 7. Gene copy number in CO_2 and HTC fed reactors obtained by qPCR analyses.

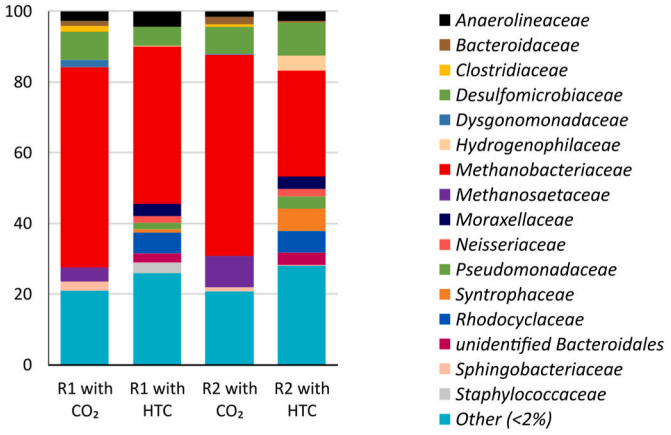

Fig. 8. Relative abundance of microorganisms fed with CO_2 and with HTC. Groups that did not reach at least 2% were grouped in the category "Other".

CRediT authorship contribution statement

Guillermo Pelaz: Conceptualization, Investigation, Methodology, Writing – original draft. **Judith González-Arias:** Conceptualization, Investigation, Methodology. **Raúl Mateos:** Conceptualization, Investigation. **Adrián Escapa:** Conceptualization, Supervision, Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.renene.2023.119047.

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