



“Gheorghe Asachi” Technical University of Iasi, Romania



## A PRELIMINARY STUDY ON ELECTROCATALYTIC CONVERSION OF CO<sub>2</sub> INTO FUELS

Fabiola Martínez\*, Carlos Jiménez, Jesús García, Rafael Camarillo, Jesusa Rincón

Department of Chemical Engineering, University of Castilla-La Mancha, Faculty of Environmental Sciences and Biochemistry, Avda. Carlos III, s/n, 45071, Toledo, Spain

### Abstract

The CO<sub>2</sub> electroreduction in gas phase using Pt on carbon black catalysts is investigated in this work. This process is expected to become a key technology to prevent anthropogenic CO<sub>2</sub> emissions. Specifically, the electrocatalytic reduction in a solventless gas phase is studied, as a first approach to later develop a photoelectrocatalytic device for the efficient conversion of CO<sub>2</sub> to fuels using solar energy for the reaction. The objective of this preliminary work has been the tuning up of the experimental setup and the development of the analytical method. To determine the reaction products three different configurations have been tested. The configuration consisting in the absorption of the reduction products in a cold trap with decane and the injection of both liquid and gas phases from the cold trap in a GC-FID-TCD allowed identifying several reduction products such as methanol, acetone, isopropanol, methyl acetate, hydrogen, and carbon monoxide. Further, it has been found that hydrocarbons such as ethylene, ethane, methane, propylene, propane, butane or pentane are not quantitatively formed during the process at conditions used in this work.

*Key words:* CO<sub>2</sub> recycling, energy compounds, electrocatalysis, electroreduction

*Received:* May, 2014; *Revised final:* October, 2014; *Accepted:* October, 2014

### 1. Introduction

Reducing emissions of greenhouse gases has long ceased to be a statement of good intentions to become a pressing need to ensure the sustainability of our society. Moreover the path to sustainability should not only be traveled by the energy sector, but the industry in general should also improve their processes through the adoption of better technologies as they become available. In this context, “capture, transport, storage and use of CO<sub>2</sub>” become a key technology pathway within the range of possibilities existent to prevent anthropogenic CO<sub>2</sub> emissions from reaching the atmosphere (Russo et al., 2013).

Regarding CO<sub>2</sub> utilization, several authors have proposed using the gas either as a technological fluid or as the raw material (carbon precursor) in the synthesis of valuable products and/or fuels (Aresta, 2010; Benson et al., 2009; Centi and Perathoner,

2009; Olah et al., 2009). However, according to the literature (Centi and Perathoner, 2009), the first two options may absorb less than 5% of current emissions of the gas. Consequently, it may be argued that, from all these alternative CO<sub>2</sub> uses, the gas conversion into liquid fuels (easy to store and transport) is the option with larger potential to reduce anthropogenic CO<sub>2</sub> emissions.

To convert CO<sub>2</sub> into fuels exist different options (Centi and Perathoner, 2009b; Halmann and Steinfeld, 2009; Lemonidou et al., 2003; Saito, 1998; Song, 2006; Song and Pan, 2004; Tan et al., 2005; Usubharatana et al., 2006) but there is one of them, the electro-photo-catalytic reduction of CO<sub>2</sub>, which has an enormous future potential. Nevertheless, it is still at its early stage of development. It should be noted, however, that this technology will only be sustainable if the electrons and protons necessary for the reaction are supplied using renewable resources,

\* Author to whom all correspondence should be addressed: e-mail: [fabiola.martinez@uclm.es](mailto:fabiola.martinez@uclm.es)

e.g. using solar energy by integrating a photoanode cell on which the photodissociation of water produces the electrons and protons necessary for the electrocatalytic reduction of CO<sub>2</sub> (Centi et al., 2007; Centi and Perathoner, 2009a). In other words, the sustainability of the technology requires direct use of solar energy in a one-step scheme and the coupling of the two processes in a single unit.

It should also be noticed that the electrochemical reduction of carbon dioxide can be accomplished by three main approaches depending on whether the conversion of CO<sub>2</sub> is performed in aqueous media, non-aqueous solutions or in a solventless gas phase. However, from the application point of view, the most interesting alternative is the solventless electrocatalytic reduction of CO<sub>2</sub> because involves developing a process able to produce longer chain hydrocarbons and/or alcohols than the former options, which may be collected without the need to distillate them from liquid solutions (Centi et al., 2007).

Taking all this into account, the ultimate goal of our work will be to develop a photoelectrocatalytic device for the efficient conversion of CO<sub>2</sub> to fuels using solar energy for the reaction. However, we are still in an early stage of development and the objective of this preliminary work is the tuning up of the experimental setup to study the electrocatalytic reduction of CO<sub>2</sub> in gas phase and the development of the analytical method to determine the reaction products. Thus, three different configurations have been tested and two gas chromatographs equipped with the MSD or FID-TCD detectors have been used. In the near future, the synthesis of advanced electrocatalysts is planned: specifically, the deposition of metals (Cu, Fe, Ni, Zn, Au, Ag, Pd, Pt, Ti) on carbon nanotubes in supercritical media will be addressed.

## 2. Material and methods

### 2.1. Experimental system

In this work, the assembly and starting up of the experimental system for electroreduction of CO<sub>2</sub> have been carried out. The main component of the system is the electrochemical cell (single fuel cell PaxiTech, 25 cm<sup>2</sup>), which is analogue to a PEM (proton exchange membrane) fuel cell (Fig. 1). It is based on the use of a proton membrane as an electrolyte (separating anode and cathode). Pt/C electrocatalysts (anode and cathode) were coated on carbon cloth (used as gas diffusion layer) and assembled (by hot pressing) to both sides of a Sterion® proton exchange membrane. The electrochemical flow cell is divided into anodic and cathodic compartments. A pump circulates a KHCO<sub>3</sub> aqueous solution (0.5 M) through the anodic zone. A mass flow meter allows controlling the CO<sub>2</sub> gas (99.998 %, supplied by Contse) flowing through the cathodic zone of the cell (flow rate: 0.5 dm<sup>3</sup> min<sup>-1</sup>).

The cell is equipped with a temperature controller and the electrical current is applied using a potentiostat-galvanostat (PGSTAT302N, Metrohm AUTOLAB), that is also used to measure voltage.

The potentiostat-galvanostat allows making cyclic voltammetries, which consists of scanning intensity while modifying voltage through different cycles between two fixed voltage values. Voltammetries give important information about electrochemical oxidation-reduction reactions occurring inside the cell (Cañizares et al., 2002).

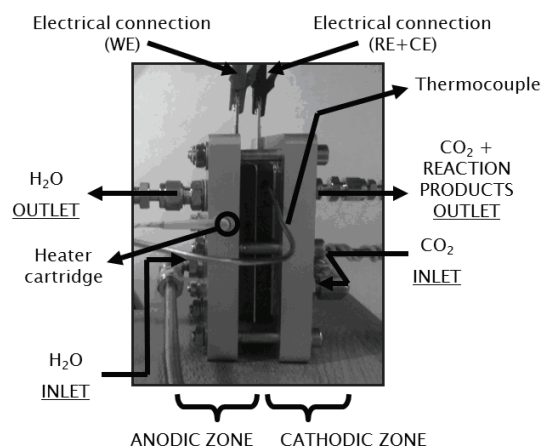


Fig. 1. Electrochemical cell (WE: Working Electrode; RE: Reference Electrode; CE: Counter Electrode)

### 2.2. Analytical system

Two different Gas Chromatographic (GC) systems supplied by Agilent were used for the measurement of reaction products during the electroreduction of CO<sub>2</sub>: a mass detector (5975C VL MSD with Triple-Axis Detector) coupled to a gas chromatograph (GC 6890); and a gas chromatograph (GC 7890A) with a system to concentrate the samples (GC Sampler 80) and with a FID and two TCD detectors.

### 2.3. Experimental procedure

The preparation of the membrane assembly includes the preparation of the electrodes (gas diffusion layer), the assembly of the electrodes with the protonic exchange membrane and its set-up in the electrochemical reactor. For the preparation of the electrodes the catalytic ink was deposited on carbon cloth (Toray TM Carbon Paper 0.28 mm thick, Teflon<sup>TM</sup> treated (20 (+/-)5 wt %) supplied by Quintech) using an airbrush. The catalytic inks were prepared using platinum 20 wt % on Vulcan (E-TEK<sup>®</sup> supplied by Quintech). The platinum load was 0.5 mg Pt cm<sup>-2</sup> in both electrodes (anode and cathode). An Sterion<sup>®</sup> membrane (180 μm thickness, based on the polymer Sterion<sup>®</sup>, a perfluorosulfonic acid which has a high ionic conductivity) supplied by Hydrogen Works, was used.

For the assembly of the electrodes with the membrane, a hydraulic press (Specac) was used applying 5.1 tons and 130 °C for 10 minutes. Three different configurations of the experimental set-up have been tested in this work to obtain the optimal conditions to determine the products obtained during the CO<sub>2</sub> electroreduction. These configurations can be seen in Fig. 2.

### Configuration 1

As shown in Fig. 2, in Configuration 1 the stream leaving the cathodic zone (that contains CO<sub>2</sub> and reduction products) is trapped in cold decane (-5°C). Later on the liquid absorbed reaction products are analyzed in a Gas Chromatograph (GC-MSD) whereas the gas phase is sent to vent. 1-pentanol was also used as absorbent liquid in the cold trap.

### Configuration 2

In this Configuration the gaseous stream leaving the cathodic zone is sent directly to the Gas Chromatograph (GC-MSD). The pipe is heated with a heating cord up to 130-140 °C to avoid condensation. Moreover, a filter was connected to the pipe to completely remove any particles that could be swept along the pipe.

### Configuration 3

In Configuration 3 the stream leaving the cathodic zone is trapped in cold decane (-5 °C). The cold decane sample (with trapped products) is preconcentrated using an automatic system (GC Sampler 80, Agilent) that allows concentrating the volatile products and adsorbing them with a fiber (SPME Fiber Carboxen). Then, the fiber content is injected in a GC-FID-TCD, so the products adsorbed on it are released and analyzed with the GC-FID.

Moreover, the gas phase from the cold trap is driven through a pipe with a heating cord and a particle filter to the GC-FID-TCD where it is injected.

## 3. Results and discussion

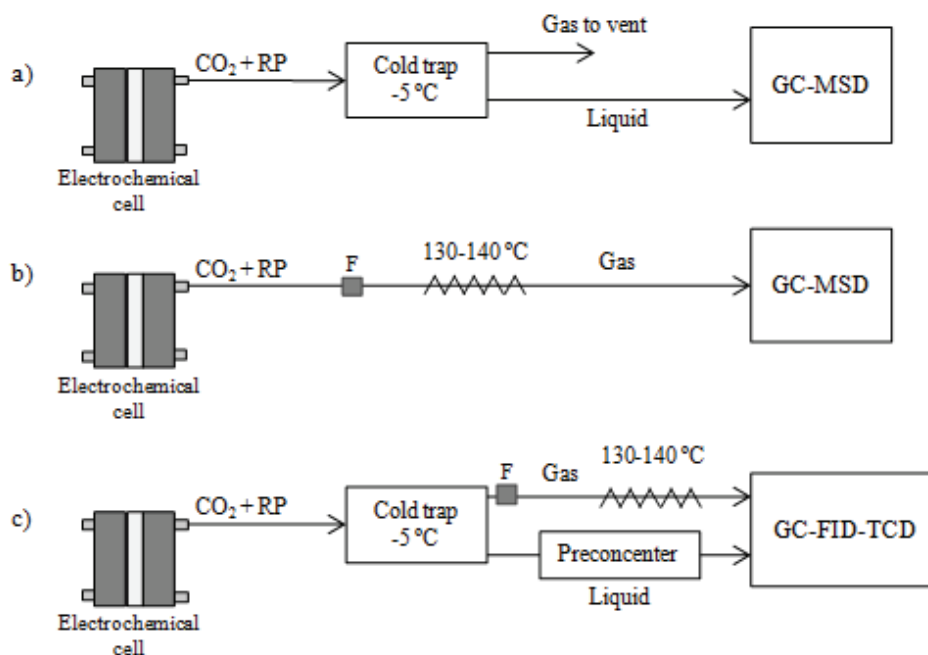
First of all, the results obtained in a cyclic voltammetry carried out in the electrochemical cell are shown. After that, the results obtained in the electrocatalytic reduction of CO<sub>2</sub> in gas phase will be analyzed taking into account the three different configurations previously explained. Thus, the optimal configuration for analyzing the reduction process may be selected.

### 3.1. Electrochemical analysis

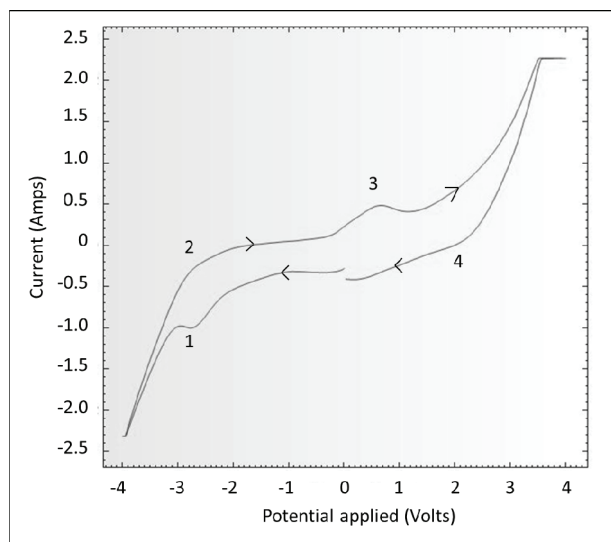
When working with electrochemical processes, two parameters have to mainly be taken into account: intensity and voltage. The production of different oxidation or reduction reactions depends on the voltage, and current intensity determine the reaction rate, that is, the number of electrons per second involved in the process. In other words, cyclic voltammeteries allows determining if, inside the cell, oxidation or reduction reactions are occurring (Cañizares et al., 2006).

In this work, the cyclic voltammetry shown in Fig. 3 was performed between -4 and +4 V to study the reactions in the cathodic zone of the electrochemical cell. As it can be seen in the figure four important zones are highlighted (zones 1-4).

Zones 2 and 4 in the voltammetry correspond to those zones in which intensity begins decreasing or increasing linearly. Both are due to water reduction (around -3 V) and water oxidation (+2 V) respectively.



**Fig. 2.** Experimental set-up configurations for the measurement of the products obtained during the electroreduction of CO<sub>2</sub>. RP: reduction products; F: filter. a) Configuration 1; b) Configuration 2; c) Configuration 3



**Fig. 3.** Cyclic voltammetry during CO<sub>2</sub> electroreduction (Experimental conditions: CO<sub>2</sub> flow rate: 0.5 dm<sup>3</sup> min<sup>-1</sup>; KHCO<sub>3</sub> concentration: 0.5 mol dm<sup>-3</sup>; VCP: -4 to +4 V; temperature: 25 °C)

It can also be observed a reduction peak at around -2.8 V (zone 1 in Fig. 3) that indicates a reduction reaction (probably the reduction of CO<sub>2</sub>) in the cathodic zone of the electrochemical cell. Attending to this assumption, CO<sub>2</sub> reduction taking place at this value of voltage, the voltage applied to the cell has been set to -2.8 V during the electrochemical experiments of this work. Nevertheless, it can be seen that this value of voltage is quite similar to the one corresponding to water reduction (around -3 V according to the data shown in the voltammetry) what implies that water reduction secondary reaction competes with CO<sub>2</sub> reduction in the cathode.

Furthermore, other oxidation peak also appears in the voltammetry (zone 3 in Fig. 3). This peak indicates the oxidation of any compound inside the cell at this value of voltage (around 0.8 V), probably due to the oxidation of some of the products generated in the reduction of CO<sub>2</sub> or some of its impurities.

### 3.2. Selection of the system configuration

The next step of this study has been the development of the analytical method to determine the products formed during the electroreduction of CO<sub>2</sub>. Specifically, the three different configurations described below have been tested.

#### Configuration 1

According to the results found in literature (Centi et al., 2007), some experiments were done using Configuration 1, in which reaction products were absorbed in decane in a cold trap. Then, the solvent with the absorbed products were measured using a GC-MSD.

For the absorption of the reaction products, 30 mL of decane were used. After 2 hours of experiment, 2 phases were obtained, the decane and a small amount of an aqueous phase (around 0.5 mL). This latter phase could have been formed due to diffusion of water through the membrane or more probably, as a consequence of previous humidification of CO<sub>2</sub>. Figs. 4 and 5 show the chromatograms obtained by the GC-MSD after injecting both liquid phases.

As expected, and shown in Fig. 4, the largest peak detected corresponds to decane, the absorbent used. That peak goes from 8.3 to 12.2 minutes. Another peak was also observed at retention time of 1.489. According to the mass detector library (NIST) it corresponds to acetone. Finally, peaks observed for retention times above 12 minutes correspond to traces of decane impurities. When analyzing the aqueous phase (Fig. 5) only two peaks were found, one for acetone and another one for decane, probably because both compounds had been partially dissolved in the aqueous phase.

In order to check if the decane peak in the chromatogram could hide some other peaks corresponding to different reaction products, some injections of solutions containing different concentrations of possible reduction products were done. The components of the solutions were methanol, ethanol and acetone dissolved in decane. Concentrations of 1 and 5 ppm of each compound were used in each solution. For both concentrations studied, only two peaks were obtained in the chromatograms: The first one, for a retention time of around 1.5 minutes, corresponded to acetone, and the second one between 7 and 16 minutes corresponded to decane. No peaks were detected by the GC-MSD for methanol or ethanol contained in the solutions. This fact confirms that the wide peak corresponding to decane (absorbent) may hide reduction products such as methanol or ethanol.

Trying to solve this problem, decane was swapped by 1-pentanol as absorbent liquid in the cold trap, although no improvement was observed with this change; in this sense, a wide peak corresponding to 1-pentanol was observed in the chromatogram for times between 4 and 10 minutes.

Thus, the main problem of this configuration is that the peak of decane, the main compound observed in the chromatogram, is too wide. This means that other compounds peaks may be hidden by the decane peak. Moreover, the peak for acetone is very small and cannot be properly seen. Thus, to solve this problem Configuration 2 was proposed.

#### Configuration 2

In order to solve the problems caused by the use of a solvent to absorb the products formed during the electroreduction of CO<sub>2</sub>, a configuration in which the gaseous products were directly injected in the chromatograph (GC-MSD) was tested.

Fig. 6 shows the chromatogram obtained after 2 hours of electrolysis. It can be seen only one peak for a retention time between 2.4 and 3.8 minutes. According to the mass detector, that peak corresponds to CO<sub>2</sub>. These results do not provide too much information and indicate that products concentration in the stream leaving the electrochemical cell is probably below the detection limit of the equipment.

It should also be noted that when using this configuration a white solid was formed inside the pipe, causing obstruction problems, probably because of the formation of carbonates from the reduction of CO<sub>2</sub> inside the cell.

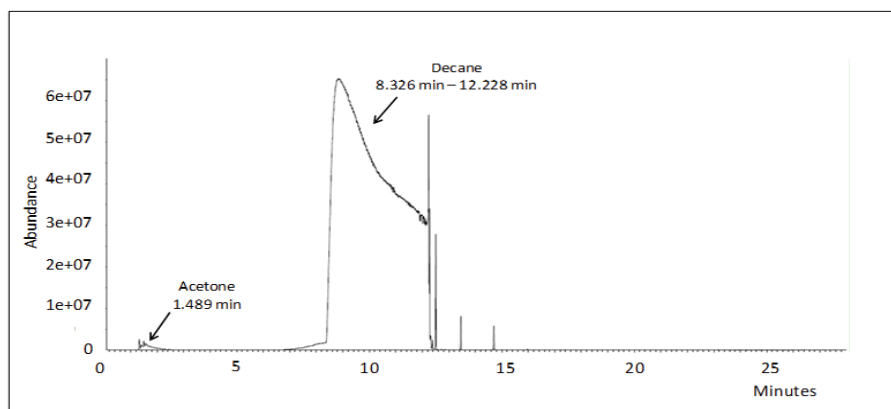
In order to solve the problem that solid formation could cause in the analytical equipment a filter was inserted into the pipe and further experiments are performed at the same conditions. However, results attained when operating with and without filter were similar.

Finally, with the aim of improving the analysis of the products formed during the electrolysis; whose concentrations were apparently below the GC-MSD detection limit, Configuration 3 was developed.

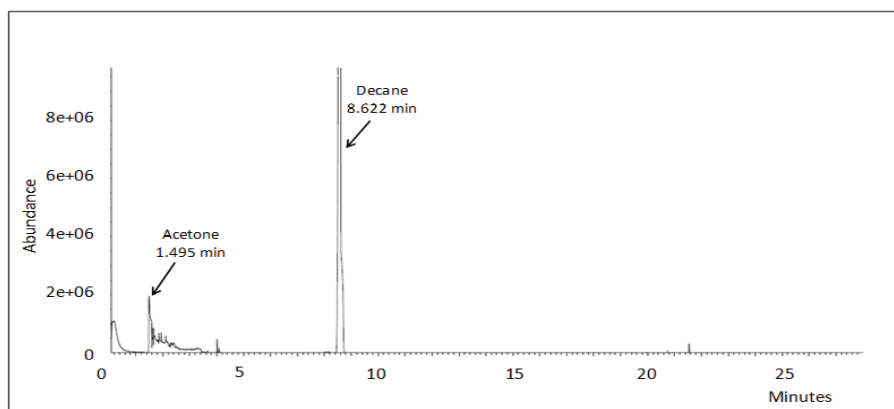
### Configuration 3

This configuration was proposed to solve the problems observed with previous configurations. First, it allowed measuring those compounds that could not be absorbed in the liquid phase (cold trap) so they would be escaping with the gas phase. Moreover, it could allow measuring very low concentrations of the products formed below the detection limits of the mass detector used in configuration 1 and 2. And finally, it allowed measuring the most volatile compounds, which would be the main CO<sub>2</sub> reduction products formed. This is a very important advantage, as it allows separating the products formed from the solvent used for absorbing them (decane).

In order to identify the reaction products absorbed in decane, mixtures of different compounds in decane with a known concentration were measured. These compounds included methanol, acetone, methyl acetate, and i-propanol. Each mixture was pre-concentrated and injected in the GC-FID-TCD at the same conditions than the liquid sample from the cold trap. Fig. 7a represents the result of joining the chromatograms of all these measurements.

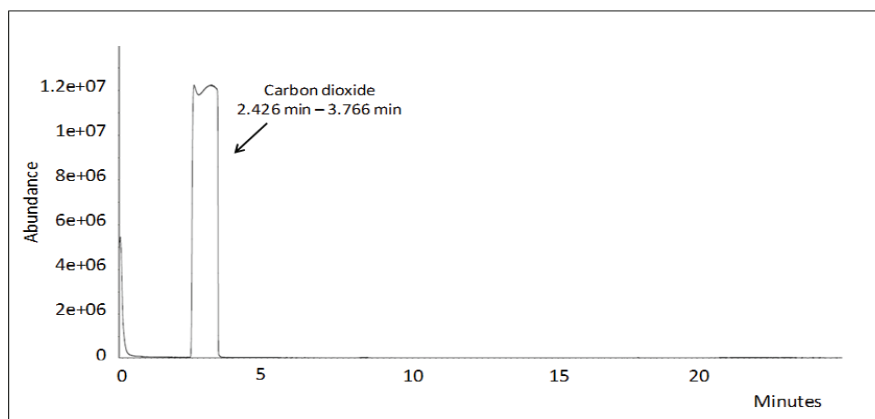


**Fig. 4.** Chromatogram obtained by the GC-MSD after injecting the decane phase from the cold trap when working with Configuration 1. Experimental conditions: CO<sub>2</sub> flow rate: 0.5 dm<sup>3</sup>min<sup>-1</sup>, KHCO<sub>3</sub> concentration: 0.5 mol dm<sup>-3</sup>, Voltage: -2.8 V, temperature: 25 °C

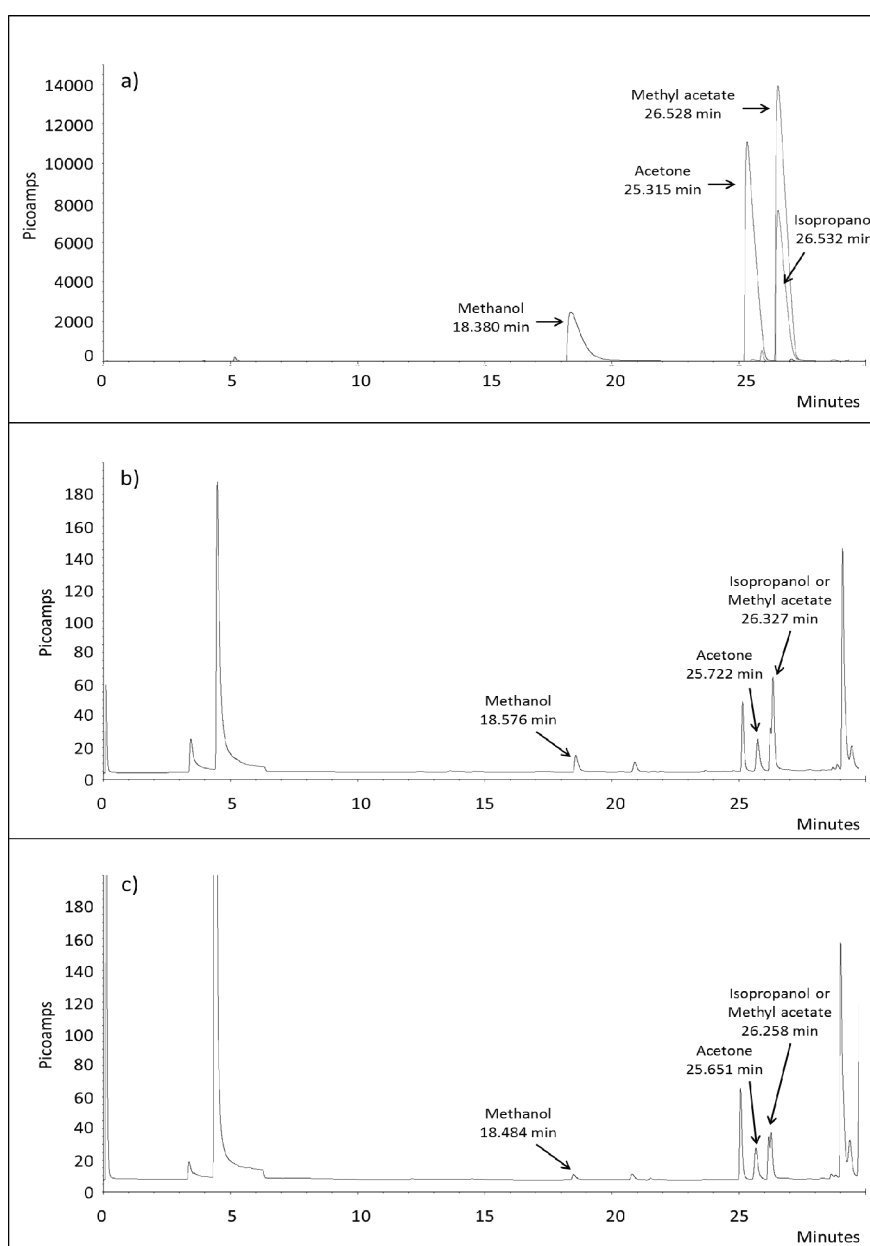


**Fig. 5.** Chromatogram obtained by the GC-MSD after injecting the aqueous phase from the cold trap when working with Configuration 1. Experimental conditions: CO<sub>2</sub> flow rate: 0.5 dm<sup>3</sup>min<sup>-1</sup>, KHCO<sub>3</sub> concentration: 0.5 mol dm<sup>-3</sup>, Voltage: -2.8 V, temperature: 25 °C





**Fig. 6.** Chromatogram obtained by the GC-MSD after injecting directly the streaming leaving the cathodic zone of the cell when working with Configuration 2. Experimental conditions: CO<sub>2</sub> flow rate: 0.5 dm<sup>3</sup>min<sup>-1</sup>, KHCO<sub>3</sub> concentration: 0.5 mol dm<sup>-3</sup>, Voltage: -2.8 V, temperature: 25 °C



**Fig. 7.** Chromatograms obtained through the FID detector after injection of: (a) Solutions of known concentration; (b) Decane phase with reaction products absorbed in the cold trap; (c) Aqueous phase formed in the cold trap. Experimental conditions: CO<sub>2</sub> flow rate: 0.5 dm<sup>3</sup>min<sup>-1</sup>, KHCO<sub>3</sub> concentration: 0.5 mol dm<sup>-3</sup>, Voltage: -2.8 V, temperature: 25 °C

It can be observed that peaks are obtained at 18.38, 25.31, 26.528 and 26.532 minutes for methanol, acetone, methyl acetate and i-propanol, respectively. According to these results, it would be very difficult to distinguish between the last two compounds because their retention times in these conditions are too similar.

As previously said, both liquid and gaseous phases from the cold trap are measured using the GC-FID-TCD. Fig. 7b shows the chromatogram of the reaction products absorbed in decane during the electroreduction of CO<sub>2</sub> using Configuration 3. Furthermore, since an aqueous phase is also formed during the process (around 1 mL), its chromatogram is also represented in Fig. 7c.

In the chromatogram of the decane phase (Fig. 7b) different peaks can be observed. Three of these peaks have been identified for retention times of 18.576, 25.722, and 26.327. They respectively correspond to methanol, acetone and compounds of the carbon fraction identified before (i-propanol or methyl acetate). Similar peaks have been formed for the aqueous phase (Fig. 7c).

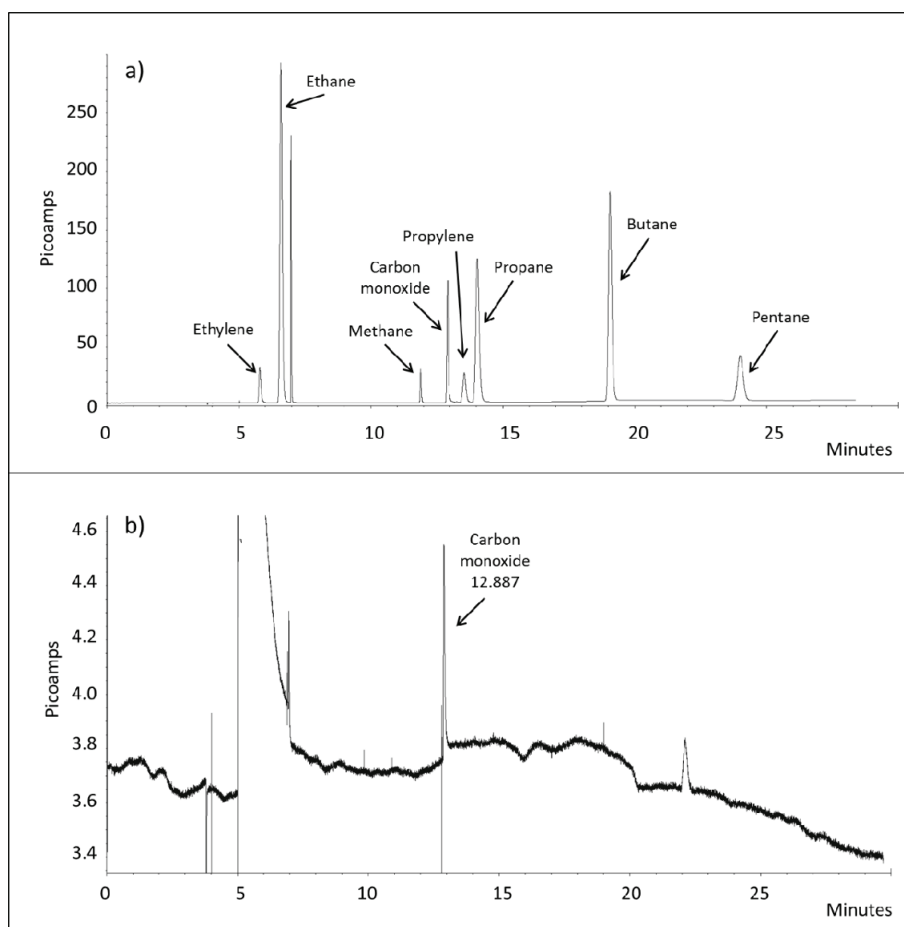
Regarding the gas phase from the cold trap, it was also injected in the GC-FID-TCD and the chromatograms attained when using the FID detector

are shown in Fig. 8b and, in Fig. 9b the TCD detector. Previously, a standard gas of known composition was injected to identify the products obtained. Most of the components of the standard gas can be observed using the FID detector (Fig. 8a). Moreover, H<sub>2</sub> was identified with the TCD detector (Fig. 9a).

The comparisons between the chromatograms attained when injecting the gas sample from the cold trap and the standard used are shown in Fig. 8 (FID detector) and Fig. 9 (TCD detector).

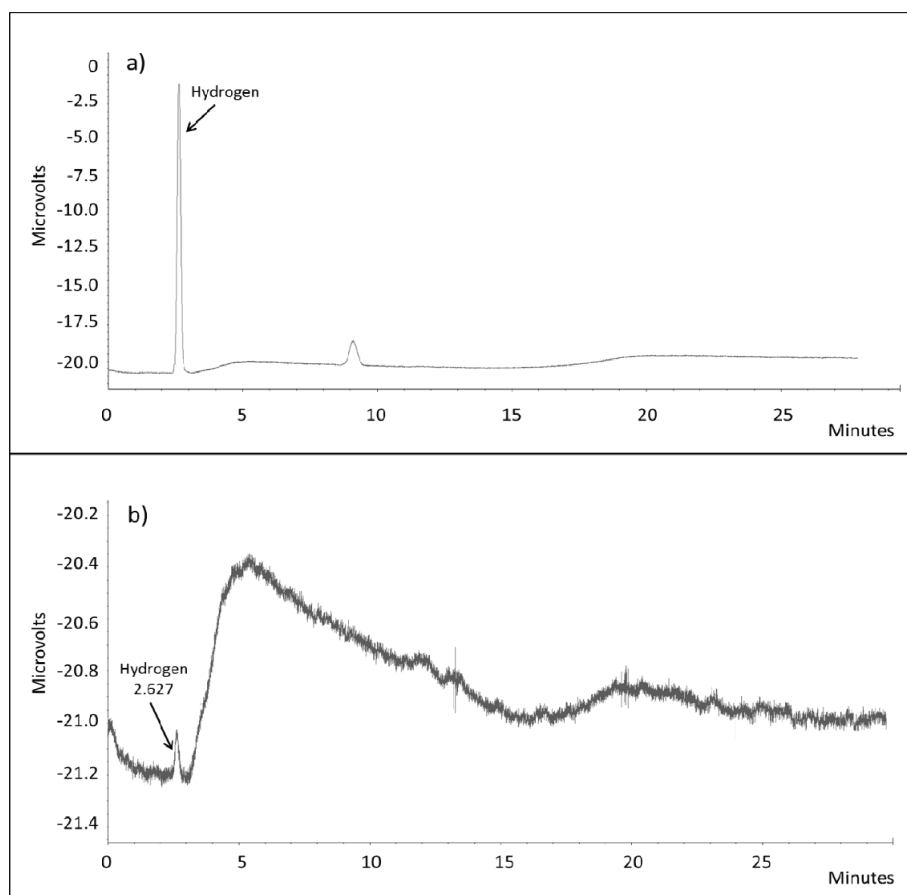
From these results it can be concluded that no ethylene, ethane, methane, propylene, propane, butane or pentane are detected using this configuration. Only hydrogen and carbon monoxide (from the reduction of water and carbon dioxide respectively) are detected in the gas phase using this method, which are the usual compounds formed when using platinum as catalyst.

It should be noted that compounds identified using this configuration correspond with some of the compounds produced in other similar works in literature (Centi et al., 2006, 2007, 2009b). Therefore, it may be concluded that Configuration 3 is the one that allows obtaining better results.



**Fig. 8.** Chromatograms obtained through the FID detector injecting a gas phase.

a) Injection of Standard gas; b) Injection of gas phase from cold trap. Experimental conditions: CO<sub>2</sub> flow rate: 0.5 dm<sup>3</sup>min<sup>-1</sup>, KHCO<sub>3</sub> concentration: 0.5 mol dm<sup>-3</sup>, Voltage: -2.8 V, temperature: 25 °C



**Fig. 9.** Chromatograms obtained through the TCD detector injecting a gas phase.

a) Injection of Standard gas; b) Injection of gas phase from cold trap. Experimental conditions: CO<sub>2</sub> flow rate: 0.5 dm<sup>3</sup>min<sup>-1</sup>, KHCO<sub>3</sub> concentration: 0.5 mol dm<sup>-3</sup>, Voltage: -2.8 V, temperature: 25 °C

#### 4. Conclusions

Electrochemical reduction of CO<sub>2</sub> to fuel can be accomplished in a solventless gas phase. Among the fuel products obtained in the process we could identify methanol, acetone, isopropanol, methyl acetate, hydrogen, and carbon monoxide.

Further, it has been found that hydrocarbons such as ethylene, ethane, methane, propylene, propane, butane or pentane are not quantitatively formed during the electrocatalytic reduction of CO<sub>2</sub> at conditions used in this work.

#### Acknowledgements

The authors gratefully acknowledge to **Ministerio de Ciencia e Innovación of Spain**, and **Junta de Comunidades de Castilla-La Mancha** for the financial support to this work through projects CTM2011-26564, PAI08-0195-3614 and PEI10-0310-5840.

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