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Enhancing ethanol selectivity in microbial electrosynthesis from CO_2 via digital process control

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ABSTRACT

The present work aimed to address the challenges of low efficiency and selectivity that are hindering the industrial adoption of microbial electrosynthesis (MES) for producing ethanol from CO_2. To this end, an electrically efficient MES cell with a low-gap stack configuration was operated and subsequently integrated into a bench scale system, enabling full control of the operating parameters to optimize ethanol production. In a preliminary test, low pH values (<5) along with low CO_2 partial pressure (< 0.2 atm) were identified as key parameters in triggering solventogenesis. Under these conditions, ethanol was produced with 64% selectivity and 57% coulombic efficiency. This resulted in an ethanol:acetic acid molar ratio exceeding 2.0, a final concentration of 3.35 g L^{-1} and a production rate up to 1.24 g m^{-2} d^{-1}. A digital process control was then implemented in the automated bench scale system, setting the pH between 4.5 and 4.7, fixing the dissolved CO_2 concentration range between 200 and 800 ppm and the total pressure to either 1.6 or 1.8 atm. Ethanol production rate boosted to 5.69 g m^{-2} d^{-1} while maintaining a similar production selectivity. Overall, the present work lays the foundation for the digital transformation of microbial electrosynthesis by showcasing the application of automated control systems to accurately regulate the operational parameters required to optimize ethanol production from CO_2.

1. Introduction

Ethanol is an organic compound of particular interest as it has broad applications in the chemical industry, as a solvent, as a cleaner agent, as a drop-in biofuel and its potential conversion to jet fuel, among others [1,2]. Additionally, ethanol acts as electron donor for the bioproduction of valuable middle chain fatty acids and other valuable compounds [3]. It has a 5 times higher market value than methane [4] and 10 times the market size of acetic acid, with perspective to continue rising. Its production from carbon dioxide (CO_2), in particular by employing biological approaches, is emerging as a sustainable alternative to conventional fossil-based processes [5]. Up to date, gas fermentation, which consists of the bioconversion of gaseous substrates into organic compounds, is the most advanced biotechnology to produce ethanol, already exploited at commercial level [6]. The main drawback of gas fermentation is that the electron donor (usually hydrogen, H_2) must be externally supplied and has low solubility in liquid media, which adds complexity, energy demand, and cost to the process. Microbial Electrosynthesis (MES) emerged as an alternative where reducing power is provided by an electrode and H_2 is *in-situ* produced.

In MES, ethanol and other alcohols have been produced at low concentrations and mainly as a by-product [7,8], while a scarce number of studies have delved into its production [9–11]. Ethanol formation in MES cells employing a mixed culture inoculum is commonly obtained through reduction of CO_2-derived acetic acid [12]. Diverse microorganisms are capable of converting H_2 and CO_2 into acetic acid (as *Sporomusa ovata* or *Acetobacterium woodii*), however only few of them possess the genetic traits to synthesize ethanol (as *Clostridium ljungdahlii* or *C. autoethanogenum*) [13]. In addition, insights in the shift mechanism from acetogenesis to solventogenesis route are still mainly unknown [14].

Few studies have focused on identifying the main operational parameters promoting ethanol formation over other metabolites [9,11]. These studies indicated that low pH and CO_2 partial pressure (pCO_2) along with high H_2 partial pressure (pH_2) and acetic acid availability are crucial parameters to trigger solventogenesis. Ethanol production from CO_2 in MES is a combined multi-step process where each stage requires different conditions, thus increasing the process complexity and

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requiring fine-tuning to optimize the solventogenic pathway. This underscores the need for real-time monitoring and control of key operational conditions within the MES systems [11]. This would streamline the production and establishing guidelines for synthesizing ethanol from CO_2. Such controls have been previously introduced to fermentation studies, resulting in significant productivity increases [15].

Additionally, the electric efficiency of the process plays a principal role for its techno-economic feasibility. Up to date, the most common configurations have been electrically inefficient, such as H-type and tubular reactors, which have exhibited different impediments as high cell voltages or uneven energy distribution. In this context, recent studies proposed the application of compact, scalable and efficient flat-plate electrochemical cells with minimum distance between electrodes (as zero- and low-gap configurations) for product synthesis [16]. These cells exhibit low ohmic resistance which reduces overpotentials and minimizes the required power input. They also have a high scalability potential as the compartments can be stacked.

Thus, to advance the MES technology devoted to ethanol synthesis, the process should be both selective and efficient. Therefore, system designs capable of integrating efficient cells, advanced sensing, control, and actuation devices should be prioritised to enable precise process management.

The present work explored, for the first time, the incorporation of a rigorous in-line digital control of operational conditions to an efficient, scalable, low-gap MES stacks. This strategy allowed to fine-tune the process parameters towards selective and efficient ethanol production, exemplifying the value of digital transformation in optimising bio-electrochemical systems.

2. Materials and methods

2.1. Experimental design and configurations

Two commercial flat-plate MES cell stacks (Electro MP Cell, ElectroCell Europe, Denmark) were used to conduct the experiments (Figure S1). Each stack consisted of three cathodic and two anodic chambers separated by a total of four reinforced cation exchange membranes (CEM, Nafion N324, US). The chambers were built with PVDF frames acting as electrolyte distributor racks and sealed with 1 mm ethylene propylene diene monomer (EPDM) rubber gaskets to prevent leakage. The cathode electrodes consisted of carbon felts of 0.01 m^2 projected area (four working faces, total working area of 0.04 m^2) in contact with a stainless-steel plate as current collector. Dimensionally stable anodes (DSA-O_2) of 0.01 m^2 were used as counter electrode (4 operating faces, total working area of 0.04 m^2). The three cathodic compartments, as well as the two anodic compartments, were interconnected and formed a total volume of 0.3 L each.

Each cell stack was operated either as a stand-alone non-controlled system (SA) or integrated into a controlled balance of plant (BoP) unit, that allowed in-line and automated control of key operational parameters (Fig. 1). In both cases, systems were operated under dark conditions to avoid photosynthetic growth and without temperature control. The cathode chamber was completely sealed to prevent oxygen (O_2) intrusion and to favour H_2 accumulation, while the anode was in contact with the environment to prevent O_2 accumulation. The liquid phase of each chamber was continuously recirculated through a pump, to get homogenization.

2.1.1. Non-controlled stand-alone system

The stand-alone (SA) cell stack system was built by connecting the cathodic and anodic compartments of the stack to their respective cathodic and anodic buffer tanks using marprene tubing. The liquid phase was continuously recirculated by means of peristaltic pumps (Watson Marlow, model 323, USA) at a flow rate of 5.2 mL min^{-1} (Fig. 1**A,** Figure S2 A). The catholyte and anolyte liquid volumes were 0.4 L each, with a headspace of 0.2 L in the cathode buffer tank. The cell was connected to a power source (IMHY3, Lendher, Spain) for electric current delivery.

2.1.2. Controlled balance of plant system

The cell stack was installed into a balance of plan (BoP) system (Fig. 1**B,** Figure S2 B), similar to the one previously described by Rovira-Alsina et al. [17], that allowed the dynamic control of operational variables. Briefly, the anode compartment was connected to a buffer tank where the pH was continuously measured. The anolyte was recirculated at 100 mL min^{-1} using a peristaltic pump (Schenchen, LabM6, China). The cathode compartment was connected to a buffer tank. The cathode section also comprised a continuously stirred probe holder unit (HYCC, USA), and a gas-liquid separation unit (Fig. 1**B**). The catholyte was continuously recirculated by a micro-pump (GJ-N27-DEELE, USA) at a flow rate of 125 mL min^{-1}. Two additional peristaltic pumps (Schenchen, LabM6, China and Grundfos, DDC-15–4, Spain) were used to fill the anode and cathode compartments at the beginning of the experiment, and when a fresh media supply was required. The total anolyte liquid volume was 2 L, while the catholyte total volume was 2.9 L with 1.0 L of headspace.

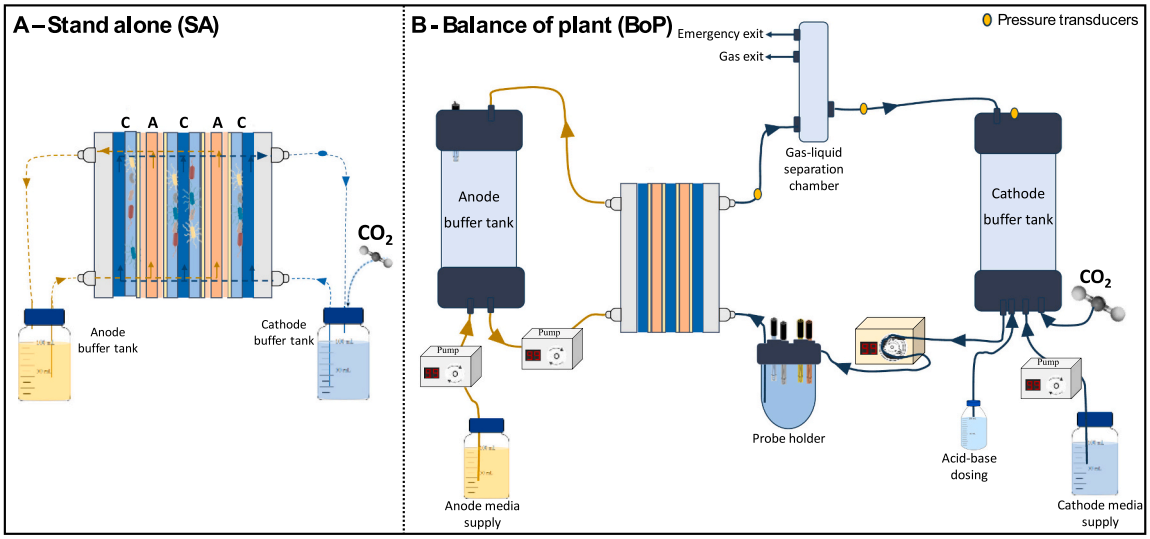

Fig. 1. Schematic representation of the (A) SA and (B) BoP configurations. C and A indicates cathode and anode chambers and electrodes.

Table 1
Summary of tests and conditions stablished with BoP system.

BoP		pH	Dissolved CO_2	Pressure (atm.)	Temperature (°C)
Test 1		Not controlled		1.8	16–25
Test 2	0–6*	< 5.0	500–2200		17–25
	6–11*	4.5–4.7			
	11–22*		200–800		
Test 3				1.6	19–25

* Days of operation under each controlled parameter range.

The system was connected to a programmable logic controller (Haiwell PLC – H02W, China) with a touchscreen display that allowed to continuously control and monitor pH, total pressure, dissolved CO_2 concentration and current applied, supplied by a power source (MQR120–24F; Mibbo, China). The control system allowed to set either a setpoint or a range to maintain, as well as the activation and waiting time of the actuators. Moreover, electrical conductivity (EC), dissolved O_2 and electric parameters including the cell voltage and energy consumed, were continuously monitored. Pure CO_2 (99.9%, AirLiquide, Spain) was sparged in the buffer tank and its dissolved concentration was continuously registered along with temperature with an in-line probe (InPro® 5000(i); Mettler Toledo, Spain). The pressure was monitored by pressure transducers (IFM, PT0505, Spain), and the overpressure was released through an electro-valve according to the custom setpoint. Two dosing pumps (DOSATec PCO, Dosatronic, Spain) controlled by an ON/OFF system actuator were used for pH control, dosing either HCl or NaOH (5 M) to the buffer tank when required. The liquid CO_2 concentration was mastered by a multi-transmitter (Multi-parameter Transmitter M200, Mettler Toledo, Spain) and the actuator was a magneto-inductive flowmeter (IFM, SM4100, Spain) installed and connected to a CO_2 gas line to maintain the desired concentration. The setting and change of all parameters could be done through the touchscreen with the system-scheme and the configuration settings. Besides, a remote-access tool (EasyAccess 2.0) was available to implement the required adjustments online, also accounting with an operation interface software (cMT viewer).

2.2. Systems start up and operation

2.2.1. Stand-alone system operation

The SA system was filled with the previously described mineral media and inoculated with 40 mL (10% *v/v*) of an enriched culture from a MES cell dominated by *Clostridium ljungdahlii/Clostridium autoethanogenum* [9]. The cell was operated under galvanostatic mode applying 60 mA (0.15 mA cm^{-2}) for a total of 87 days. Two tests were performed. In the first one, the system was operated in fed-batch conditions and CO_2 (99.9%, AirLiquide, Spain) was sparged in the catholyte for 3 min after each sampling time (2–3 times per week), and thereafter added in excess, by closing the outlet valve, to reach a pCO_2 of 1.5 atm. The pH was not controlled and let naturally decrease to trigger solventogenesis. Sodium 2-bromoethanesulphonate (Na-BES, 1 g L^{-1}) was added when CH_4 was detected, to avoid methanogenic activity. The reactor was kept at room temperature (26 ± 2 ºC). The second test was started up by replacing half of the catholyte and the whole anolyte with fresh media aiming at direct solventogenesis initiation. Therefore, working conditions in terms of current and CO_2 supplied were maintained, while initial pH was lower (4.7), and product concentration was higher (acetic acid ca. 45 mM C).

2.2.2. Controlled balance of plan system operation

The BoP system was inoculated with 150 mL of SA catholyte obtained at the end of that system operation. The BoP operation was in galvanostatic mode, at an applied current of 430 mA (1.075 mA cm^{-2}), according to the previous SA current applied and scaled by the catholyte volume. CO_2 was initially added to the cathode buffer tank by sparging thrice per week and adjusting the pressure to 1.6 atm after sampling. Later, CO_2 was added on demand, based on dissolved CO_2 concentration in the catholyte set in the control system.

Three sequential tests were performed (Table 1). First, the operation parameters (pH, EC and temperature) were simply monitored, and only the pressure threshold was controlled by setting a limit of 1.8 atm. In the second test, the pressure was again controlled at 1.8 atm, the dissolved CO_2 concentration was set in the range of 500–2200 mg L^{-1}, and the pH was maintained slightly below 5.0 to boost acetic acid production. After acetic acid accumulation, when ethanol started to be detected, the pH was decreased to the range 4.5–4.7, and dissolved CO_2 between 200 and 800 mg L^{-1}, to boost solventogenesis. In Test 3, the same setpoints were maintained from the beginning, except pressure that was decreased to 1.6 atm. The system was operated at ambient temperature (16–25 ºC).

2.3. Chemical analysis and calculations

The cells were sampled twice to thrice a week. Liquid samples (5 mL) were taken from both anolyte and catholyte. Cathode gas samples (5 mL) were also collected on the same days. Gas pressure was manually measured in the cathode headspace of both systems by a differential pressure sensor (differential pressure gauge, Testo 512, Spain). Liquid withdrawn by sampling was replenished with fresh media to uphold a constant volume.

Gas composition was analysed through a micro-GC (Micro GC 490, Agilent technologies, USA). Liquid samples were taken to measure the optical density, the pH and the EC. Then, the samples were filtered (0.2 μm) and analysed to determine the concentration of carboxylates and alcohols using a GC (GC 7890 A, Agilent Technologies, USA). Further details on both analyses can be found in Romans-Casas et al. [9].

Gases partial pressures were determined using the ideal gas law, based on each compound relative concentration in the cathode headspace and the total pressure. Besides, to determine the total amount of a gaseous compound, the portion dissolved in the liquid phase was calculated using Henry's law at 25 ºC. Production rates were calculated as the increment in the concentration of the compound *i* between two consecutive sampling points divided by the time span and normalized to the electrode surface (400 cm^2). Coulombic efficiency (CE) was calculated according to Patil et al. [18]. Product selectivity was determined as the percentage of carbon recovered in a specific product in relation to the total carbon recovered in products.

3. Results and discussion

3.1. Ethanol production from CO_2 in a MES stack

The stand-alone system was set-up to determine the capability of the cell stack to produce ethanol and compare the productivity to that achieved in previous tests and systems [9–11]. To do so, two sequential tests were conducted, Test 1 and Test 2, lasting 60 and 26 days, respectively (Fig. 2).

In Test 1, acetic acid production started immediately after inoculation, reaching a concentration of 38 mM C in only three days (Fig. 2**B**). However, after that initial event, acetic acid concentration did not increase until day 25 due to the onset of methanogenesis where an abrupt

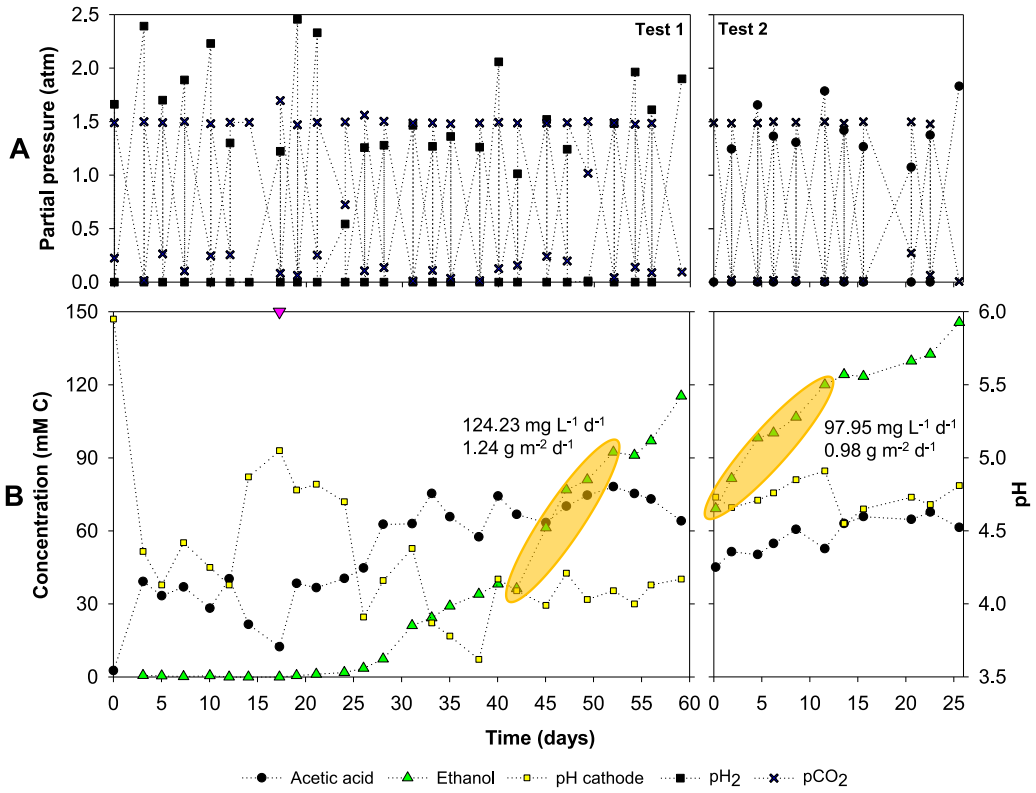

Fig. 2. Partial pressure (pH_2 and pCO_2) (A), pH and main organics concentrations (B) obtained over time in the stand-alone cell. Inverted pink triangle indicates the Na-BES addition to inhibit methanogenesis.

OD increase to 0.25 was observed (Figure S3). At that point Na-BES was added and thereafter, the methanogenic microorganisms were inhibited and CH_4 production ceased, as confirmed by the headspace analysis and by the OD decrease from 0.25 to below 0.05. For the rest of the test, OD slightly increased and oscillated between 0.03 and 0.16.

Following this event, acetic acid production was restored almost immediately after Na-BES addition, and the pH naturally decreased to mildly acidic values slightly below 5.0, due to the acid formation and accumulation [10,19]. The acetic acid production rate reached 128.49 mg L^{-1} d^{-1} (1.29 g m^{-2} d^{-1}). This rate was low when normalized to the electrode surface, but in line with previous studies when normalized to the catholyte volume [10,20], suggesting that acetogenesis was mostly occurring in the bulk liquid.

Despite CO_2 consumption, with pCO_2 values decreasing to below 0.3 atm in most feeding cycles (Fig. 2**A**), acetic acid did not accumulate above 77 mM C. The plateau of acetic acid concentration was likely due to its further conversion to ethanol, which was triggered from day 26 onwards as a response to the pH decrease to below 4.5. At such pH, most acetic acid is present in the toxic undissociated form, hampering the acetogenesis pathway and triggering the solventogenic detoxifying mechanism [21,22]. Solventogenesis began when the acetic acid titer was 38.44 mM C, as observed in previous studies from our group [11]. The ethanol production rate was initially low, most likely due to a prolonged activation period and to the excessively low pH, which dropped to < 4.0 after five days. On day 42, after the pH increased above 4.5, ethanol was consistently produced reaching a final concentration of 115.38 mM C (2.66 g L^{-1}) by the end of the operation. A maximum production rate of 124.23 mg L^{-1} d^{-1} (1.24 g m^{-2} d^{-1}) was observed between day 42 and 52, which was comparable to previously reported values in the literature [9,23]. However, by the end of the test, the EtOH:HAc molar ratio reached 1.8, with an average ethanol production selectivity of 50.32% (on a carbon basis) and peaks of above 90% (days 33–38), greatly surpassing the values achieved in previous works [8,10]. This was attributed to the joint effect of low pH and pCO_2, and high pH_2, and to the use of a cell configuration that ensured H_2 availability across the whole system, from the electrochemical cell to the buffer tank. Other byproducts, such as butyric and caproic acids, were detected at low concentration (< 7 mM C each, Figure S4), probably, due to the inhibition of the chain elongating routes at such low pH (< 4.2) [24].

On day 60 of operation, the Test 2 was initiated by exchanging 50% of the catholyte and the whole anolyte for fresh media. This resulted in an initial cathode pH of 4.7, and in a decrease of ethanol and acetic acid concentrations to 69 and 45 mM C, respectively. This strategy aimed at validating the solventogenesis onset while avoiding the need to perform an acetogenesis step. Thus, ethanol production restarted promptly, suggesting the presence of an enriched solventogenic community in the cell, resilient to changes, that can be exploited to restart the cells in case of failure (*e.g.,* power cut or recirculation clogging). After 26 days of operation, ethanol concentration doubled and reached 145.56 mM C (3.35 g L^{-1}). Its production rate was slightly lower than before, perhaps due to lower acetic acid concentration availability or to the higher initial ethanol concentration, that may have negatively affected the production kinetics [25]. Nevertheless, the EtOH:HAc molar ratio achieved between days 21 and 26 was the highest (2.11 ± 0.23), with an average product selectivity of 64% and production peaks above 97%.

The results obtained surpassed the threshold EtOH:HAc ratio of 2, more suitable for the production of elongated compounds (*i.e.,* butyric and caproic acid) [3]. In addition, high EtOH:HAc ratios are beneficial for the downstream processing to obtain commercial ethanol [1].

In this study, an uptrend in ethanol production was identified in extended cycles characterized by low pCO_2 and high pH_2 thereby, corroborating findings from previous studies [11]. Furthermore, these ranges can change over time due to microbial dynamics in the cell, biofilm formation and product accumulation. Moreover, the optimal pH, pH_2 and CO_2 ranges, and the acetic acid and ethanol productivities, are strongly dependent on the microbial community catalyzing the reactions, including the main growth pattern (biofilm or planktonic), the relative abundance of acetogenic and solventogenic species, and their

capability to sustain the pathways of interest. Since maintaining the optimal ranges for key process parameters is essential to trigger solventogenesis, technology digitalization was proposed hereby as a strategy to ensure a meaningful and adaptable in-line control of key operation parameters at the different stages of operation.

3.2. Advancing the technology: optimizing acetic acid and ethanol formation in a controlled MES

After confirming that the stack cell is suitable for efficient ethanol production, an identical cell was installed in a bench scale plant that allows a dynamic control of the key operational parameters (Fig. 1**B**). For test 1 (Table 1), the operational conditions were set similar to the initial conditions of the previous experiment (SA) to fine-tune, study and learn the operational capabilities of the system, but the applied current was increased proportionally to the catholyte volume. Normalizing the current density based on the cathode surface is the standard procedure for electrochemical cells. However, normalizing it to the cathode volume could be preferable in MES, specially when targeting compounds different than acetic acid and methane, where the actual biochemical reactions mostly occur in the bulk liquid [26]. Subsequently, key parameters setpoints were changed, in accordance with the literature and the previous findings, to target ethanol production.

The BoP system was inoculated with 5% of SA catholyte. After inoculation, the pH increased abruptly to 8.0, most likely due to the relatively high current applied, requiring manual adjustment with HCl, since the online pH monitoring was unavailable on days 5–10. After adjusting pH to below 6.0, the OD mildly increased and fluctuated, particularly on days 17–25 of operation (Figure S5 A). At the same time, acetic acid was produced at a constant rate of 17.72 g m^{-2} d^{-1} (244.43 mg L^{-1} d^{-1}) until day 18, reaching a concentration of 91 mM C (Fig. 3**B**). After that, acetic acid production slowed down and pH started to slightly increase until day 24, when it surpassed 6.5 and had to be manually adjusted. The pH increases likely occurred as the acid production was insufficient to counteract the protons consumption for H_2 formation in the cathode. Consequently, acetic acid production trend

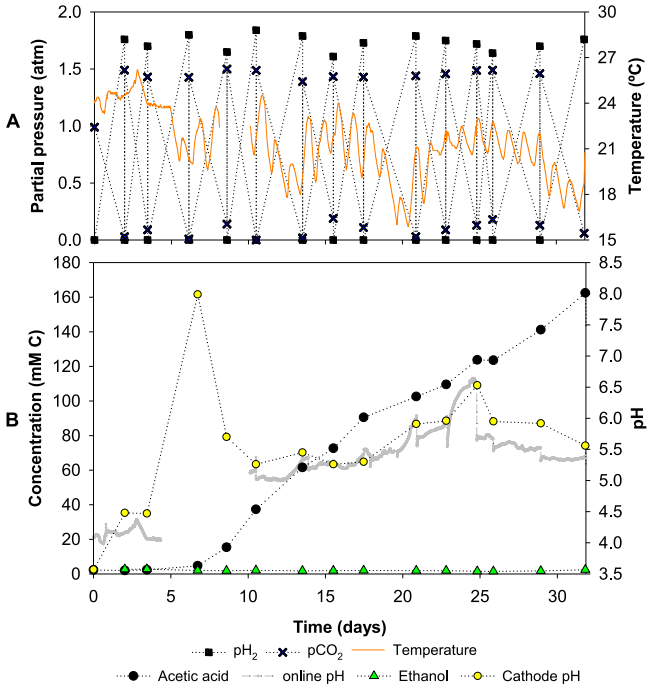

Fig. 3. Operational parameter monitoring and product concentrations obtained in the BoP MES system, Test 1. Temperature, pH_2 and pCO_2 (A); online and punctual pH, acetic acid and ethanol production (B).

slowed down due to the product accumulation [19]. Nevertheless, acetic acid accumulated to a final concentration of 162.8 mM C (4.88 g L^{-1}) by the end of the experiment. Acetic acid production rate reached a maximum of 348.10 mg L^{-1} d^{-1} (25.24 g m^{-2} d^{-1}), which is higher than in the SA experiments and in the same range of previous studies [7, 27–29]. This was most likely due to the higher pH registered (mildly acidic) and the lack of acetic acid consuming reaction, such as ethanol production and chain elongation. In fact, the concentration of other organics (i.e. butyric and propionic acids and the correspondent alcohols) remained low (Figure S5 B). This can be attributed to the fact that, differently from the SA test, CO_2 was constantly dosed and available throughout the test.

Along the whole run, the gas phase composition was systematically analysed. In each fed-batch cycle, CO_2 decreased below 0.2 atm, and H_2 accumulated up to the set pressure of 1.8 atm, while the excess gas, containing H_2 and CO_2, was released. CH_4 was not detected in any of the samples taken. Besides, the system temperature was continuously monitored yet not controlled, with the ultimate goal to examine the resilience of the culture employed under oscillating sub-optimal temperatures (16–25 °C).

Once the BoP MES system capacity of producing acetic acid was confirmed, a new test (Table 1, test 2) was initiated targeting ethanol production by determining and setting the most favourable conditions for solventogenesis. The applied strategy consisted of in-line pH and dissolved CO_2 concentration control, while the threshold pressure was maintained at 1.8 atm throughout the experiment.

Initially, pH was maintained slightly below 5.0 (Fig. 4**B,** Test 2), while the CO_2 feeding regime was maintained as in previous tests (500–2200 mg L^{-1}). At the beginning of this test, the acetic acid concentration was 94 mM C (2.85 g L^{-1}), considerably higher than the threshold of 20 mM C previously reported to trigger ethanol synthesis [9,11]. Despite this, on the first five days of operation, acetic acid concentration slightly increased, while ethanol production did not occur. Hence, from day 6 of operation, pH was further decreased to the range 4.5–4.7 to increase the share of undissociated acetic acid, necessary to trigger solventogenesis [24]. The OD remained low throughout the test (Figure S6 A). Still the ethanol production rate remained low and only improved when the CO_2 concentration naturally decreased to below 500 mg L^{-1}, supporting the conclusion that solventogenesis requires fine-tuning control of several process parameters. This was in line with previous findings stating that high H_2 and low CO_2 availability conditions enhance ethanol formation [30].

From day 12, besides controlling pH in the range 4.5–4.7, the CO_2 supply was configured to keep a low dissolved CO_2 concentration between 200 and 800 ppm in the catholyte (Fig. 4 **A,** Test 2). This specific range was selected as low dissolved CO_2 concentration (200 mg L^{-1}) favour ethanol production by acetic acid reduction, while higher concentrations (800 mg L^{-1}) are needed for CO_2 conversion to acetic acid, restoring its concentration in the catholyte. The applied changes boosted ethanol synthesis, achieving a linear production rate of 78.49 ± 20.26 mg L^{-1} d^{-1} (5.69 ± 1.47 g m^{-2} d^{-1}), three-fold higher than the rate obtained in the SA system. It is also worth to highlight that ethanol was produced with an average 59.5% product selectivity, on a carbon basis, with peaks above 94% and accumulated to 19.98 mM C (0.46 g L^{-1}) (Fig. 4**B,** Test 2). Additionally, the concentration of side products remained low (Figure S6 B).

Thus, the applied conditions were suitable to produce ethanol, reaching higher production rates without compromising the product selectivity in MES systems. Hence, emphasising the crucial role of in-line control operational conditions to target specific products in MES.

Even though it has been demonstrated that pH_2, and therefore the total accumulated pressure, plays a key role on ethanol synthesis, helding a high pressure is complicated in MES systems, specially at large scale. Thus, in Test 3 (Table 1) the total pressure was set at 1.6 atm (instead of 1.8) to evaluate the influence of lower reducing power accumulation. In this test, the temperature oscillated between 19 – 25 °C

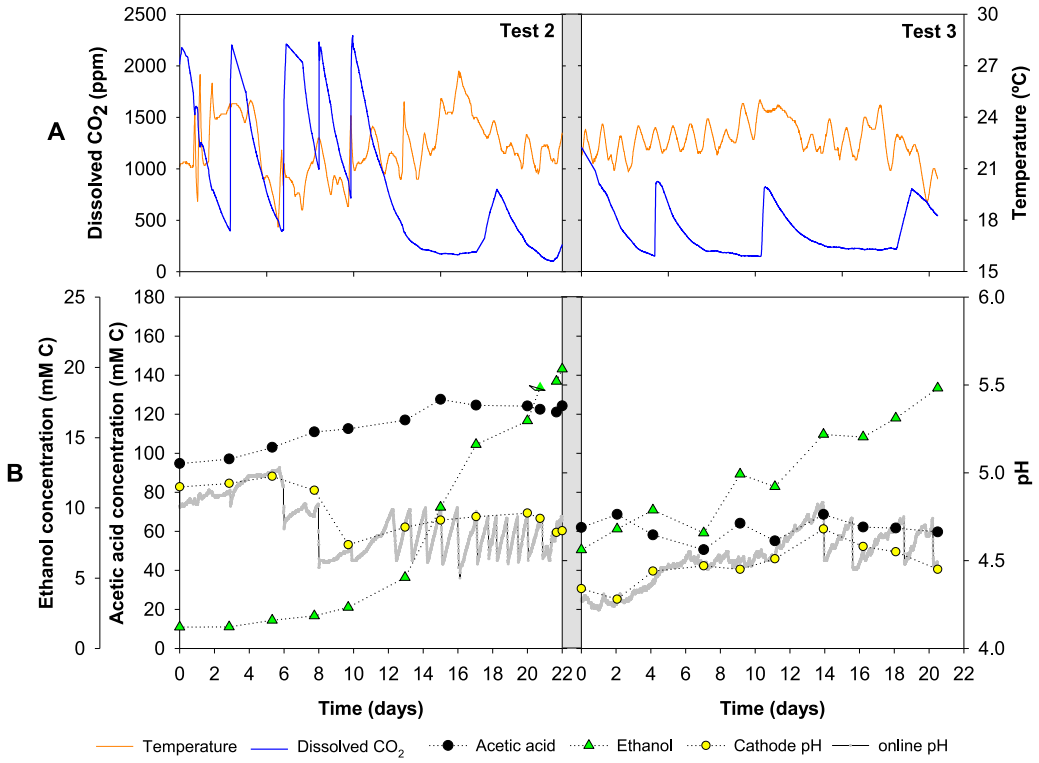

Fig. 4. Performance of the BoP MES system in test 2 and 3. Online temperature and dissolved CO_2 (A), and main product concentrations with online and punctual pH (B) are represented.

and from the very beginning, the range of the dissolved CO_2 in-line control was set between 200 and 800 mg L^{-1} (Fig. 4**A,** Test 3), pH was initially down to 4.2 but was then controlled between 4.5 – 4.7, and the initial acetic acid concentration, after replacing half volume with fresh media, was 61.97 mM C (1.86 g L^{-1}) (Fig. 4**B,** Test 3). Regardless of the low initial pH, ethanol production resumed immediately. Acetic acid concentration remained stable along the experiment, with minor fluctuations and without any substantial increment, likely due to the low CO_2 concentration in the media. Ethanol production started immediately and a concentration of 18.53 mM C (0.43 g L^{-1}), similarly to the previous test, was achieved. However, the lower pressure applied (1.6 *vs* 1.8 atm), and therefore less H_2 availability, along with the lower initial acetic acid concentration, resulted in a diminished ethanol production rate (31.13 ± 14.91 mg L^{-1} d^{-1}, or 2.26 ± 1.08 g m^{-2} d^{-1}). The concentration of other minor compounds, such as butyric acid, remained low (< 6 mM C) (Figure S6 B). Hence, the results confirmed the crucial role of pressure accumulation on this process and the need to develop systems and control devices capable of held higher overpressure.

The results obtained by applying stepwise control demonstrated that solventogenesis activation requires the joint and synergic control of pCO_2, pH and pressure. In MES, CO_2 availability is the primary driver on the formation of acids and alcohols, as it acts as the sole initial carbon source. When its concentration in the electrolyte is high, acetogenesis is promoted. Under such conditions, in presence of sufficient reducing power (i.e., methanol or ethanol), the formation of acids with a longer carbon chain, such as butyric or caproic acids, may also occur under the adequate pH conditions [31]. Conversely, when CO_2 concentration is low, and acetic acid concentration exceeds 0.6 g L^{-1} (20 mM C), carbon fixation slows down and the microbial reaction can shift to solventogenesis, where acetic acid is reassimilated and reduced to ethanol using H_2 as electron donor [11]. However, ethanol continuous and significant synthesis requires higher acetic acid titers, above 1 g L^{-1} [9]. Solventogenesis requires the presence of undissociated acetic acid (so a pH near or below its pKa of 4.76) and high H_2 concentrations, obtained by operating the MES cells pressurized [9]. Nevertheless, complete CO_2 depletion is detrimental in the medium-to-long term, as continuous acetic acid formation for the maintenance of a baseline CO_2 concentration is needed to avoid acetic acid depletion, which would in turn stop ethanol production. This further highlights the need of integrating control strategies to dynamically balance carbon supply and reducing power in MES systems, which can lead to higher and directed product selectivity.

3.3. *Perspectives and hindrances*

To date, ethanol has been mainly produced by chemical synthesis from fossil-fuel based precursors, or biologically from crops, competing with food production [5]. Research focusing on ethanol production in MES cells is scarce, most probably because of the complexity of the multi-step biological pathway requiring control of several operation parameters. The potential production of ethanol from CO_2 does not only contribute as an alternative to carbon utilization, but also as a strategy to achieve carbon-neutrality [32]. The few experiments targeting ethanol as the main compound were conducted in small systems, with low volumes and small electrode surface areas [10,23], or using electrically inefficient configurations, such as tubular reactors [11], or H-type cells, that are difficult to scale-up [9]. In certain studies, ethanol accumulation was hindered by its utilization as electron donor for the production of elongated carboxylic acids [33,34].

In this study, an efficient commercial stack cell design borrowed from electrolysis, with a low gap between electrodes, was used to assess its suitability for bioelectrochemical ethanol production while minimizing the electric energy expenses, paving the way towards technology scale up. The efficient stack cell design allowed to keep cell voltages below 3.6 V (Table 2), lower than other MES cell configurations operated at similar current density. For instance, a recent study applying 1 mA cm^{-2} and working with a more conductive electrolyte, therefore facing a lower ohmic drop, presented higher cell voltage (above 4.0 V) [35]. An average CE of 41.37 ± 20.69% and 52.89 ± 22.53 was achieved in the SA MES cell experiments. The CE of the BoP MES cell was

Table 2
Performance parameters of SA and BoP MES cell tests.

		Current applied (mA cm^{-2})	Cell Voltage (V)	Global CE (%)	Ethanol	
					Max. CE (%)	kWh kg^{-1}
SA	Test 1	0.15	2.3 ± 0.2	41.4	36.5	90.2
	Test 2		2.5 ± 0.3	52.9	57.6	136.3
BoP	Test 1	1.08	3.2 ± 0.4	30.1	-	-
	Test 2		3.3 ± 0.1	26.2	19.7	153.7
	Test 3		3.5 ± 0.1	17.8	9.1	485.3

low (Table 2), due to the constant H_2 release required for pressure maintenance, which cannot be quantified and analyzed in line, thus, conferring a limitation of the setup. Product specific CEs were only relevant for acetic acid and ethanol as the other compounds detected along the study represented minor amounts . The acetic acid specific CE was < 5% in both tests, as it acted as intermediate compound for ethanol production. The only exception was for the BoP Test 1, where acetic acid was the principal organic compound formed (with 22.8% CE) and no elongation took place, which is in line with values reported in the literature [27,36]. Ethanol reached a linear CE of 32–35% in the SA tests, in line with previously reported results [8,9,23]. However, the ethanol CE was lower in the BoP, being limited to 15.7% in Test 2 and 5.1% in Test 3, most likely due to the joint effect of diverse factors, including lower pressure and microbial kinetics. This highlights the importance of process automation improvement for efficient electron utilization, as new functionalities such as the recirculation of released gas.

Digitalization through in-line control of key parameters is a remarkable technological advancement for the MES field. Precise control of key operation conditions could pave the ground for the development of strategies tweaking the operational parameters to target specific products, in this case, ethanol. Despite the promise, the energy required for ethanol production in this study (90.2 kWh/kg) (Table 2), is still far from economic feasibility. These values are substantially higher than the ones required for bioethanol production from more stablished processes such as conventional corn and starch fermentation, which is typically an order of magnitude lower [37], and have undergone further optimization in the recent times [38]. It is also higher than processes in development, such as gas fermentation [2]. Nevertheless, MES offers advantages in terms of carbon circularity and the potential integration with surplus renewable electricity under flexible operation approaches, while allowing the production of H_2 on-site, not requiring external dedicated electrolyzers. This platform can serve not only for carbon utilization but also as an energy storage vector. However, significant improvements in electricity-to-product conversion efficiency are mandatory to enable future development and scale-up, such as the reuse of excessive gas for increasing the reducing power utilization.

In this context, developing strategies to decrease such energetic consumption is vital. A potential tactic would be to reduce H_2 wastage by overpressure, e.g. by electric current interruption. Thus, accurately assessing the H_2 concentration in the system becomes crucial to avoid excessive production. The direct approach, which can be easily integrated into the BoP, is the in-line measurement of dissolved H_2. A practical alternative is to analyze the gas phase composition and, along with pressure data, estimate the dissolved H_2 concentration by the Henry's law [39]. The automated BoP system enables monitoring and control of dissolved H_2 concentration alongside with pressure and allows to automatically shutdown of the power source to avoid excess H_2 production. Therefore, integrating this strategy into the system would maintain the required reducing power while decreasing the electric power consumption, as observed in proof-of-concept on-off experiments [26]. It would also enable real-time tracking of available reducing equivalents and the dynamic fine-tuning of operational conditions according to the targeted product at each stage of operation.

This is the first study focusing on MES system digitalization for ethanol production, opening a new field with enormous development potential. Next-generation, dynamic control systems that can adapt to the fluctuating conditions in MES cells must be developed, and huge amounts of experimental data must be generated to calibrate and train them appropriately.

4. Conclusions

This work confirmed the critical role of precisely controlled operational conditions in achieving selective ethanol production in MES systems. An efficient flat-plate stack was equipped with an in-line monitoring and control mechanisms to allow a strict control of the operation conditions, thereby promoting ethanol formation from CO_2 and electricity. Dissolved CO_2 concentration in the catholyte (between 200 and 800 mg L^{-1}) and pH (between 4.5 and 4.7) were identified as pivotal factors influencing selectivity. Instead, pH_2 was mostly linked to the ethanol production rate. The applied strategy resulted in an unprecedent product selectivity of 60% and an overall EtOH:HAc ratio above 2.0. These results demonstrate the potential for further downstream processing and product recovery. Notably, this is the first study to explore the digitalization of MES systems for ethanol production, laying the groundwork for a promising new research direction.

CRediT authorship contribution statement

Meritxell Romans Casas: Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. **Paolo Dessì:** Writing – review & editing, Investigation, Conceptualization. **M. Dolors Balaguer:** Writing – review & editing, Supervision. **Sebastià Puig:** Writing – review & editing, Supervision, Resources.

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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2026.103391.

Data availability

Data will be made available on request.

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