

# Clean4G: Scale-up of an electrocracking process of liquefied biomass. Hydrogen and biorefinery application in cement industry

# Jéssica Vicente

jessica.vicente@tecnico.ulisboa.pt

### Instituto Superior Técnico, Universidade de Lisboa, Portugal

November 2021

## Abstract

The increasing emissions of greenhouse gases into the atmosphere are causing huge consequences like climate change. The electrochemical reduction of  $CO_2$  can use the  $CO_2$  that otherwise was going to be emitted to the atmosphere and transform the gas into value-added products. In the current research, it was studied the electrochemical reduction of  $CO_2$  simultaneously with the oxidation of an emulsion of liquefied biomass of eucalyptus. Fundamental studies were conducted in platinum, nickel, copper, and graphite. It was concluded that the best material to use as a cathode would be copper and the best material to be used as anode would be graphite. Gas generation was detected during the electrolysis at 55 °C without  $CO_2$  bubbling. The electrolytes were analyzed, and it was not detected a significant difference in the emulsion before and after the electrolysis. The analysis of the exiting gas of the electrolysis cell concluded that it does not occur the reduction of the bubbled  $CO_2$ , however, exists the production of hydrogen. The analyzes carried out do not allow concluding that there was production of compounds through the electrolysis at 25 °C with  $CO_2$  bubbling.

Keywords: electrocracking; liquefied biomass; bio-oil electrolysis; CO<sub>2</sub> reduction; hydrogen generation.

# 1. Introduction

The increasing emissions of greenhouse gases are a huge problem in the modern world. The consequences of the increasing concentration of these gases in the atmosphere affect not only the climate but also the different ecosystems on the planet. In 2015 were emitted approximately 50 billion tons of carbon dioxide equivalents, and of those, 74.5% correspond only to  $CO_2$  emissions [1]. To decrease the volume of these emissions and to diminish the consequences of the greenhouse gases to the planet where created agreements and goals by the United Nations Framework Convention on Climate Change, which is composed of 197 countries. These goals are established individually for each country [2].

The cement industry is one of the chemical industries that emit more  $CO_2$  into the atmosphere. The global emissions from this industry correspond to 3% of the global emissions

of greenhouse gases in 2016, which make up an emission of approximately 1.5 billion tons of  $CO_2$  per year [1]. There have been efforts to reduce these emissions by studying new ways to use the carbon dioxide emitted.

In this work, the objective is to combine liquefied biomass with  $CO_2$  to obtain added-value products. This objective would be achieved by combining two electrochemical processes into one system. In the anode occurs the electrocracking of the organic materials present in the biomass and simultaneous in the cathode occurs the electrochemical reduction of  $CO_2$ . The carbon dioxide is originated in the production of cement and the liquefied biomass is formed by a liquefaction process using the wastes produced by the quarry exploration that is necessary to obtain the raw material to produce cement.

#### 1.1. Electrochemical reduction of CO<sub>2</sub>

The electrochemical reduction of CO<sub>2</sub> is a reaction that has been studied since the 90's decade. It has originated several studies over the years. Is a complex reaction because it can originate up to 16 products in aqueous solutions depending on the electrodes, the temperature, the electrolyte, the pressure, and the tension applied in the system. At the anode usually occurs the oxygen evolution reaction (OER). At the cathode occurs the reduction of CO<sub>2</sub>. The products that may be obtained are formate, carbon monoxide, methanol, glyoxal, methane, acetate, glycolaldehyde, ethyl glycol, acetaldehyde, ethanol, ethylene, hydroxy acetone, acetone, alcohol allylic, propane, and 1-propanol. However, the hydrogen evolution reaction can also occur in the cathode and competes with the reduction of CO<sub>2</sub> [3].

The metals used as cathodes have a huge influence on the products formed during the electrochemical reduction of  $CO_2$ . Copper is known to produce in larger quantities hydrocarbons such as methane and ethylene, while platinum, nickel, iron, and titanium produce mainly hydrogen [4].

The use of an aqueous electrolyte is the most common in the studies regarding this subject because of the high conductivity of the solution. However, the use of an organic electrolyte brings several advantages: the solubility of the  $CO_2$  in these solutions is higher and the number of products that can be produced increases because in the anode it can occur the oxidation of those organic compounds to added-value products instead of the production of oxygen that as a very low economic value [5, 6].

## 1.2. Biomass and electrocracking

Biomass is an organic material that can be originated from multiple sources. The most abundant type of biomass is lignocellulosic biomass. This biomass comes from forest and agriculture residues as well as residues of food processing [7]. This type of biomass has in its composition approximately 90% of lignocellulose, which is mainly composed of cellulose, hemicellulose, and lignin [8].

It is a very important source of energy that can be used as an energy source through direct combustion or it can be used in several processes to produce biofuels. The thermochemical conversion of biomass is used to produce syngas and bio-oil, there are 3 types of these processes: gasification, pyrolysis, and liquefaction. Liquefaction is a process where occurs the thermal and catalytic decomposition of large molecules into smaller and unstable species that polymerize again forming a bio-oil. The process occurs at temperatures between 250 to 450 °C and pressures from 5 to 20 atm [7].

To valorize even more the bio-oil produced during the liquefaction process, some studies use the electrocracking process. The electrocracking has the objective of breaking molecular bonds through the passage of an electric current, transforming the initial molecule into smaller molecules.

Guerra et *al.* use the electrocracking concept to produce syngas simultaneously with water electrolysis, using a solution of 1.2 M NaOH and 20% liquefied cork biomass. It was obtained a syngas with the following composition: 66.7%H<sub>2</sub>; 25.3% CO e 8% O<sub>2</sub>. After the electrolysis, the molecular structure showed changes in the FTIR spectrum [9].

## 2. Experimental Procedure

During the studies, it was used a Squidstat<sup>TM</sup> Plus potentiostat and in the experiments with temperatures higher than 25 °C it was used a heat circulation bath from Lab Companion. The carbon dioxide and the compressed nitrogen used were from Air Liquide (Alphagaz) with a purity higher than 99%. The potassium hydroxide 85% was from labkem and the industrial bio-oil used was obtained from the hydrothermal liquefaction of eucalyptus biomass and came from the brand Energreen. The emulsion used in the laboratory tests had a composition of 50 vol.% of 2 M KOH and industrial bio-oil.

Before the beginning of the experiment, the pH of the emulsion and the aqueous solution of 1 M KOH were measured in the different conditions of bubbling studied (without any bubbling, with  $N_2$ bubbling and CO<sub>2</sub> bubbling), it was used a digital pH meter from *Hanna Instruments*, model HI11311.

The first part of the studies consisted of the determination of the proper materials to use as cathode and anode in the electrolysis to be done.

During these tests, it was used a typical 3electrode cell composed of a saturated calomel electrode from *Hanna Instruments* (SCE, model HI5412), a platinum mesh with an area of 50 cm<sup>2</sup> as a counter electrode, and different materials for the counter electrode. The materials to use as cathodes were: platinum (1 cm<sup>2</sup>), nickel (1.92 cm<sup>2</sup>), and copper (0.88 cm<sup>2</sup>). The materials to be used as anode were: platinum (1 cm<sup>2</sup>), nickel (1.92 cm<sup>2</sup>), and graphite (7.6 cm<sup>2</sup>).

For all the materials studied it was done a full scan of the potential window, consisting in the application of cyclic voltammetry in a wider range of potentials to realize the reactions that may occur as well as the potential at which they occur. The potential sweep occurs in the sequence: OCP  $\rightarrow$  1 V vs. SCE  $\rightarrow$  -1.5 V vs. SCE  $\rightarrow$  OCP, at a scan rate of 50 mV s<sup>-1</sup>. For the materials to be used as anodes were performed 8 cyclic voltammograms (CVs) at different scan rates: 5 mV s<sup>-1</sup>, 10 mV s<sup>-1</sup>, 20 mV s<sup>-1</sup>, 50 mV s<sup>-1</sup>, 100 mV s<sup>-1</sup>, 200 mV s<sup>-1</sup>, 500 mV s<sup>-1</sup>, and 1000 mV s<sup>-1</sup>. The potential sweep occurs in the sequence:  $0.7 \rightarrow 0.5$ V vs. SCE  $\rightarrow$  0.7. With the materials to be used as cathode were executed linear scan voltammetry (LSVs) from the OCP to -1.5 V vs. SCE at a scan rate of 1 mV s<sup>-1</sup>.

The CVs and the LSVs were conducted in 2 different electrolytes, the liquefied emulsion, and a solution of 1 M KOH for 3 different conditions: without any bubbling, with  $N_2$  bubbling, and with CO<sub>2</sub> bubbling. The CVs at different scan rates were performed only for the emulsion and at 2 different conditions: without any bubbling and with the bubbling of CO<sub>2</sub>.

The fundamental studies included recording polarization curves and chronoamperometry measurements. To determine the current stability over time of the copper electrode, it was performed a 1-hour chronoamperometry, at a potential of -0.6 V vs. SCE with and without  $CO_2$  bubbling, at two temperatures: 25 °C and 55 °C. The polarization curves were performed at two temperatures: 25 °C and 55 °C and under two conditions: with and without bubbling of  $CO_2$ , between 0 V e 2.5 V. For the polarization curves, an assembly with two electrodes was used, with copper as the cathode and nickel or graphite as the anode, with constant agitation.

A 9-hour long electrolysis was carried out at a potential of 2 V. The effect of temperature was studied, performing the electrolysis at two different temperatures: 25 °C and 55 °C. The electrolysis was carried out with CO<sub>2</sub> bubbling and with N<sub>2</sub> bubbling. For the electrolysis with N<sub>2</sub>, the bubbling occurred only for 10 minutes prior to the electrolysis to deaerate the solution. With CO2 an intensive bubbling of 10 minutes was carried out to saturate the solution before starting the electrolysis, during the electrolysis a lower flow was maintained in the cell. All electrolysis was carried out using an electrolytic copper tube as the cathode  $(35.98 \text{ cm}^2)$  and a graphite cylinder as the anode (82 cm<sup>2</sup>). The tests were carried out in a closed cell with only one gas inlet and outlet. The cell outflow was measured only in the tests with N<sub>2</sub> bubbling with the *RITTER* gas meter.

To determine the gaseous products formed, the gas chromatography technique was used using a *Shimadzu 9A* equipment, which has a thermal conductivity detector and a flame ionization detector. Mass flow controllers (*Bronkhorst*) were used to control the flow of gases. The equipment was previously calibrated with the expected products, to know at what time the peaks of each compound would occur. Three different tests were carried out at room temperature. The first two tests used an inlet flow of 30 mL/min CO<sub>2</sub>, while the third test used an inlet flow of 6 mL/min CO<sub>2</sub> + 24 mL/min N<sub>2</sub>. The first test used an applied tension of 4 V.

Conductivity, pH, and dry solids content of the electrolyte samples were measured before and after the 9 h electrolysis. The moisture content of the samples was performed on a VWR scale model 1400108. CVs and studies of the anodic zone to the electrolytes were carried out before and after the 9 h electrolysis using a 3 system electrode, with a saturated calomel electrode from Hanna Instruments (model HI5412), a platinum mesh with an area of 50  $cm^2$  as a counter electrode and a platinum electrode as the counter electrode with an area of 1 cm<sup>2</sup>. In CVs, the potential scan occurs in the sequence: OCP  $\rightarrow$  1 V vs. SCE  $\rightarrow$  -1.5 V vs. SCE  $\rightarrow$  OCP, at a scan rate of 50 mV s<sup>-1</sup>. In the anode zone studies, 3 CVs were performed at various speeds (5 mV s<sup>-1</sup>, 50 mV s<sup>-1</sup>, 500 mV s<sup>-1</sup>). The potential sweep occurs in the same sequence  $OCP \rightarrow 0.5 \text{ V vs. SCE} \rightarrow -1.5 \text{ V vs. SCE} \rightarrow OCP.$ 

FTIR analyzes were performed on the electrolyte samples before electrolysis and after 3 h, 6 h, and 9 h of electrolysis, in *a PerkinElmer* FTIR spectrometer. The analysis was performed between 4000 to  $400 \text{ cm}^{-1}$ .

#### 3. Results and discussion

The pH values read for the emulsion and for the 1 M KOH solution, with and without  $CO_2$  bubbling are shown in Table 1. The pH of the solution decreased in both the emulsion and the 1 M KOH solution with the bubbling of  $CO_2$ . This pH variation was expected because the  $CO_2$ , when dissolved in the electrolyte, reacts with the water in the solution, forming carbonate.

 Table 1. pH values of emulsion and 1M KOH solution,

 with and without CO2.

	Without CO <sub>2</sub>	With CO <sub>2</sub>	Variation
pH Emulsion	13.85	9.30	4.55
pH 1 M KOH	14.14	13.45	0.69

## 3.1. Full CV scans

The full CV scans obtained for the 4 materials studied in the emulsion at 3 different conditions are represented in figure 1. To conclude that the activity came only from the reactions that took place in the bio-oil and not from the 2M KOH solution present in the emulsion, CVs were carried out only from the 1 M KOH solution. In the results obtained, no peak of reduction is observed in the four materials studied, even with the bubbling of carbon dioxide in the solution.

At the CV for the platinum electrode, it is possible to observe some electrocatalytic activity between -1 V vs. SCE in emulsion and emulsion +  $CO_2$ electrolyte. It is possible to observe an oxidation peak only in the curve of the emulsion +  $CO_2$ .

In the CV for nickel, it is possible to observe in the anodic zone currents characteristic of the oxygen evolution reaction starting at 0.5 V vs. SCE for all conditions studied, except in the medium with the emulsion bubbled with carbon dioxide. By bubbling carbon dioxide into the medium we observe the inhibition of OER. The non-bubbling and nitrogen bubbling emulsions show some catalytic activity. There is an oxidation peak at approximately -0.7 V vs. SCE and an oxidation peak at approximately -1.2 V vs. SCE the same for both electrolytes. The peaks obtained may be the oxidation of some matter present in the electrolyte, as they do not appear in the 1 M KOH solution.



Figure 1. CVs of the 4 materials studied in the emulsion at 3 different conditions at  $T_{amb}$  and 50 mV s<sup>-1</sup>.

The CV for copper without bubbling in the emulsion shows a peak reduction at approximately -0.3 V vs. SCE. The spikes can be the result of an oxidation layer of the metal itself that is reduced.

At the graphite electrode, it is not detected any electrochemical activity.

#### 3.2. Study of the anodic zone

In the study of the anodic zone, the potential materials to be used as anode were studied. In Figure 2 is the CVs at various scan rates of the platinum electrode.



Figure 2. CVs run at different potential scan rates with and without CO<sub>2</sub> bubbling, using a platinum electrode.

The platinum was the only electrode that showed electrochemical activity in the CVs, the nickel and graphite electrodes did not show any peak of reduction or oxidation. In cyclic voltammetry performed with the platinum electrode without gas bubbling, it is possible to observe an oxidation peak at approximately -0.2 V vs. SCE and a reduction peak at approximately -0.4 V vs. SCE. These two peaks can be the result of a redox reaction of some carbonaceous compound present in the liquefied emulsion, where the compound is first oxidized and then reduced. The same is not reproducible in the emulsion with CO<sub>2</sub> bubbling.

In this case, it is only possible to observe an oxidation peak at approximately 0.2 V vs. SCE only at a speed corresponding to 5 mV s<sup>-1</sup>, this peak can be neglected because it does not occur at any higher speed. This initial oxidation peak may be the result of some deposit that was on the electrode surface that came out after the first cyclic voltammetry.

### 3.3. Study of the cathodic zone

The linear scan voltammetry performed in the 3 different materials studied at  $T_{amb}$  and 1 mV/s, in the emulsion under the various conditions studied are represented in Figure 3.



**Figure 3**. LSVs of the 3 different materials studied at  $T_{amb}$  and 1 mV s<sup>-1</sup>, in the emulsion under the various conditions studied.

With the LSVs it was possible to determine the Tafel curves and to calculate parameters with the Tafel equation. It was determined the Tafel coefficient (b), the charge transfer coefficient ( $\alpha$ ) and the exchange current density (j<sub>0</sub>). The parameters determined for each electrode and condition are in Tables 2, 3, and 4 for platinum, nickel, and copper, respectively.

 Table 2. Determination of the Tafel coefficient, the charge transfer coefficient, and the exchange current density for the platinum electrode under the various conditions studied in the two electrolytes.

	b (mV dec <sup>-1</sup> )	j <sub>0</sub> (mA cm <sup>-2</sup> )	α
Emulsion	317	0.103	0.19
Emulsion + N <sub>2</sub>	235	0.026	0.25
Emulsion + CO <sub>2</sub>	335	0.060	0.28
1 M KOH	335	3.178	0.98
1 M KOH + N <sub>2</sub>	422	6.300	0.97
1 M KOH + CO <sub>2</sub>	332	0.568	0.99

**Table 3.** Determination of the Tafel coefficient, the charge transfer coefficient, and the exchange current density for the nickel electrode under the various conditions studied in the two electrolytes.

	b (mV dec <sup>-1</sup> )	$j_0 (mA \ cm^{-2})$	α
Emulsion	1144	0.216	0.05
Emulsion + N <sub>2</sub>	215	0.020	0.28
Emulsion + CO <sub>2</sub>	276	0.002	0.21
1 M KOH	273	0.038	0.25
1 M KOH + N <sub>2</sub>	173	0.065	0.38
1 M KOH + CO <sub>2</sub>	239	0.106	0.25

**Table 4.** Determination of the Tafel coefficient, the charge transfer coefficient, and the exchange current density for the copper electrode under the various conditions studied in the two electrolytes.

	b (mV dec <sup>-1</sup> )	j <sub>0</sub> (mA cm <sup>-2</sup> )	α
Emulsion	318	0.015	0.19
Emulsion + N <sub>2</sub>	281	0.007	0.21
Emulsion + CO <sub>2</sub>	1591	0.022	0.04
1 M KOH	335	4.254	0.18
1 M KOH + N <sub>2</sub>	174	0.020	0.34
1 M KOH + CO <sub>2</sub>	209	0.466	0.28

#### 3.4. Polarization Curves

In the polarization curves performed, the effect of temperature on currents generated with and without bubbling carbon dioxide was studied. Two systems were analyzed, copper was used as the cathode and the anode material was varied. In all tests performed, the current density increases with temperature. Higher currents are achieved without bubbling  $CO_2$  regardless of the material or temperature at which the test takes place. Comparing the Cu-Graphite system and the Cu-Nickel system it is possible to conclude that the current density in the second system is always higher than the current density in the first system, regardless of the temperature of the emulsion or the bubbling conditions.

#### 3.5. Chronoamperometry

In the four chronoamperometry measurements carried out, it is possible to immediately see a sharp decrease in the current, followed by a stabilization of the current. In the two conditions studied (with and without  $CO_2$  bubbling), on the curves at 55 °C it is possible to observe that the current density generated is higher than the current density generated at 25 °C. Although the current at which stabilization occurs is lower in the tests with  $CO_2$  bubbling, the current density generated in the initial minutes of the tests with  $CO_2$  bubbling. The currents obtained are reduced in all curves, however, current stabilization is always achieved in the 60 min test.

#### 3.6. Electrolysis

The electrolysis had a duration of 9 hours and was performed at two temperatures: 25 °C and 55 °C, with two bubbling conditions, with and without  $CO_2$ . In electrolysis at 25 °C, the equipment did not detect the production of any gas during 9 hours. Electrolysis at 55 °C produced a total of 160.23 mL of gas over 9 hours. The electrolysis was divided into 3 parts so that it was possible to take a sample every 3 h of the electrolyte. In the three parts, a constant gas production is visible for approximately up to the first 100 min, after which there is no gas production.

#### 3.7. Gas chromatography

In the 3 tests carried out, the existence of 3 similar peaks was verified in the chromatogram obtained: at ~1.8 min, at ~2.9 min, and at ~12 min, which corresponds to the compounds of hydrogen, oxygen, and carbon dioxide, respectively. The observed peaks were integrated, and the area of each peak obtained was calculated, the results are shown in Table 5.

 Table 5. Area of the peaks obtained in the chromatogram.

Inlet flow	Δ <b>Ε</b> (V)	Area H <sub>2</sub> peak (mV.s)	Area O <sub>2</sub> peak (mV.s)	Area CO2 peak (mV.s)
30 mL/min CO <sub>2</sub>	2	0.378	3.514	2233.714
30 mL/min CO <sub>2</sub>	4	3.165	3.073	2063.014
6 mL/min CO <sub>2</sub> + 24 mL/min N <sub>2</sub>	4	2.383	5.310	535.193

Observing the results obtained in the integration of the identified peaks, it is possible to verify that the area corresponding to the  $H_2$  peak increases almost 10 times when the voltage is doubled from 2 V to 4 V. When a change is made in the CO<sub>2</sub> flow, there is a decrease in  $H_2$  in the sample obtained by the chromatogram.

The oxygen peak is approximately constant between the first and second tests, despite increasing the voltage in the system, which indicates that there is a leak in the system and that atmospheric  $O_2$  is contaminating the produced sample. When changing the gas flow the peak area increases which could be the result of some movement of the system which could have increased the leakage even further. The fact that the leakage increased between the second and third tests may also justify the decrease in the peak area corresponding to H<sub>2</sub> between the same tests, although the voltage remains the same. Due to the high fugacity of hydrogen, it is possible that some of it was lost.

The carbon dioxide peak in the chromatogram has a very high integration area compared to the other compounds. The peak area assigned to the  $CO_2$  of the first and second trials is approximately equal, in the third trial the  $CO_2$  peak area decreases because of the decrease in the  $CO_2$  inlet flow. In the three tests performed, no compound described in the literature as a product obtained in the electrochemical reduction of carbon dioxide was detected.

## 3.8. Electrolyte analysis

To study the possibility of the formation of compounds from the electrochemical reduction of  $CO_2$  in the liquefied, analyzes were carried out on the electrolyte resulting from 9 hours of electrolysis under the different conditions studied.

The pH of the emulsion remains approximately constant under the various electrolysis conditions studied.

Conductivity increases in all analyzed electrolytes. The increase in conductivity can be explained by the production of hydrogen, which reduces the concentration of water in the solution, increasing the concentration of KOH in the solution and consequently increasing the conductivity.

In the CVs recorded in the initial emulsion and in the final emulsions of the different electrolysis performed, the voltammograms do not present a significant change in the curves, despite the different conditions to which the electrolyte was subjected.

The percentage of moisture remained approximately constant, considering that the emulsion is made with an industrial liquefied of variable composition.

## 3.9. FTIR

In the performed electrolysis, samples were taken every 3 hours to later analyze by FTIR. All the FTIR spectrums have six similar peaks at the same wavenumber.

In almost all assays, the absorbance peaks remain unchanged, except in the spectrum corresponding to the electrolysis emulsion with  $CO_2$  bubbling at a temperature of 25°C (Figure 4), where it is possible to observe a slight decrease in the absorbance peak associated with the C-H bond at approximately 2900 cm<sup>-1</sup> and a slight increase in peak at approximately 1450 cm<sup>-1</sup> which corresponds to the deformation of the C-H bond and the disappearance of the bond corresponding to the C=O bond.



**Figure 4.** FTIR of the emulsion after 9 h of electrolysis with  $CO_2$  bubbling at a temperature of 25 °C.

#### 3.10. Humidity content

The results of the moisture content of the emulsion after 9 h of electrolysis under varying conditions are summarized in Table 6.

**Table 6.** Moisture percentage of the emulsion after 9h of electrolysis under variable conditions.

Electrolysis conditions	Humidity (wt.%)	
Without electrolysis	77.46	
T=25 °C with $N_2$	72.19	
T=55 °C with $N_2$	76.48	
T=25 °C with CO <sub>2</sub>	83.74	
T=55 °C with CO <sub>2</sub>	71.82	

The percentage of moisture remained approximately constant in all tests, considering that the emulsion is made with an industrial liquefied of variable composition. Except for the electrolysis test at a temperature of 25 °C and with  $CO_2$  bubbling where the percentage of humidity increases. Due to the oxidation of some bonds or the occurrence of depolymerization reactions, some molecules present in the electrolyte released water molecules, which contributed to the increase in the moisture content of the electrolyte.

#### 4. Conclusions

In the fundamental studies carried out, it was sought to understand which would be the best materials to be used as electrodes, both for the cathode and for the anode, to carry out bio-oil electrolysis. The objective would be to achieve the electrochemical reduction of the bubbled CO<sub>2</sub> gas with simultaneous oxidation of the organic matter present in an alkaline emulsion of industrial biooil.

In the linear scan voltammetry experiments, copper and platinum electrodes led to similar values for the Tafel parameters. Although platinum had higher current density values, copper was chosen to be used as the anode due to the results reported in the literature of greater hydrocarbon production with this electrode.

Even though the currents generated by the Cu-Graphite system are lower than those of the Cu-Nickel system in the polarization curves performed, it was concluded that the best material to be used as anode for the electrolysis performed would be graphite. The reason was because of the higher stability of this material. Graphite does not show changes in the CVs under the various conditions studied and manages to function as an anode without producing oxygen, using a bio-oil alkaline emulsion as the electrolyte.

In the electrolysis carried out without bubbling  $CO_2$ , only gas was produced at a temperature of 55 °C. Although this output gas flow was not analyzed, it is possible to conclude that the gas produced was pure hydrogen, because in gas chromatography analyses, when reducing the carbon dioxide flow, the hydrogen production was not affected. This means that the production of hydrogen takes place without the bubbling of  $CO_2$  and that the gas produced in electrolysis without the bubbling of  $CO_2$  would be pure hydrogen.

When analyzing the electrolyte, it was not possible to observe a distinct difference in the results of the analysis methods performed, except for conductivity. However, in electrolysis with bubbling CO<sub>2</sub> at 25 °C it was possible to observe a change in the FTIR spectrum after electrolysis, particularly a decrease in the peak associated with C-H bonds, a slight increase in the peak corresponding to the deformation of the C-H bond and the disappearance of the shoulder of the connection corresponding to the C=O connection. These results obtained by FTIR agree with the results obtained in the sample moisture content tests. The same sample is the only one that increases the moisture content after electrolysis, which indicates the oxidation of some bonds or occurrence of depolymerization reactions during

electrolysis, which increases the moisture content of the emulsion.

Through the analyzes carried out, it is not possible to conclude that the production of compounds has occurred through the electrochemical reduction of  $CO_2$ . However, the results suggest the occurrence of the electrocracking of the bio-oil during electrolysis at 25 °C with  $CO_2$  bubbling.

Although the electrochemical reduction was not observed in the performed electrolysis, the studied system can be used to produce hydrogen without the bubbling of CO<sub>2</sub>. The fact that the gas generated is only pure hydrogen allows the use of a much simpler electrochemical cell, without membranes or separators. Not using these pieces of equipment in the process reduces production costs because these pieces are not only expensive but also need to be replaced regularly.

## References

- [1] H. Ritchie e M. Roser, "CO<sub>2</sub> and Greenhouse Gas Emissions," Our World In Data, Oxford Martin School, University of Oxford, 2020. [Online]. Available: https://ourworldindata.org/co2-and-othergreenhouse-gas-emissions. [Acedido em 8-2021].
- [2] A. Savaresi, "The Paris Agreement: a new beginning?," *Journal of Energy & Natural Resources Law*, vol. 34, nº 1, pp. 16-26, 2016.
- [3] K. P. Kuhl, E. R. Cave, D. N. Abram e T. F. Jaramillo, "New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces," *Energy & Environmental Science*, nº 5, pp. 7050-7059, 2012.
- [4] H.-R. M. Jhong, S. Ma e P. J. Kenis, "Electrochemical conversion of CO<sub>2</sub> to useful chemicals: current status, remaining challenges, and future opportunities," *Current Opinion in Chemical Engineering*, vol. 2, n° 2, pp. 191-199, 2013.
- [5] M. Konig, J. Vaes, E. Klemm e D. Pant, "Solvents and Supporting Electrolytes in the Electrocatalytic Reduction of CO<sub>2</sub>," *iScience*, vol. 19, pp. 135-160, 2019.

- [6] Á. Vass, B. Endrodi e C. Janáky, "Coupling electrochemical carbon dioxide conversion with value-added anode processes: An emerging paradigm," *Current Opinion in Electrochemistry*, vol. 25, nº 100621, 2021.
- [7] D.M. Alonso, J. Q. Bond e J. A. Dumesic, "Catalytic conversion of biomass to biofuels," *Green Chemistry*, nº 12, p. 1493– 1513, 2010.
- [8] A. Brandt, J. Gräsvik, J. P. Hallett e T. Welton, "Deconstruction of lignocellulosic biomass with ionic liquids," *Green Chemistry*, vol. 15, n° 3, pp. 550-583, 2012.
- [9] L. Guerra, K. Moura, J. Rodrigues, J. Gomes, J. Puna, J. Bordado e T. Santos, "Synthesis gas production from water electrolysis, using the Electrocracking concept," *Journal of Environmental Chemical Engineering*, vol. 6, nº 1, pp. 604-609, 2017.