Joana da Costa Franco Afonso

Licenciatura em Ciências da Engenharia Química e Bioquímica

Catalytic hydrogenation of carbon dioxide to form methanol and methane

Dissertação para obtenção do Grau de Mestre em Engenharia Química e Bioquímica

Orientador: Manuel Nunes da Ponte, Professor Catedrático, FCT/UNL

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Agradecimentos

A realização deste trabalho só foi possível devido ao apoio, directo ou indirecto, de algumas pessoas, às quais gostaria de agradecer.

Ao Professor Doutor Manuel Nunes da Ponte e à Doutora Ana Reis Machado, pela oportunidade de ingressar no seu grupo de trabalho e realizar esta tese. Tenho a agradecer-lhes toda a simpatia, disponibilidade e interesse demonstrados, assim como todo o conhecimento transmitido.

Ao Professor Doutor Luís Branco, por toda a simpatia, disponibilidade e apoio.

À minha mãe e irmã por o apoio incondicional, por terem sempre acreditado em mim e por toda a força que me deram. Também por todo o amor, carinho e paciência.

Ao meu pai, que à sua maneira me apoiou e incentivou.

Ao Pedro, por todo o apoio, companheirismo e amor, sem os quais não teria sido possível chegar ao fim desta etapa.

À minha família, por o apoio e encorajamento.

Por último, mas não menos importantes, obrigada aos meus amigos. Quero agradecer-lhes por todos os bons e maus momentos partilhados, por toda a compreensão, força e coragem que me deram.

A todos um MUITO OBRIGADA!

Abstract

This work was divided into 2 distinct parts, the first consisting in the electro-reduction of high pressure CO_2 dissolved in an ionic liquid and the second in chemical catalysis of carbon dioxide reduction with hydrogen, using homogeneous and heterogeneous catalysts. In both cases new facilities were built with new and/or recycled materials.

This it is an exploratory work, which aimed to produce methane or methanol through the reduction of CO_2. For this, we used carbon dioxide with hydrogen biphasic mixtures of ionic liquid / (CO_2 + H_2) at high pressure, 140 bar, and lower temperatures, 413K. A ratio of CO_2: H_2 = 3:1.

In the electrochemical experiments, three different cathode materials, different amounts of water in ionic liquid and two different gases were tested. We can see that the water content did not change the electrochemical potential window and AuPt may be the best of the tested materials, since it generated higher currents.

In the case of heterogeneous catalysis, the ionic liquid was impregnated into the catalyst. We used Pd, Rh and Ru catalysts supported on alumina. The reactions were conducted for 24h or 72h. Methane was obtained in reactions without ionic liquid, when Pd and Ru were used catalysts, Ru being the best; with 3.30% yield.

In homogenous catalysis, the catalysts were immobilized in an ionic liquid. We used [Ru(cod)Cl$_2$]$_n$ and Ru(methylallyl)$_2$(cod) catalysts with and without PPh$_3$ ligand. The reactions were conducted for 24h and 38h. The products of the reaction were not identified, however, But there is the possibility of having obtained methanol.

Keywords: CO_2, ionic liquids, electrochemical reduction, heterogeneous catalysis, homogenous catalysis.

Resumo

Este trabalho foi dividido em 2 partes distintas, a primeira consistiu na electrorredução do CO_2 dissolvido a alta pressão em líquidos iónicos e a segunda na catálise química da redução do dióxido de carbono com hidrogéneo, usando catalisadores homogéneos e heterogéneos. Em ambos os casos foram construídas novas instalações com materiais novos e/ou reutilizados.

Este trata-se de um trabalho exploratório, que tinha como objectivo produzir metano ou metanol através da redução do CO_2. Para isso usou-se dióxido de carbono com hidrogéneo em misturas bifásicas de líquido iónico/(CO_2+H_2) a altas pressões, 140 bar, e baixas temperaturas, 413K. num rácio de CO_2: H_2=3:1.

Nas experiências de electroquímica foram testados três materiais de cátodo diferentes, diferentes quantidades de água no líquido iónico e dois gases diferentes. Pudemos verificar que o teor de água não alterou o potencial da janela electroquímica e que AuPt pode ser o melhor dos materiais testados, uma vez que foi o que gerou correntes mais elevadas.

No caso da catálise heterogénea, o líquido iónico foi impregnado no catalisador. Usaram-se catalisadores de Pd, Rh e Ru suportados em alumina. As reacções tiveram duração de 24h ou 72h. Obteve-se metano nas reacções sem líquido iónico onde se usaram os catalisadores de Pd e Ru, sendo que o último foi o que teve maior produção de metano; 3,30% do hidrogéneo que estava disponível para reagir deu origem a metano.

Na catálise homogénea, os catalisadores estavam imobilizados no líquido. Os catalisadores utilizados foram [Ru(cod)Cl_2]$_n$ e Ru(methylallyl)$_2$(cod) com e sem o ligando PPh$_3$. Estas reacções foram feitas durante 24h e 38h. Os produtos da reacção não foram identificados, no entanto existe a possibilidade de se ter obtido metanol nas reacções onde se usou o ligando.

Palavras-chave: CO_2, líquidos iónicos, redução electroquímica, catálise heterogénea, catálise homogénea.

List of Symbols and Abbreviations

[bmim][BF$_4$] – 1-Butyl-3-methylimidazolium tetrafluoroborate

[bmim][NTf$_2$] – 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

[emim][BF$_3$Cl] – 1-ethyl-3-methyl-imidazolium trifluorochloroborate

GC – Gas Chromatography

HS-GC – HeadSpace Gas Chromatography

IL – Ionic Liquid

MOFs – Metal–organic Frameworks

NMR – Nuclear Magnetic Resonance

PPh$_3$ – Triphenylphosphine

[Ru(cod)Cl$_2$]$_n$ – (1,5-Cyclooctadiene)ruthenium(II) chloride

Ru(methylallyl)$_2$(cod) – Bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II)

scCO$_2$ – Super critical carbon dioxide

SCIL – Solid catalyst with ionic liquid layer

SILP – Supported ionic liquid phase catalysts

TCD – Thermal conductivity detector

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1. Introduction

Global energy consumption is increasing rapidly due to population and economic growth. Currently, most of the energy is obtained by the burning of non-renewable fossil resources, which implies the production of greenhouse gases. [1] Scientists and Government agencies recognize the high contribution of carbon dioxide as a greenhouse gas to global warming. [2] Figure 1.1 shows surface temperature projections in different scenarios for the 21st century.
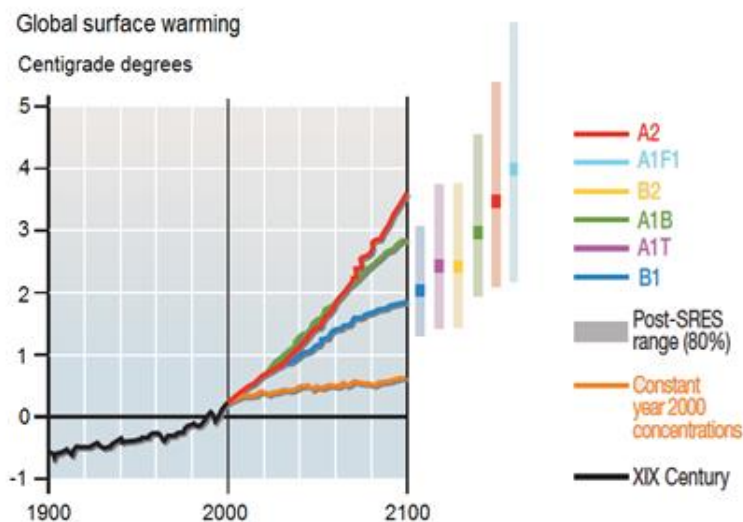
Figure 1.1 – Surface temperatures projection. (A1) very rapid economic growth and global population, and introduction of new and more efficient technologies: (A1F1), intensive use of fossil fuels (A1T) non-fossil energy sources, (A1B) balance across all energy sources, (A2) economic growth and technological changes are more fragmented and slower than in other occurences. Continuously increasing global population. (B1) Rapid changes in economic structures toward a service and information economy, with reductions in material intensity, and the introduction of clean and resource-efficient technologies. The emphasis is on global additional climate initiatives solution to economic, social, and environmental sustainability, including improved equity, but without additional climate initiatives, (B2) emphasis is on local solutions to economic, social, and environmental sustainability. Adapted from **[3]**.

Human activity has a direct consequence on the concentration of greenhouse gases. Since anthropogenic greenhouse gases accumulate in the atmosphere, they produce net warming by strengthening the natural "greenhouse effect". The concentration of carbon dioxide in the atmosphere has been increasing since the last century compared to the rather steady level evident during the pre-industrial era. Nitrous oxide and methane have also suffered an increase.

As reported in several publications of the Intergovernmental Panel on Climate Change, impacts of the increased Greenhouse Gases (GHG) concentrations may be slow to become apparent. In fact, interacting climate, ecological and socio-economic systems are inherently stable and they take a long time to react to changes in global changing conditions. The time scales associated with climate processes and feedbacks are very long, of the order of centuries. This poses however the problem that, once set in motion by anthropogenic causes, such as greenhouse emissions, global warming and sea level rise will continue for many years, even if stabilization of the atmospheric concentration of

CO_2 is achieved in the near future. Some changes in the climate system would be irreversible in the course of a human lifespan. For example, in the worst case scenario, it is expected an average temperature increase of between 2.4^{o}C and 6.4^{o}C by 2100. [3]

According to the statistics published by the International Energy Agency, [4] in 2010, 43% of CO_2 emissions from fuel combustion were produced from coal, 36% from oil and 20% from gas. In the same year, there was an increase of about 4.9% over the previous year in CO_2 emissions from the combustion of coal, which represented 13.1 $GtCO_2$. Coal is indeed the worst offender of the fossil fuels in terms of CO_2 emissions per unit of energy produced. However, it is currently the preferred energy source in the most populous developing countries, such as India and China, where intensive industrial production of energy is growing rapidly and access to large coal domestic reserves is easy. If nothing is done, estimates are of an increase of 15.3 $GtCO_2$ emissions from coal alone by 2035. The same publication reports that reducing CO_2 emissions from coal to 5,6Gt by 2035 could be possible by the use of more efficient plants and end-use technologies as well as increased use of renewable and nuclear energy and, last but certainly not the least, carbon capture and storage technologies. [4]

1.1. CO_2 Sources

In its first special report on carbon dioxide capture and storage, [5] the Intergovernmental Panel on Climate Change calls the attention to the importance to map the emissions where carbon dioxide concentration is higher, because these are more amenable to the use of capture technologies. It is quite obviously impracticable to capture CO_2 directly from the atmosphere, where its concentration is currently around 400 ppm. At the emission point (power plants and factories, for instance) the concentrations of carbon dioxide are usually of the order of 15% or less. These concentrations correspond to the normal combustion processes, where atmospheric oxygen (at 20 % concentration in air) reacts with carbon in fossil fuels, to produce carbon dioxide. The future proportion of high and low-content CO_2 sources will largely depend on the rate of introduction of hydrogen, biofuels, and the gasification or liquefaction of fossil fuels, as well as future developments in plant sizes.

In the energy sector, the use of biomass as fuel is still very low; the selection of fuels in the industrial sector is sector-specific. For example, in the refining and chemical sectors the primary fuels are gas and oil, in the cement industries all fossil fuels are used, and in some parts of the world coal, as mentioned above, is the dominant form.

To achieve the goal of reducing CO_2 emissions from the power and industry sectors, through its carbon capture and storage, it is necessary to understand where emissions arise and what their geographic relationship with potential storage opportunities is. If this relationship is good, then it is possible to significantly reduce these emissions through carbon capture and storage. However, when storage points are not available at short distances, the transport of carbon dioxide trough pipelines will introduce a significant addition to cost and energy consumption, rendering the process impracticable.

1.2. CO$_2$ Capture

The CO$_2$ capture involves the capture of this gas resulting from combustion and/or preparation of fossil fuels, as well as power generation and natural gas processing. Industrial processes such as the production of hydrogen, ammonia, steel, iron or cement, also produce carbon that can be captured.

There are four basic systems of CO$_2$ capture, these are: post combustion capture; pre-combustion capture; oxyfuel combustion capture; industrial process streams capture. Figure 1.2 shows a simplified diagram of these systems.
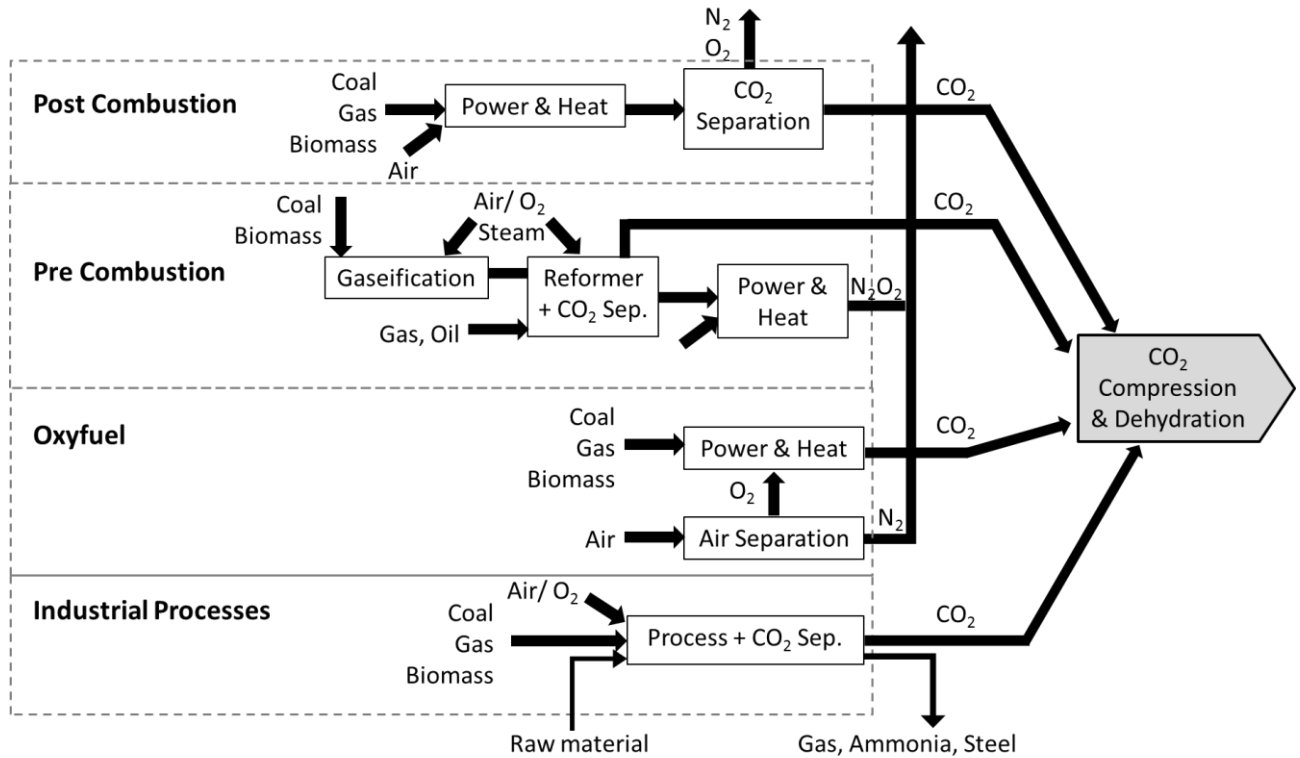

Figure 1.2 – CO$_2$ capture systems. Adapted from **[5]**.

After combustion, CO_2 is captured from flue gases produced from the combustion of fossil fuels and biomass. When combustion gases are produced, they are not directly dumped into the atmosphere; instead they pass through a device that separates much of the CO_2, which is then stored in a reservoir; the remaining flue gases are released into the atmosphere. For this process, a chemical sorbent process is used. The 2005 report of the IPCC [5] identified the main systems of reference for post-combustion capture as the then installed capacity of 2261 GW of oil, coal and natural gas power plants and in particular, 155 GW of supercritical pulverized coal fired plants and 339 GW of natural gas combined cycle plants, which represented the types of high efficiency power plant technology where CO_2 capture can be best applied.

In the second system above mentioned, pre-combustion capture, there is the reaction of fuel with oxygen or air and/or steam. This reaction originates essentially synthesis gas (syngas), composed of carbon monoxide and hydrogen. These systems were considered strategically important by the report. Reference systems for the application of pre-combustion capture were existing natural gas, oil and coal-based syngas/hydrogen production facilities and other types of industrial system. [5]

In a oxy-fuel system, combustion is performed with almost pure oxygen instead of air, giving a result of combustion gas that is mostly made up of carbon dioxide, and water in the case of hydrocarbon fuels. The oxygen used cannot be pure, because if it was, when gas was burned, the temperature of the flame would reach very high temperatures, but CO_2 and/or H_2O-rich flue gas can be recycled to the combustor to moderate this. The membranes and chemical looping cycles that are being developed are new techniques that are used for the supply of oxygen to the fuel. These new techniques, associated with low temperature (cryogenic) air separation are used to produce oxygen. The power plant systems of reference for oxy-fuel combustion capture systems which are the same as those mentioned above for post-combustion capture systems.

The capture of carbon dioxide from industrial processes has been made for 80 years or more. However, since there are no incentives or requirements to store this gas, most of the captured CO_2 is released into the atmosphere. The purification of natural gas, such as the production of synthesis gas containing hydrogen to produce ammonia, alcohols and synthesis of liquid fuels are a few examples of this type of CO_2 capture. The techniques used for the capture of the gas in these industries resemble the techniques used in pre-combustion CO_2 capture. The production of cement and steel, among others, also lead to the production of carbon, but this is not captured. The techniques used in the above systems can also be used in this system to capture CO_2 from streams.

1.3. CO_2 Storage or Reduction?

Storage (or sequestration) of carbon dioxide after its capture from flue gases will require several steps: purification, compression, transport in pipelines and injection into underground reservoirs. Purification is needed because the acidity of wet carbon dioxide is incompatible with long lives of the huge and expensive compressors required to pump CO_2 into pipelines. Transport through pipelines is itself a hazardous process, as carbon dioxide is denser than air and may accumulate in low lying areas, in case of a serious leak. CO_2 is non-breathable and accidents with a large number of

human fatalities may happen in case of rupture of any pipeline going through densely populated areas. Moreover, underground storage will certainly be opposed by many environmentalists and neighbour associations, due to fears of leakages through geological fractures and the risk of accidents at the surface.

In this context, transformation of carbon dioxide into useful products through reduction reactions is progressively being proposed as an alternative. Carbon dioxide as a C1 carbon source has been mentioned for decades. And in fact, life has found a solution for that problem many millions of years ago through photosynthesis. The carbon source of most living organisms is indeed atmospheric CO_2.

Industrial chemical processes using carbon dioxide as a reactant exist, with the production of urea occupying a very prominent first place in terms of quantities of CO_2 used. The sheer volume of current greenhouse gas emissions is however much bigger than the whole production of carbon-containing chemicals. Thus, even if the production of the Chemical Industry could be entirely based on CO_2, it would use only a small fraction of anthropogenic carbon emissions.

The only industry that is large enough to make a significant impact in emission reductions is the energy industry itself. Carbon dioxide reduction products contain carbon and can be used as a new energy source. Methods that can be used to convert CO_2 into fuels are photosynthesis, chemical catalysis and electroreduction.

Carbon dioxide is a stable molecule, with a highly negative Gibbs energy of formation. In order to make it react, either highly energetic reactants, such as hydrogen, must be used or energy directly supplied to the system, in the form of light or electricity. For instance, electrochemical reduction of CO_2 gas on a solid electrode has been employed to produce methane, and others as shown in Figure 1.3. [6]
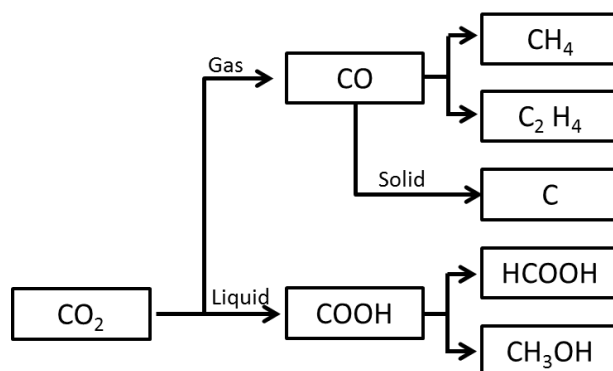
Figure 1.3 – Reaction products and intermediates for CO_2 reduction reactions. Adapted from **[6]**.

Different products may be formed, each corresponding to different changes in thermodynamic functions. The final products of electrochemical reduction depend on the conditions used, such as electrocatalyst, reduction potential, temperature, pressure and electrolyte. [6] Most proposed routes for chemical reduction of CO_2 leading to fuels use hydrogen. The various hydrogenation reactions of CO_2 are:

$$CO_2(aq) + H_2(aq) \rightarrow CO(aq) + H_2O(l)$$
$$\Delta G^o = 11 kJmol^{-1}; \ \Delta H = 11 kJmol^{-1}; \ \Delta S^o = -0,8 Jmol^{-1}K^{-1}$$

$$CO_2(aq) + 3H_2(aq) \rightarrow CH_3OH(l) + H_2O(l)$$
$$\Delta G^o = -79 kJmol^{-1}; \ \Delta H = -106 kJmol^{-1}; \ \Delta S^o = -88 Jmol^{-1}K^{-1}$$

$$CO_2(aq) + 4H_2(aq) \rightarrow CH_4(l) + 2H_2O(l)$$
$$\Delta G^o = -193 kJmol^{-1}; \ \Delta H = -230 kJmol^{-1}; \ \Delta S^o = -125 Jmol^{-1}K^{-1}$$

Figure 1.4 – Thermodynamic parameters for the hydrogenation of CO_2. **[2]**

As to proposed catalysts, a range of high-surface-area macro- and microporous materials, such as inorganic materials (e.g. alumina, silicas, and zeolites), organic materials (e.g. activated carbon materials), and complex metal–organic frameworks (MOFs) have been tried. [2]

The most desirable products for energy production are methane and methanol. Methane is a precursor to many useful organic chemicals, it can be used as fuel and it is used in the generation of electricity in fuel cells. Special applications have been proposed for space travel, to obtain drinking water by combining the on-board hydrogen rocket fuel with carbon dioxide produced by the astronauts. [7] Eight electrons are however needed to reduce the fully oxidized carbon into methane; the kinetic limitations are significant, so the use of catalyst is essential to achieve acceptable rates and selectivities.

Hydrogenation of CO_2 to methanol is thermodynamically more favourable, needing only six electrons. Methanol has the disadvantage that, contrarily to methane, there is no complete infrastructure already built to handle it for transport and end-user utilization. As a liquid fuel, It would however have some distinct advantages over methane and use the infrastructure of petrol distribution already in place.

Much is said about the reaction of carbon dioxide to produce methane and methanol. Most studies on the methanation reaction of CO_2 have been conducted at high temperature (> 200° C). [8] It would be important to carry out CO_2 reductions at lower temperatures (< 200 °C), in order to improve the flexibility of the operation, especially when the CO_2 and/or H_2 sources are intermittent, and to improve the energy efficiency of the process.

The methanation reaction of CO_2 has been studied, using as catalysts different noble metals, such as Ru, Pd and Rh over a variety of supports. Solymosi et al. [9] gave special attention to surfa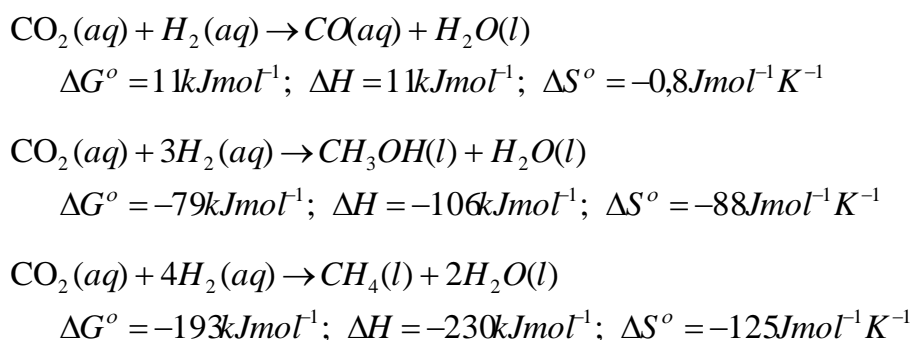ce processes that occur during the removal of the CO_2 atoms by H_2. They saw that hydrogenation of CO_2 in Ru/Al_2O_3 occurred to a measurable rate above 443 K producing almost exclusively CH_4, proposes that the synthesis of CH_4 from $H_2 + CO_2$ occurs through the formation of surface C and its subsequent hydrogenation. More recently, Eckle et al. [10] conducted an experiment, which led them to conclude that, under the conditions of the reaction, Ru/Al_2O_3 Catalyst is what has the lowest activity among tested. They also concluded that the selectivity was higher for the catalyst Ru / zeolite with this CO_2 conversion was less than 10% over a 40°C temperature window. Nobuyuki Ichikuni et al. [11] studied the differences in catalytic activity, depending on the type of impregnation. They concluded that the

6

catalytic activity of Ru/Al_2O_3 fine particles prepared by spray reaction (SPR) were much higher than those obtained by conventional impregnation (IMP) under the same conditions. Which indicates that the SPR is an excellent method plausible and an excellent method for preparing high-activity catalysts.

Hydrogenation of CO_2 on Pd supported by Al_2O_3, TiO_2, SiO_2 and MgO was investigated by Erdöhelyi et al. [12] The dispersion of Palladium is important, when it is very dispersed the reaction product is methane, when it is a little spread out the product can be methanol or water-gas shift. The dispersivity of $Pd-Mg/SiO_2$ catalyst has also been studied in the methanation reaction of CO_2 with hydrogen. [7] The catalyst at 450^oC, presents 95% selectivity for CH_4, with a CO_2 conversion of 59%. Palladium supported on silica reduces mainly CO_2 to CO.

Rhodium catalysts have also been studied. Solymosi et al. [13] investigated the hydrogenation of CO_2 in Rh/Al_2O_3 to a measurable rate above 443 K, with only methane product. This support was compared with others, concluding that the most effective has been TiO_2 and SiO_2 less effective. Iizuka et al. [14] also did a study on the catalyst of rhodium in different supports. Their aim was to compare the reactivity of different catalysts in the reaction of hydrogen with carbon dioxide and carbon monoxide. Recently the effect of addition of O_2 to the mixture of CO_2/H_2 has been studied. When the gas is added in small quantities it has a beneficial effect on CO_2 methanation reaction, however, if a large amount is added, this will have a negative effect. The relationship between Rh particle size and intrinsic catalytic activity has also been studied. [8]

In respect to homogeneous catalysis, Jessop et al. [15] were pioneers. They performed a study where formic acid was produced from a mixture of supercritical carbon dioxide and hydrogen, using a ruthenium catalyst, where ligands had been modified to include groups with high solubility in high pressure CO_2. Previously, Leitner et al. [16] performed CO_2 hydrogenation in aqueous solutions of amines using $RhCl(TPPTS)_3$ and rhodium-based catalyst $[RhCl(COD)_2]_2/TPPTS$ and $[RhH(COD)]_4/TPPTS$. Joó et al. [16] studied this same reaction in aqueous solutions of free amines. They concluded that in acidic media reactions are slower. With hydrogenation of CO_2 is also possible to obtain formic acid, Zhang et al. [17] did this study. The conditions of the reaction were: 6MPa (CO_2/H_2) to 60^oC, during 5h; used ruthenium chloride catalysts or ruthenium complexes. Tai et al. [18] also made studies in this sense, they tested 44 different phosphines in combination with 3 precursors of Ru(II) different and $[RuCl_2(C_6H_6)]_2$. Only 6 of the phosphines tested resulted in high rates of production of formic acid.

1.4. Ionic liquids and carbon dioxide reduction

Ionic liquids (IL) are composed entirely of ions and exist in the liquid state at room temperature. They typically contain a bulky organic cation which is poorly coordinated to an organic or inorganic anion. [19] Recently they have attracted much interest because they can be used as solvents, replacing traditional organic solvents. Because their vapour pressures are very low, they can replace volatile organic compounds as more environmentally benign solvents in many chemical processes. Product recovery from ionic liquid media may be difficult for temperature sensitive substances that cannot be distilled out. On the other hand, liquid-liquid extraction using organic

solvents may result in exactly the type of pollution that the use of ionic liquids is supposed to avoid. [20] The combination of ionic liquid and supercritical carbon dioxide for achieving more convenient reaction and product recovery, reported recently, has further extended the research and application scope of ionic liquids. [21] [22] [23] In the course of these studies, it was discovered that carbon dioxide may be highly soluble in many ionic liquids.

The solubility of carbon dioxide in ionic liquids is usually through absorption. Although most be through physical absorption involves the weak association between CO_2 and IL, some IL absorb through chemical reaction. [24] Some studies show that the supercritical CO_2 ($scCO_2$) is highly soluble in ionic liquids, however these liquids are not soluble in $scCO_2$, so it is possible to extract many organic compounds of ILs. This property is very important because it makes it possible to separate $scCO_2$-soluble chemicals from ILs using $scCO_2$ without any cross-contamination. [25]

For the imidazolium- and pyridinium-based ILs the solubility of the gas is mainly controlled by interactions with the anion. [26] [27]

Other characteristic important to note that the ionic liquids are their high ionic conductivity and wide electrochemical window. [21] [28]The conversion of CO_2 in methanol with an electrochemical photocell was studied by Ogura et al. [29] The electrocatalytic reduction of CO_2 proceeds via a limited surface of a metal complex in the presence of a homogeneous catalyst. Naitoh et al. [30] investigated the electrochemical reduction of carbon dioxide in methanol at low temperature. Electrolysis was performed with a copper cathode and an anode of Platinum in methanol catholyte containing benzalkonium chloride and in 0.1 M hydrogen carbonate or 80 mM benzalkonium chloride anolyte. In one carbon-based energy cycle concept, it was studied the reaction of electrolytic hydrogen with CO_2, to form methanol and water [31], another concept was the formation of methane by means of electrolytic hydrogen reaction with CO_2 (with condensation of water to shift the equilibrium and achieve good yields). [32] Hori et al. were able to make the direct reduction of CO_2 to methane and ethylene with current densities of 5-10 mA cm^{-2} and efficiency of current up to 69%, at 0ºC. [33] [34]

Ionic liquids have been used in various electrochemical applications such as solar cells, electrochemical sensors, solvents in electrochemical experiments (due to the fact that ionic liquids have a large amount of charge carriers, when these are used as solvents no supporting electrolytic is required for these experiences), among others. Has been studied the possibility of using a liquid-liquid interface with an aqueous phase with the intent of this function as a electroanaytical tool for quantitative anion detection, could still replace the volatile organic solvents previously used. O'Mahony et al. [19] studied the effect of water on electrochemical window and potential limits of ILs. They established an order for the hydrophobicity of the anions, being the more hydrophobic the [FAP]$^-$ and the least ate halides. They concluded that the increase in water causes electrochemical window decreases. Snuffin et al. [35] performed electrochemical experiments with the [emim][BF$_3$Cl], they found that CO_2 can be dissolved and electrochemically reduced to atmospheric pressure and room temperature.

Mixtures of high pressure carbon dioxide and ionic liquids were first used for green processing by Brennecke et al. [20] Selective hydrogenations can be conducted in this type of mixtures. [36]

Some recent proposals of catalysts for CO_2 hydrogenation seem interesting to adapt to ionic liquid media. Putting the concept of the promotion of Ru homogeneous CO hydrogenation by iodide salts and the aim of produce one-carbon products, the CO_2 hydrogenation was done at 513K with $Ru_3(CO)_{12}$ catalyst in N-methylpyrrolidone, 1,3-dimethy1-2-imidazolidin, N-ethyl-2-pyrrolidone) for 3h. [37] There have been advances in discovery of new highly active catalysts for the production of formic acid and formates and in direct reduction of CO_2 with silanes to methanol at ambient conditions. The obtained formic acid or its derivatives next were converted into methanol with a high yield. [38] Also at lower temperature (413K) [Ru(acac)$_3$] with the tridentate ligand Triphos (Triphos,1,1,1-tris(diphenylphosphinomethyl)ethane) and the ruthenium(II)-complex [(Triphos)Ru-(trimethylenemethane)] [39] in methanesulfonic acid and EtOH, or MeOH for 24h was successfully applied.

2. Experimental

The start of my thesis work coincided with the launching of a new programme in the research group I was about to join. This programme aims at devising new methods to reduce carbon dioxide, by chemical or electrochemical catalysis, to fuel products, such as methanol and methane. Several researchers are involved in this project. Part of my work was therefore carried out in close collaboration with other researchers, while another part was essentially performed by myself, although under supervision by senior group members. Each piece of work reported here involved the previous design and assembling of a new high pressure apparatus.

The experimental work was divided in two distinct parts:

I – In the first part, I collaborated in the setting up of laboratory facilities to carry out the electroreduction of high pressure carbon dioxide dissolved in ionic liquids. This work involved: (1) building a new, simple high pressure cell with incorporated cathodes of different materials and a zinc sacrificial anode (see Figure 2.1); (2) assembling a specially designed high pressure apparatus to collect samples of reaction products, and to increase several times their concentration in relation to carbon dioxide, in order to facilitate detection and analysis (see Figure 2.6); (3) characterising several cathode materials immersed in ionic liquids through voltammetry measurements.

II – In the second part, I focused my attention on chemical catalysis of carbon dioxide reduction with hydrogen, using either heterogeneous or homogeneous catalysts. This part of the work was exploratory, experimenting with diverse catalytic systems, with the main objective of trying to find out simple, but promising routes to implement the reaction. Ionic liquids were used as solvents in homogeneous systems, or as selectivity modifiers, in heterogeneous systems. This part of the work has also included assembling a new high pressure apparatus, bringing together several pre-existent pieces (see Figure 2.7 and 2.8).

In this chapter, the assembled apparatus will be described, as well as the experimental procedures followed for the voltammetric measurements and for the high pressure hydrogenations.

2.1. Chemicals

Hydrogen and carbon dioxide were supplied by Air Liquide with a stated purity of 99.98 mol%. These substances were used as received without any further purification.

Silicon oil was bought to Labor Spirit.

Carbon fabric type B1 used was bought from Clean Fuel Cell Energy Lt.

Ag_3Cu and AuPt were prepared by Catalonia Institue for Energy Research under the framework of a FP7 research project

The catalyst used were Palladium (0.5 wt.%) on alumina in 3.2mm pellets, Rhodium (0.5 wt.%) on alumina in 3.2mm pellets and Ruthenium (0.5 wt.%) on alumina in 3.2mm pellets . All of them were bought from Sigma-Aldrich.

The studied ionic liquids [bmim][BF$_4$] and [bmim][NTf$_2$] were supplied by Solchemar. These liquids were used as received, without any further purification.

2.2. Voltammetry

The high pressure electroreduction cell was an adaptation of a pre-existent small reactor. This reactor is made of stainless steel and has a volume of 150 cm^3. Its scheme and picture are shown in Figure 2.1 and 2.2, respectively. This cell was placed in a thermostated oven, for temperature control. The voltammetric measurements were performed with three electrodes inside the cell (3, 4 and 5, in Figure 2.1), a pressure transducer, a temperature sensor. The ionic liquid solvent inside the cell was magnetically stirred, using an external stir plate and a magnetic bar.
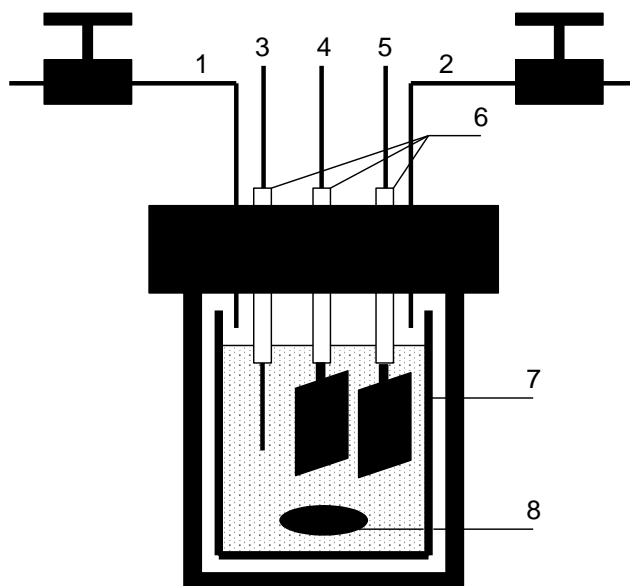

Figure 2.1 – Scheme of the high-pressure electrochemical cell: (1) gas inlet; (2) gas out; (3) quasi-reference electrode; (4) cathode: working electrode; (5) anode: counter electrode; (6) Teflon packing; (7) glass beaker; (8) stirrer. Adapted **[25]**.
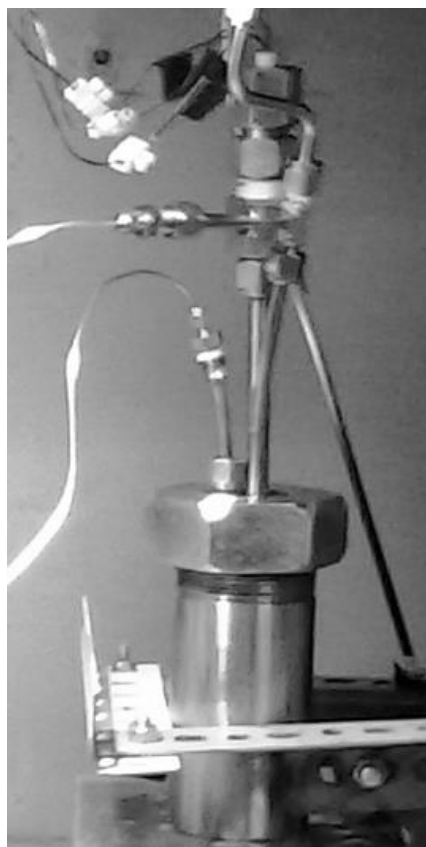
Figure 2.2 – Picture of the apparatus used for voltammetry experiments.

2.2.1. Voltammetry Procedure

First, CO_2 was introduced in the cell up to 30 bar, and released, in order to purge the cell to remove oxygen in the system. This was repeated three times. When the temperature of the air bath and the pressure of the cell are at desired values for the experiment, we waited 1 hour for proper stabilisation. A voltammetric measurement was then carried out. Pressure varied from 7 to 60 bar, depending on the type of gas: lower pressures for test experiments with argon, the highest pressure was used with carbon dioxide. Temperature was always 45°C. The program *NOVA* was used for electrical current measurement (AUTOLAB 84469 used the power source). The scan rate at which they were carried out voltammetry measurements were 20, 50 and 100 mV.s^{-1}.

2.3. Calibration

Precise knowledge of the volumes of all vessels connected to the device used for the recover of gas samples for chemical analysis are needed in order to calculate the reaction yield, that is, the final concentration of methane in the (chemical or electrochemical) reaction vessels. The applied calculation methodology uses those values to obtain total quantities of carbon dioxide and methane. Calibration of those volumes was therefore carried out, using a low pressure gas expansion method. The calibration gas was argon. A high pressure vessel of well known volume, measured by weighing

with water, was used as reference (CB in Figures 2.3 and 2.4). A pressure digital meter, with a measurement precision of < 0.1% FS at room temperature, registered pressure values at different stages of the expansion method.

Schemes of the different apparatus requiring calibration are shown in Figures 2.3, 2.4 and 2.5.
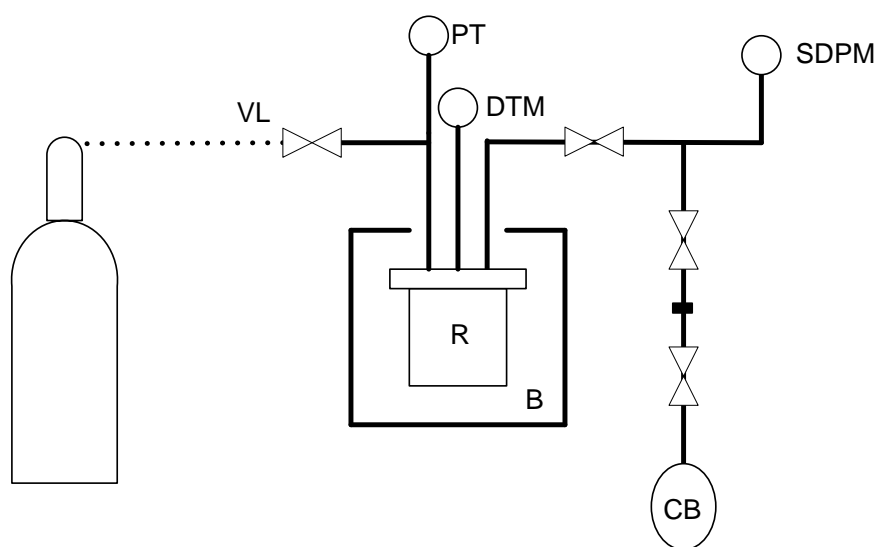
Figure 2.3 – Scheme of the calibration of high pressure installation: (VL) Ar inlet and output and vacuum line, (PT) pressure transducer, (DTM) digital temperature meter, (R) reactor, (B) bath, (SDPM) sensitive digital pressure meter, (CB) calibration balloon.

Figure 2.4 – Scheme of the calibration of expansion zone vessel: (VL) Ar inlet and output and vacuum line, (PT) pressure transducer, (EV) expansion vessel, (SDPM) sensitive digital pressure meter, (CB) calibration balloon.
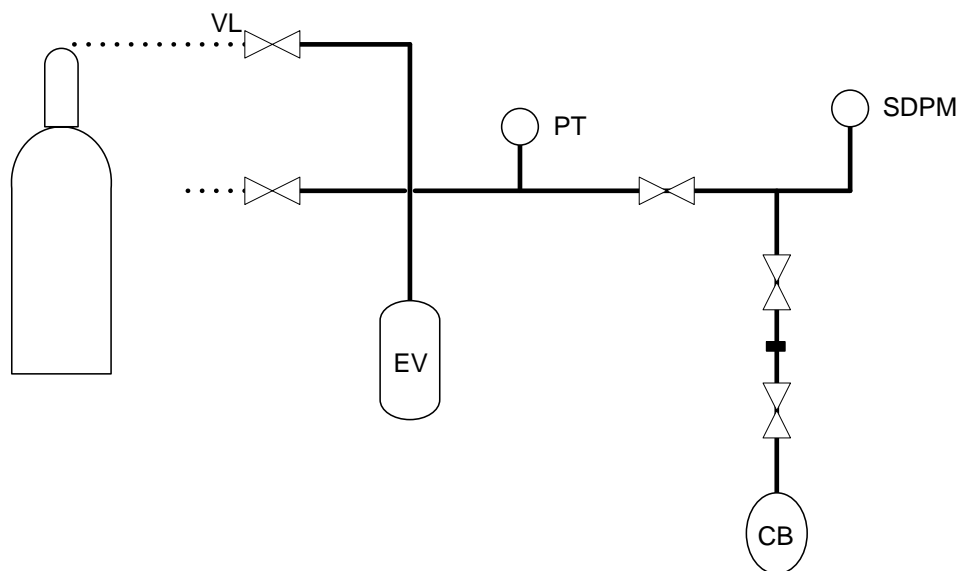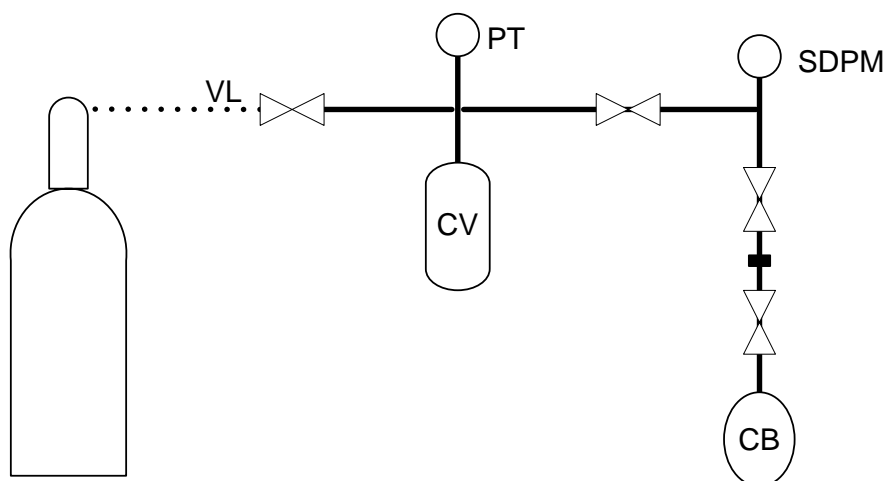
Figure 2.5 – Scheme of the calibration collecting vessel apparatus: (VL) Ar inlet and output and vacuum line, (PT) pressure transducer, (CV) collecting vessel, (SDPM) sensitive digital pressure meter, (CB) calibration balloon.

2.3.1. Calibration Procedure

The procedure starts with the connection of the calibrated balloon, as shown in Figures 2.3, 2.4 and 2.5, followed by the addition of Argon[1]. Pressure was registered and the calibrated vessel valve was then closed, the remaining volume was then connected to the vacuum pump, until a very low pressure was attained. The gas inside the calibrated vessel was expanded into the volume to be calibrated and pressure measured again.

Values of the calibrated volumes of the different apparatuses are given in the following Table.

Table 2.1 – Volume values obtained for the various devices.

Devices	Volume (cm^3)
Chemical reaction vessel	30
Collecting Vessel (1)	80
Collecting Vessel (2)	48
Electrochemical reaction vessel	150
Expansion Vessel (1)	140
Expansion Vessel (2)	1015

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[1] The pressure has to be less than 2,5 bar.

2.4. Gas analysis technique

Large amounts of CO_2 were used to carry out the voltammetric measurements and the hydrogenation reactions. Direct sampling from the reaction vessel would thus contain carbon dioxide in such excess that the detection of the reaction products and measurement of their concentrations by gas chromatography would be very difficult. In order to solve this problem and to facilitate the GC analysis of the products, we built an apparatus that allowed us to substantially reduce the amount of CO_2 present in the collection vessel.

This apparatus consists of an expansion vessel with the volume of 140 cm^3. When the voltammetric measurements or the hydrogenation reactions were finished, the reactor was connected to this expansion vessel, which was then immersed in a cryogenic mixture of ice, salt and N_2. At these temperatures, CO_2 would liquefy, contrarily to the reaction gaseous products, like methane, which stayed in the gas phase. Samples for analysis were than taken from the gas phase. By removing large quantities of CO_2 from this phase, the concentration of products such as methane was amplified several times, allowing its easier detection by GC.

By establishing an equilibrium pressure, gas concentrations are the same in any part of the installation, i.e. the concentration of CO_2 and other gases is equal in the expansion vessel and the cell. With the information concerning the gas concentration detected in GC analysis and using the calibration curve we can obtain the information of the number of moles of the product that we obtained. Knowing the density of the CO_2/H_2 mixture at high pressure and doing some calculations we obtain the number of moles of hydrogen which were available to react, so we can know the yield of the reaction relative to limiting reagent, H_2.

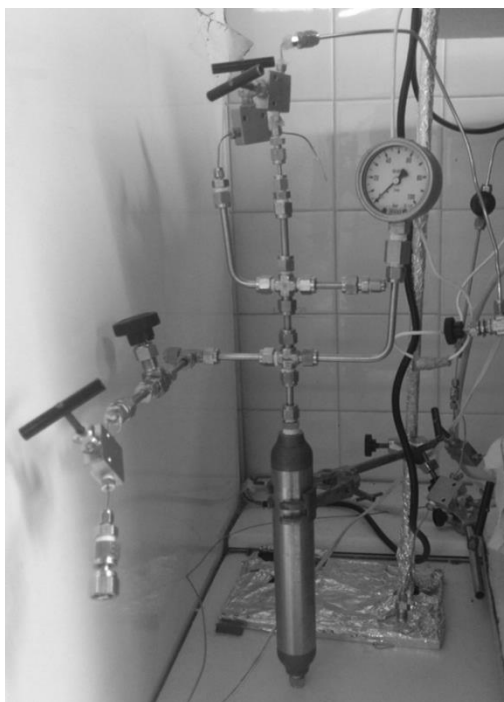Figure 2.6 shows the installation that was created.

Figure 2.6 – Picture of the apparatus that allowed us to substantially reduce the amount of CO_2 present in the collection vessel.

2.5.   Hydrogenation

Hydrogenations were performed in a high pressure stainless steel reactor, inside a fume hood. This reactor has the volume of 30 cm^3, as given in Table 2.1, and it is immersed in a thermostated silicone oil bath. The mixture inside the reactor is stirred, using an external stir plate and a magnetic bar. The scheme of this apparatus is shown in Figure 2.7.
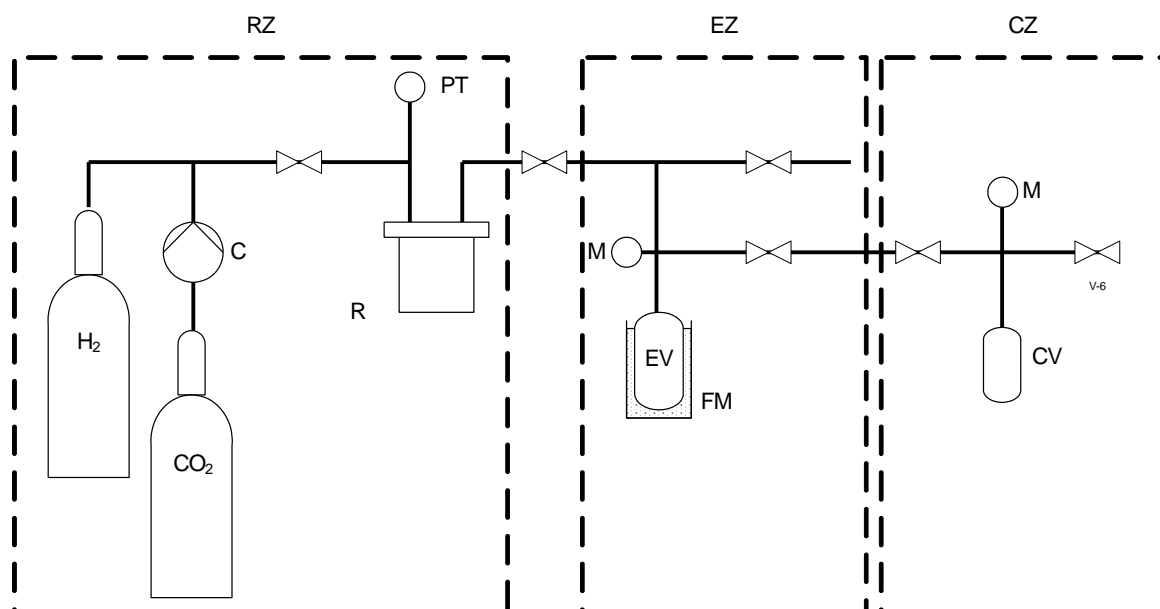

Figure 2.7 – Scheme of the hydrogenation apparatus: (RZ) reaction zone, (EZ) expansion zone, (CZ) collecting zone, (C) CO$_2$ compressor, (R) reactor, (PT) pressure transducer, (M) manometer, (EV) expansion vessel, (FM) freezing mixture, (CV) collecting vessel.
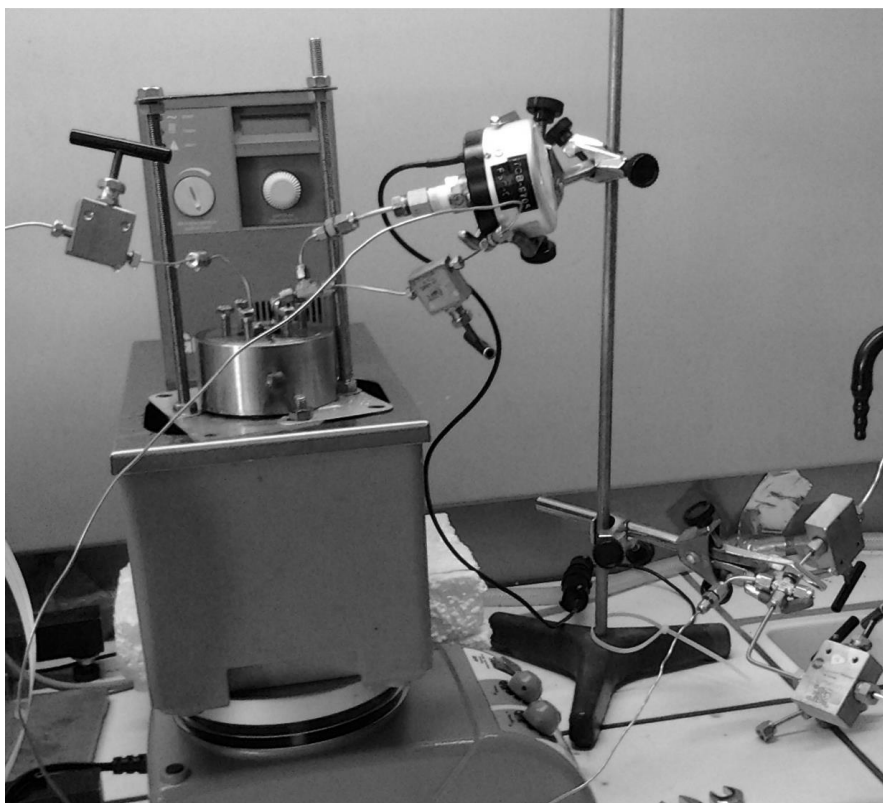
Figure 2.8 – Picture of the apparatus used for hydrogenation.

2.5.1. Hydrogenation Procedure

The reactor was assembled, as show in figure 2.7 and 2.8, it is important to confirm that the output valves are closed. After you make sure that the output valves are closed, we inserted CO_2 to a pressure of 30 bar. We wait a few seconds until pressure stabilizes. So, we inserted 20 bar of H_2 and look forward a few more seconds until the value of the pressure remained constant. Finally, we insert a further 30 bar of CO_2. When the pressure was stable at 80 bar, we put the reactor inside the bath and we turn on the same. Until the temperature inside the reactor reaches 140°C, pressure was increasing. When the pressure reached stabilized we turn on the stirrer inside the reactor and start counting the time of the reaction. Passed 24 or 72 hours, depending on the reaction we wanted to do, we turned off the stirrer and the temperature of silicone oil bath.

It was necessary to wait some time until the reactor was at room temperature. While we waited, we made vacuum in collecting vessel and the expansion zone vessel. Subsequently we opened slightly the valve that connects the reactor and the expansion zone vessel. The gases from the reactor began to pass to the expansion vessel until the pressure had the same value in both places. Then we put the freezing mixture in the expansion vessel to the pressure down. When this stabilized again open the valve which connects the expansion vessel and the collection vessel until the pressure in the latter was of 2 bar. Close the valve and take the collection vessel for analysis.

2.6. Identification methods

The qualitative identification of products obtained was carried out by Gas Chromatography HeadSpace (HS-GC) and Nuclear Magnetic Resonance (NMR).

The HS-GC used was TRACE GC Ultra. The column used was a 100% Dimethyl Polysiloxane fused silica capillary column (dimensions: 30 m x 0.32 mm internal diameter x 3.0 µm film thickness). The carrier gas was hydrogen (1mL/min) and the oven program was 50ºC (1 min) to 130ºC (2min) at 10ºC/min.

The nuclear magnetic resonance analyses were performed on a Bruker Avance III 400.

The quantitative analysis was carried out by gas chromatography. An Agilent Micro GC 3000 was used equipped with a backflush 1 µl injector. The separation of the compounds present in the gas current was done in two columns. One of the columns was a MolSieve 5A 10 m x 0.32 mm with Plot U 3 m x 0.32 mm pre-column, with argon as carrier gas (Channel 1). The other column is a Plot U 8 m x 0.32 mm column with a Plot Q 1 m x 0.32 mm pre-column with helium as carrier gas (channel 2). After separation on the column, the sample gas flows through a thermal conductivity detector (TCD).

On channel 1, the column and injector temperature were 100°C and 90°C, respectively. Sampling time was 10 s, injector time was 200 ms, run time 180 s and pressure equilibration time was 10s. Column and post-run pressure were 30 psi and 40 psi. Detector sensibility was standard and the data rate was 50 Hz. Baseline off set was 0mV; backflush time was 9.5 s. Channel 2 only differs in the column temperature, this was of 60ºC, post-run pressure was 32 psi and the detector sensitivity was high.

Figure 2.9 – TRACE GC Ultra used in HS-GC analysis.

20

3. Results and Discussion

The first part of this work addressed the electrochemical reduction of CO_2. It is known that different products can result from this type of electrolysis, which depends critically on the materials used to build the electrode. Thus, voltammetric experiments were performed in order to characterize cathodes made of different metals. The influence of the amount of water present in the ionic liquid was also checked, as hydrogen produced at the cathode from water may also influence the products and the yield of reaction. In this way, tests were conducted with three different cathodes, with different amount of water in the liquid.

The second part of this work addressed the chemical reduction of CO_2 using homogeneous or heterogeneous catalysis methods. Experiments were conducted with different catalysts, under the same conditions of pressure and temperature. Homogeneous catalysis was carried out using ionic liquids as solvents. In the case of heterogeneous catalysis, catalysts were used as such or coated with ionic liquids.

3.1. Voltammetric experiments

Cyclic voltammetry is an electrochemical technique where an electric current generated by a varying applied potential is measured. Usually, a cyclical scanning of the potential is implemented, and the result of the experiment is a current versus potential curve. For these experiments, three different electrodes are needed, a working electrode, where the potential is applied, a counter electrode, and a reference electrode, all usually immersed in one liquid solution. Using a potentiostat system, the potential is varied at a certain scan rate (measured in Volts per second), up to a certain pre-defined value, and then brought back to the original value. The imposed electrical potential imposes an electric current that generates electrochemical reactions at the surface of the working electrode. The shape of the curve current vs. applied potential depends critically on these electrochemical phenomena, and may reveal important information concerning the interaction between the electrode materials and the reacting species in solution.

In the course of this work, three different cathode materials were characterized using voltammetric methods. The liquid solution was based on the ionic liquid 1-butyl-3-methylimodazolium tetrafluoroborate [bmim][BF$_4$]. Small quantities of water (0.5 or 1.7 mole percent) were added, and the ionic liquid was in contact with either argon, at a pressure of 7 bar, or carbon dioxide, at a pressure of 60 bar. The Ar-based experiments were used as a control, since no electrochemical reactions are expected involving this solute. The differences between the experiments with Ar and those with CO_2 should therefore translate the effect of the electrochemical reactions involving carbon dioxide dissolved in the ionic liquid at 60 bar. The differences in solution water content were also designed to check the effect of water concentration, especially since the production of H_2 at the cathode is a competing/cooperative reaction in regard to carbon dioxide reduction.

Table 3.1 – Voltammetric experiments using the ionic liquid [bmim][BF$_4$] as solvent, in contact with the referred gases at the stated pressure, silver as the reference electrode and zinc as counterelectrode.

Entry	Working cathode	Counter anode	Gas phase	Pressure (bar)	Water (%)	Scan rate (mV.s^{-1})
1	Carbon fabric	Zn	CO$_2$	60	0.5	20; 50; 100
2	Carbon fabric	Zn	Ar	7	0.5	20; 50; 100
3	Ag$_3$Cu	Zn	CO$_2$	60	0.5	20; 50; 100
4	Ag$_3$Cu	Zn	Ar	7	0.5	20; 50; 100
5	AuPt	Zn	CO$_2$	60	0.5	20; 50
6	AuPt	Zn	CO$_2$	60	1.7	20; 50
7	Carbon fabric	Zn	CO$_2$	60	1.5	20; 50
8	Carbon fabric	Zn	CO$_2$	60	2.5	20; 50
9	Carbon fabric	Zn	CO$_2$	60	3.5	20; 50

This experiment matrix was set up in order to allow us to compare:

(1) water content, by comparison between runs 1, 7, 8, and 9, and also between runs 5 and 6;

(2) carbon dioxide vs. argon, using runs 1 and 2, for carbon fabric; and 3 and 4, for Ag3Cu;

(3) electrode materials, using runs 1, 3, and 5.

It should be mentioned that the results of the experiments with the lowest used scan rate, at 20 mV s^{-1}, turned out to be more precise than the others, and so all comparisons were made based on that rate.

Figure 3.1 shows the cyclic voltammograms obtained for runs 5 and 6, with a AuPt working electrode and water contents of 0.5 and 1.7 %, respectively.
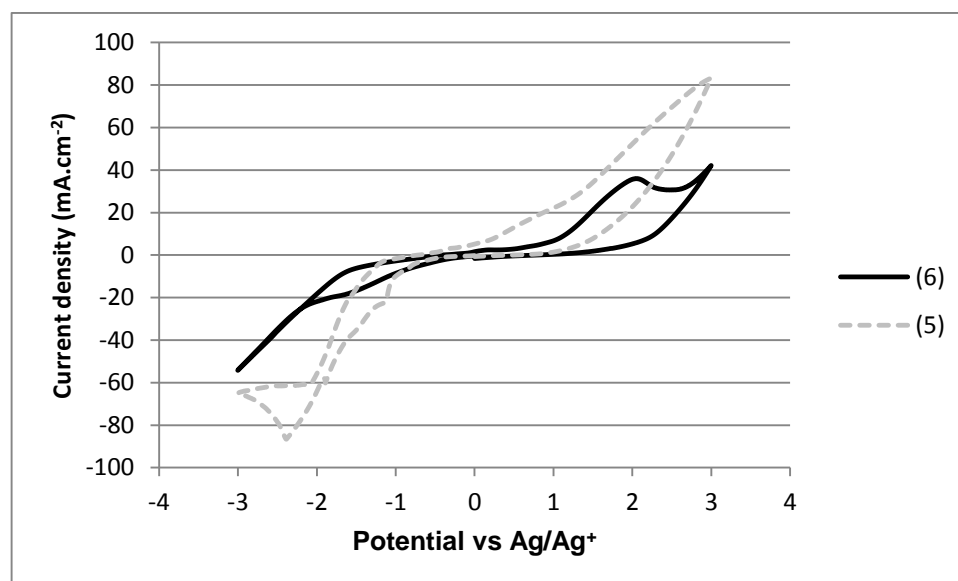

Figure 3.1 – Cyclic voltammograms in [bmim][BF$_4$] with a AuPt catalyst and a water content approximately (6) 1,7% and (7) 0,5%. Scan rate, 20 mV s^{-1}.

The water content did not change the electrochemical potential windows. The result is however surprising, because it indicates a current density decrease with increased water content. This result is contrary to what would be expected. In fact, the experiments performed by Schröder et al. [40] show, as expectable, that the current increases with the increase of water in ionic liquid, due to the reduction to hydrogen. On the other hand, comparison between runs 1, 7, 8, and 9 could not be done, due to the highly irregular profiles of the curves obtained in runs 7 to 9.

As a consequence, the only conclusion we may have reached was that experiments with much larger water contents should be performed, in order to try and devise the effect of water content in the presence of dissolved carbon dioxide.

Figure 3.2 shows cyclic voltammograms in [bmim][BF$_4$] with a carbon fabric cathode, runs 1 and 2, and Ag$_3$Cu, runs 3 and 4 in Table 3.1.
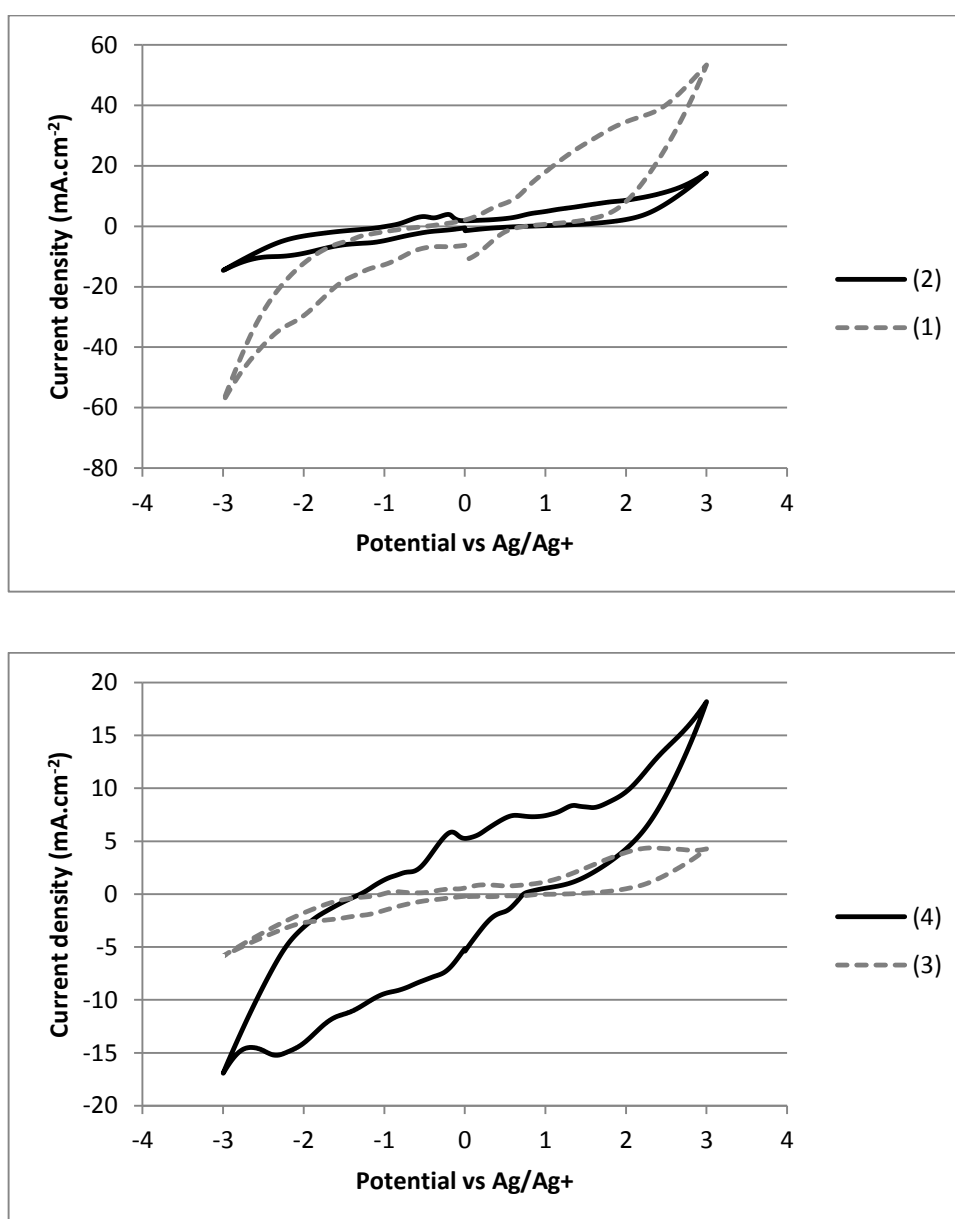

Figure 3.2 – Cyclic voltammograms in [bmim][BF$_4$] with a Carbon fabric after 60 minutes exposure to (2) Argon, (1) CO$_2$; with Ag$_3$Cu after 60 minutes exposure to (4) Argon, (3) CO$_2$; Scan rate, 20 mV.s^{-1}.

These experiments have shown that carbon fabric does promote the electrochemical reduction CO_2, with a reaction onset potential around -1 V, while Ag_3Cu seems totally ineffective for this purpose.

Figure 3.3 compares the results of the experiments with CO_2 for the three different types of cathode used in this work, with all other conditions equal.
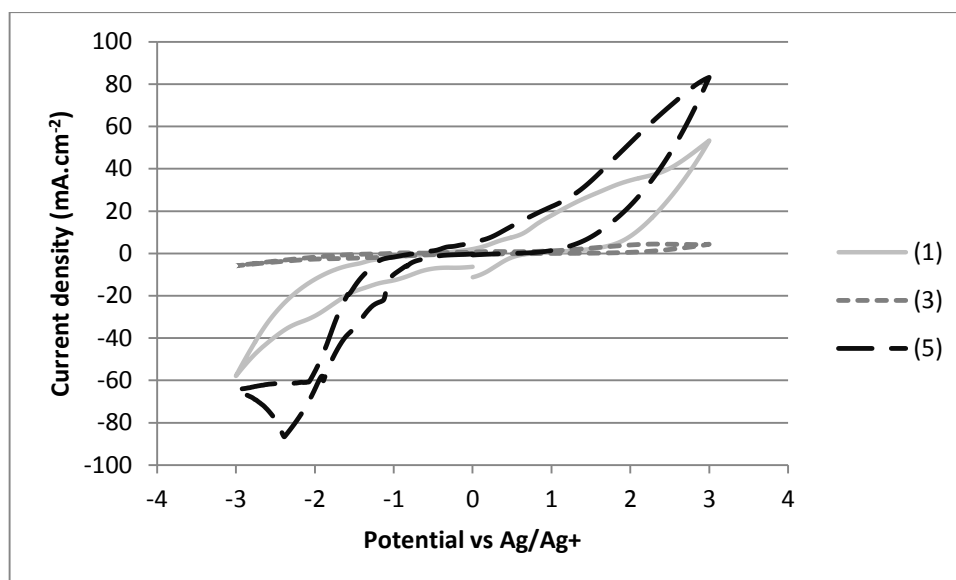

Figure 3.3 – Cyclic voltammograms in [bmim][BF$_4$] with a Carbon fabric after 60 minutes exposure to (1) CO_2; with Ag_3Cu after 60 minutes exposure to (3) CO_2; with AuPt after 60 minutes exposure to (5) CO_2. Scan rate, 20 mV.s^{-1}.

It is apparent what had already been verified in Figure 3.2, namely that Ag_3Cu is not an adequate material for the reduction of CO_2. Carbon fabric and AuPt, are both suitable materials, with similar onset potentials. These preliminary findings also indicate that AuPt might be the best of the tested materials, as it generates higher currents.

3.2. Hydrogenation Experiments

This part of the work aimed at exploring the possibility of reducing carbon dioxide with hydrogen using either homogeneous or heterogeneous catalysts at relatively mild conditions. One of the objectives was to obtain a preliminary assessment of whether the use of ionic liquids as solvents or as catalyst modifiers could prove beneficial for this purpose.

Hydrogenation of CO_2 was performed with and without the addition of other solvents. Hydrogenation was carried out with different types of catalysts and ionic liquids.

Tables 3.2 and 3.3 summarize the experiments that were carried out and the respective reaction conditions.

Table 3.2 – Heterogeneous Reaction. * Reaction yield regarding hydrogen as the limiting reagent.

Heterogeneous Reaction Conditions							
No.	Catalyst	Solvent	Pressure (bar)	Time (h)	Temp. (K)	Produced CH_4 (mmol)	Yield (%)*
1	Rh/Al_3O_2	CO_2	80	24	413.15	-	-
2	Ru/Al_3O_2	CO_2	80	24	413.15	0.694	3.30
3	Pd/Al_3O_2	CO_2	80	24	413.15	0.170	0.81
4	Ru/Al_3O_2	CO_2/[bmim][BF_4]	80	24	413.15	-	-
5	Rh/Al_3O_2	CO_2/[bmim][BF_4]	80	24	413.15	-	-
6	Pd/Al_3O_2	CO_2/[bmim][BF_4]	80	24	413.15	-	-
7	Pd/Al_3O_2	CO_2/[bmim][BF_4]	80	72	413.15	-	-
8	Pd/Al_3O_2	CO_2	80	72	413.15	0.148	0.70

Table 3.3 – Homogeneous reaction.

Homogeneous Reaction Conditions						
No.	Catalyst	Ligand	Solvent	Pressure (bar)	Time (h)	Temp. (K)
9	$Ru(methylallyl)_2(cod)$	-	CO_2/[bmim][BF_4]	80	24	323.15
10	$Ru(methylallyl)_2(cod)$	PPh_3	CO_2/[bmim][NTf_2]	80	39	413.15
11	$[Ru(cod)Cl_2]_n$	PPh_3	CO_2/[bmim][NTf_2]	80	24	413.15

Reaction yields were calculated relative to hydrogen, as this is the limiting reagent. The quantities of hydrogen and carbon dioxide produced in the reaction were obtained by GC analysis. The GC calibration curve is given in Annex 11. Using the calibrated volumes of the sampling apparatus, described in chapter 2, and the density of the carbon dioxide + hydrogen mixtures, calculated using the GERG-2004 equation of state, [41] the GC determined gas concentrations were translated into concentrations in the reaction mixture at the end of the reaction.

$$\text{Yield}(100\%) = \frac{mol\ CH_4\ produced}{mol\ H_2}x100$$

Figure 3.4 – Equation for calculating the yield of methane.

In the reactions with heterogeneous catalysts, we started by trying to use only the catalyst pellets without IL (reactions 1, 2 and 3). Through the GC analysis, we can see that there was

production of methane in the reactions when ruthenium and palladium catalysts were used. Ruthenium was the most active catalyst. This result was not expected, since rhodium was expected to be one of the most active metals. [8] The smallest yields were obtained with palladium catalysts.

In the three following reactions, ionic liquid-coated catalysts were used. The method of forming the ionic liquid layer is called SCIL or SCILL [36]. In none of these reactions was there any production of methane, even when reactions were repeated allowing longer times.

The experiments with homogenous catalysts were carried out either in [bmim][BF$_4$] or [bmim][Ntf$_2$], under a pressure of 80 bar of carbon dioxide. In reactions 9 and 10 (see Table) Ru(methylallyl)$_2$(cod) and [Ru(cod)Cl$_2$]$_n$ precursors were used. In reaction 9, 15 mg of precursor weredissolved in 3 mL of IL. For reaction 10, a ruthenium phosphine complex [39] was previously prepared. In order to do this, we used toluene, because triphenylphosphine and Ru(methylallyl)$_2$(cod) are not miscible. Finally, for reaction 11, IL, triphenylphosphine and [Ru(cod)Cl$_2$]$_n$ were added to the reactor, without pretreatment.

We start by analyzing the results obtained by GC. These show that there was no formation of methane, only H$_2$ and CO$_2$ were detected. The following analysis was done with HS-GC. For reaction 9, we can observe two peaks, one peak at 6.45 minutes and another at 9.53 minutes (Annex 5). The results do not allow us to conclude if other potential compounds, such as methanol, were present in the sample, so we did an analysis of NMR.

We start by analyzing the proton NMR spectrum (Figure 3.6). To facilitate the interpretation a letter was assigned to each proton.
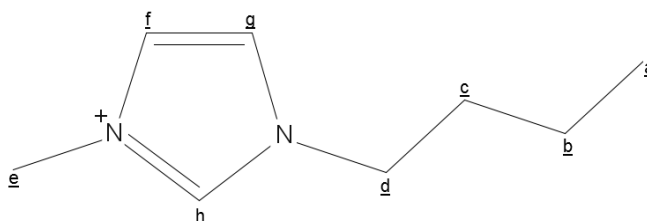

Figure 3.5 – Molecular structure of [bmim]$^+$.

The sign at 0.9 is a triplet, so we can say that this corresponds to the <u>a</u> proton. The next peak, with an area of 2.17 is a sextet, therefore corresponds to the proton <u>b</u>, the quintet, also with two protons, so with an area approximately equal to 2 (2.24) corresponds to the <u>c</u>. The peak at 4 ppm corresponds to proton <u>d</u>. To complete the analysis of aliphatic protons, we can see that the peak to 1.65 ppm corresponds to <u>e</u>. Between 5 and 10 we can see the peaks corresponding to the protons of the aromatic ring. To 8.80 ppm have the <u>h</u> peak, peak <u>f</u> and <u>g</u> are very close and are located between 7.20 and 7.30. With this analysis we can conclude that the Ionic Liquid when subjected to certain conditions, did not suffer any changes in its structure.

However, there are still two peaks that were not analyzed, one at 3.92 and another at 1.65. Among the possible reaction products, we can say that the peak to 1.65 is water that formed in the reaction. However, nothing we can conclude on another peak because methanol would be expected to

3.49 [42], let's analyze this sample carbon spectrum (Annex 6), to try to understand whether it is methanol or not. In this spectrum, we can see the eight peaks of carbon that would be expected, are peaks of [bmim]+ and still a large peak at approximately 77, which corresponds to chloroform. Regarding the methanol, it was expected at 50.04, however, this peak is also observed for the ionic liquid, thus, we cannot conclude whether or not there was formation of methanol.

Analyzing the spectrum obtained in HS-GC for the Ionic Liquid after reaction 10 (Annex 7), we can see that there are 3 peaks. The highest peak, to 6.44 minutes is mostly toluene, but only, because the previous reaction also gets a peak in that area and no toluene was added. This represents 79.37% of the sample. There is another peak in common to both reactions, at 9.53 minutes. This peak is possibly methanol, but it is not yet possible to say with any certainty, so we went to the NMR analysis. Comparing the proton spectrum of reactions 9 and 10 (Figure 3.7), we can see that the peaks in common are Ionic Liquid, once again, the liquid is not decomposed under the conditions of the reaction. We can also see a few more peaks: at 3.4 ppm should be methanol, toluene at 2.36 ppm. Analyzing the carbon spectrum of reaction 10 (Annex 8), we can see the peaks of toluene and Ionic Liquid. If you increase the zoom, we can see that there is a small peak at 50, but as we have a large peak for the IL in this area, we cannot say that it is methanol.

With respect to reaction 11, comparing the proton spectrum of this reaction and reaction 9 (Figure 3.8), we see that the peaks of the ionic liquid are maintained. There are other two peaks, one can be methanol (3.25 ppm) and an unknown peak at 2.2 ppm. Analyzing the carbon spectrum (Annex 10), we see the peaks corresponding to the Ionic Liquid and to chloroform, once again we can not confirm that there was formation of methanol.
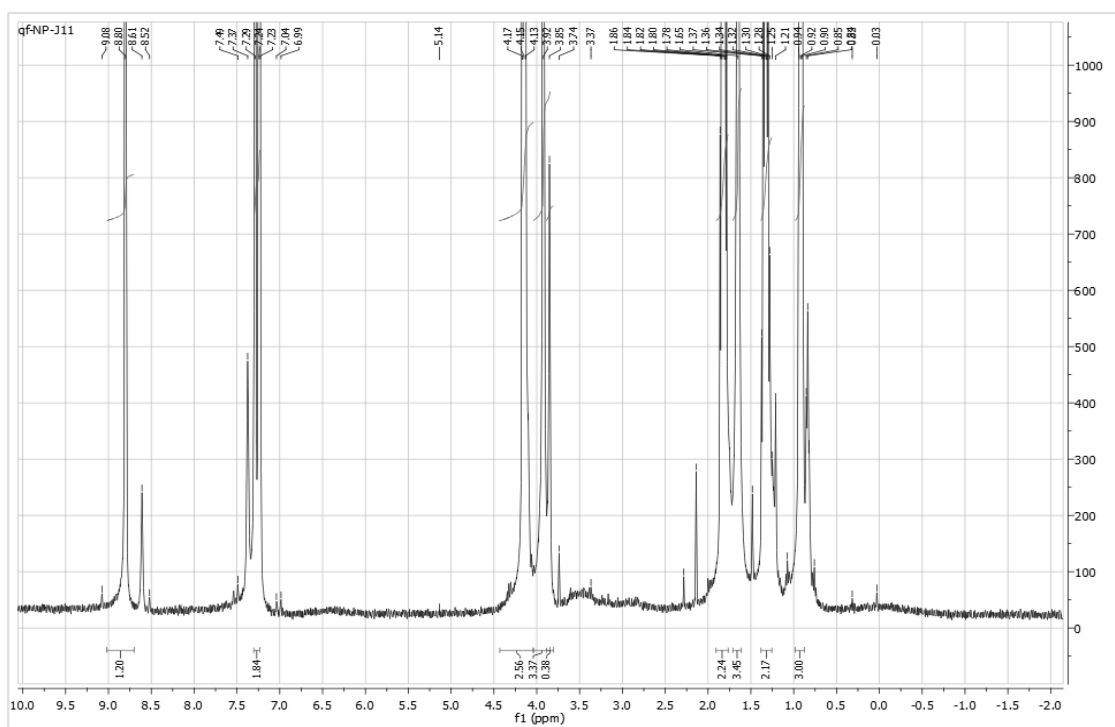

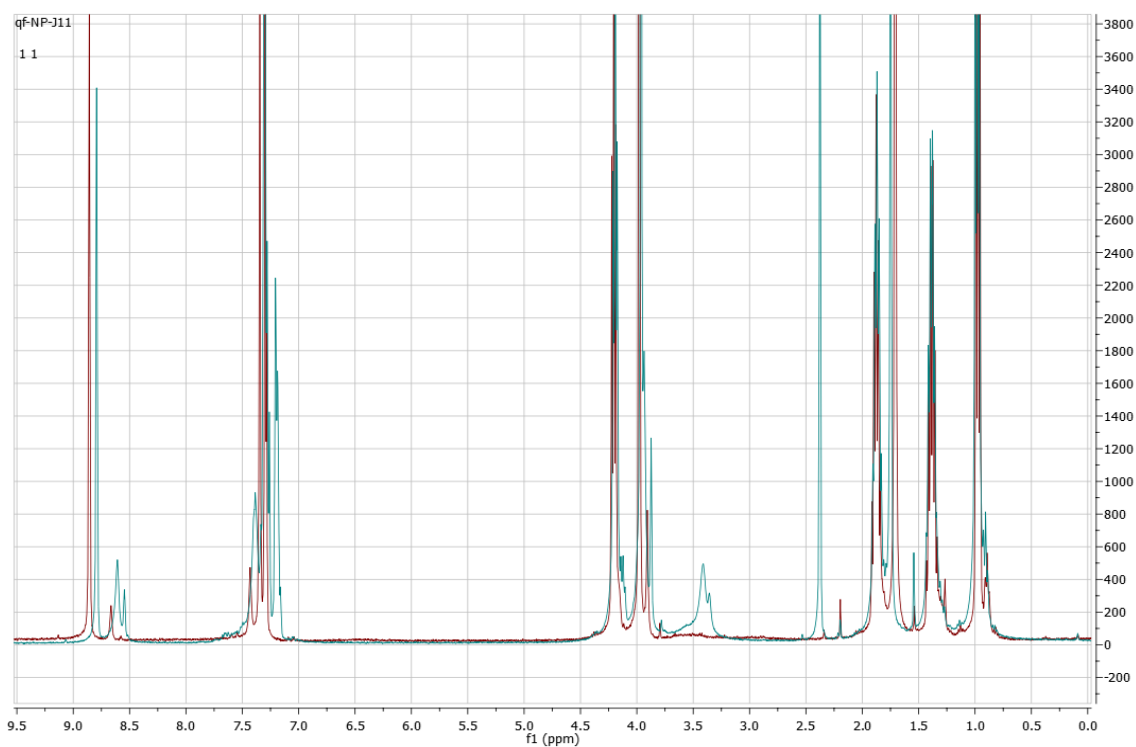**Figure 3.6 –** Proton NMR spectrum, reaction 9.

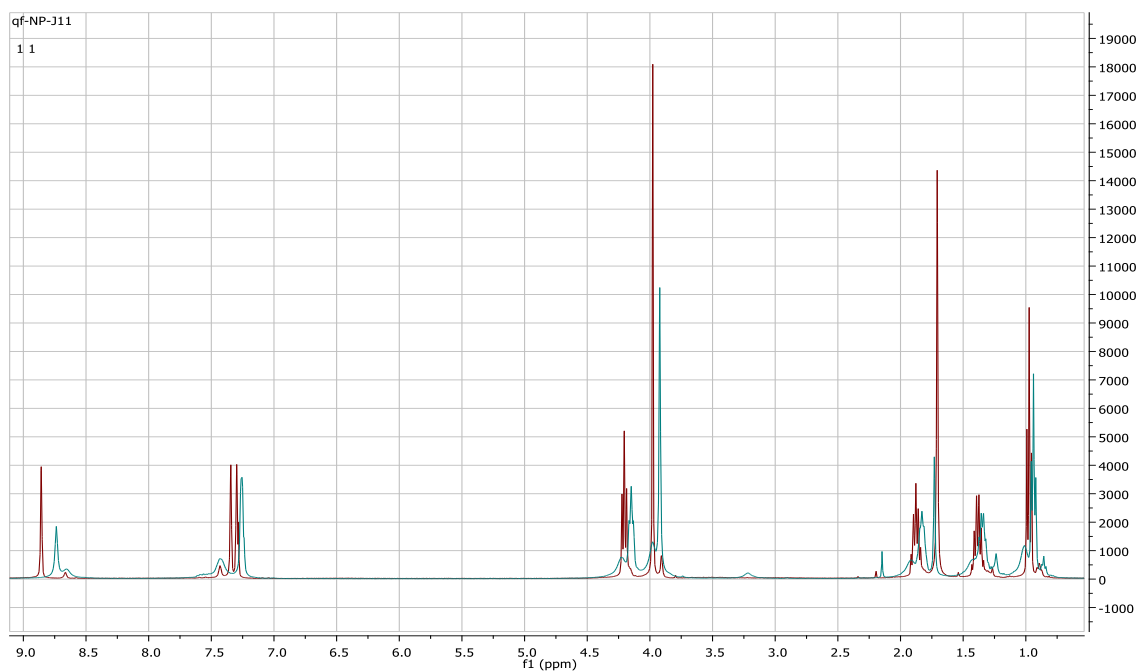**Figure 3.7 –** Proton NMR spectrum, reaction 9 (red) and 10 (blue).

Figure 3.8 – Proton NMR spectrum, reaction 9 (red) and 11 (blue).

4. Conclusions

In the first part of this work, we established that two materials, carbon fabric and a gold-platinum alloy are potentially interesting cathode constituents for carbon dioxide electrochemical reduction. Cyclical voltammetry at high pressures was proven to be a good technique for exploratory work in this area.

As to direct hydrogenation of CO_2, heterogeneous catalysis with palladium, rhodium and ruthenium was carried out in an atmosphere of supercritical carbon dioxide and hydrogen, in a ratio of 3:1. Reactions were performed at low temperature, 140°C, at high pressure, 80 bar, during different periods of time.

Of all catalysts tested, the most active is ruthenium, followed by palladium. The yields of the reactions were 3.30% and 0.81%, respectively. For rhodium, there was no production of methane, therefore it can be said that the catalyst does not have activity under the reaction conditions.

In the reactions carried out with the impregnated catalyst, there was no production of methane because the catalyst clogs pores, creating a barrier to the mass transfer. The increased reaction time does not cause the barrier to break. Reactions were performed in batch, which means that CO_2 was not available to react to all; it would be possible to increase the yield of the reaction if we had a thin layer of ionic liquid by the catalyst and a continuous flow of carbon dioxide was passing, so that the whole was available to react.

We have also homogeneous transition-metal catalyst systems based on a single ruthenium phosphine complex, with the objective of producing methanol. In relation to these catalysts we cannot reach definite conclusions about their activity for methanol production, since in all the reactions we may have reached the desired product, but the analysis results are not conclusive. It would be necessary to perform other tests, as well as use different ionic liquids.

The NMR Spectra allow us to still check that there is no Ionic Liquid deteriorate under the conditions of the reaction.

5. References

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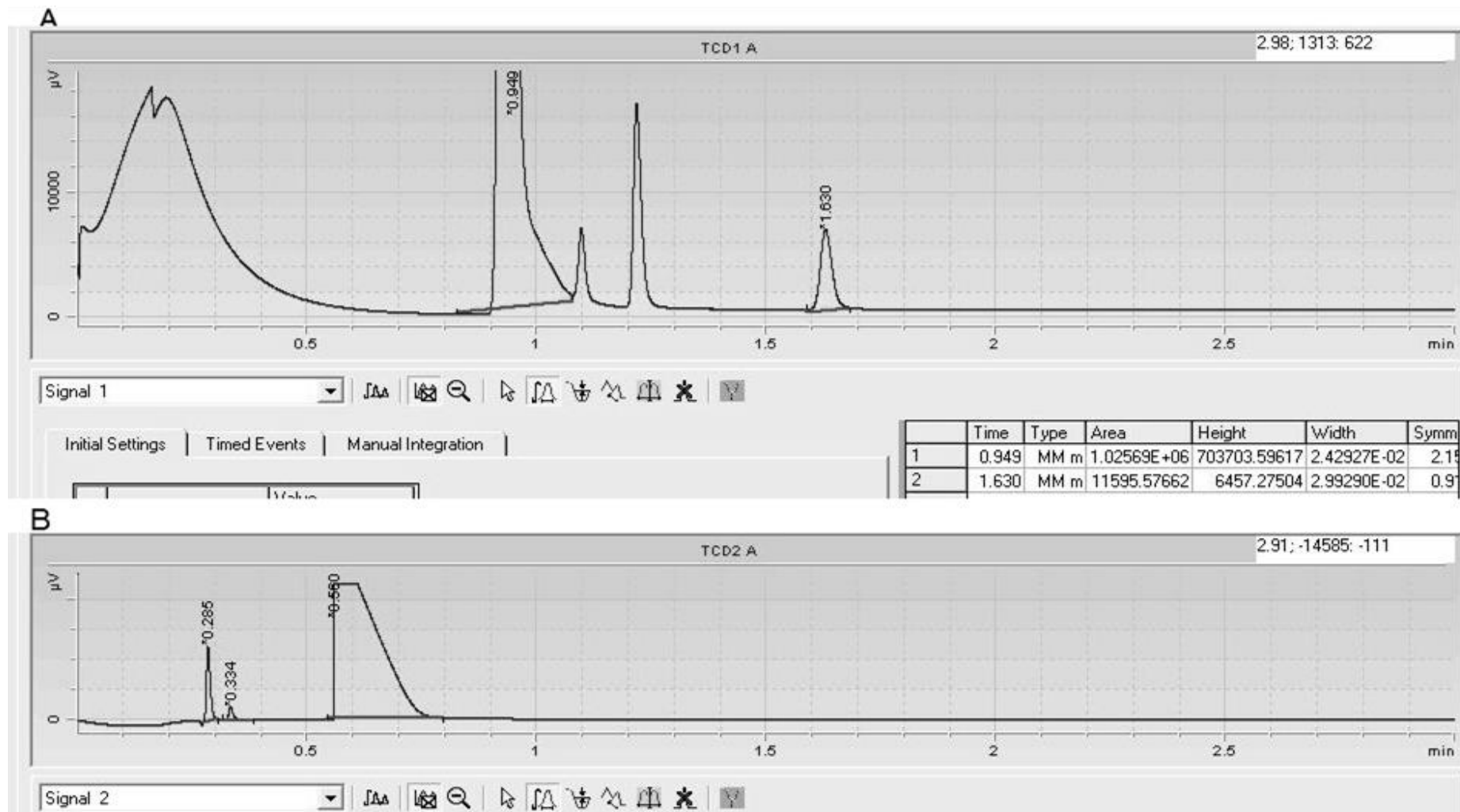
6. Annex

Annex 1

Figure 6.1 – GC Spectra of the reaction 2. A: Signal 1 – rt=0,949 H_2 ; rt=1,630 CH_4; B: Signal 2 – rt=0,550 CO_2.
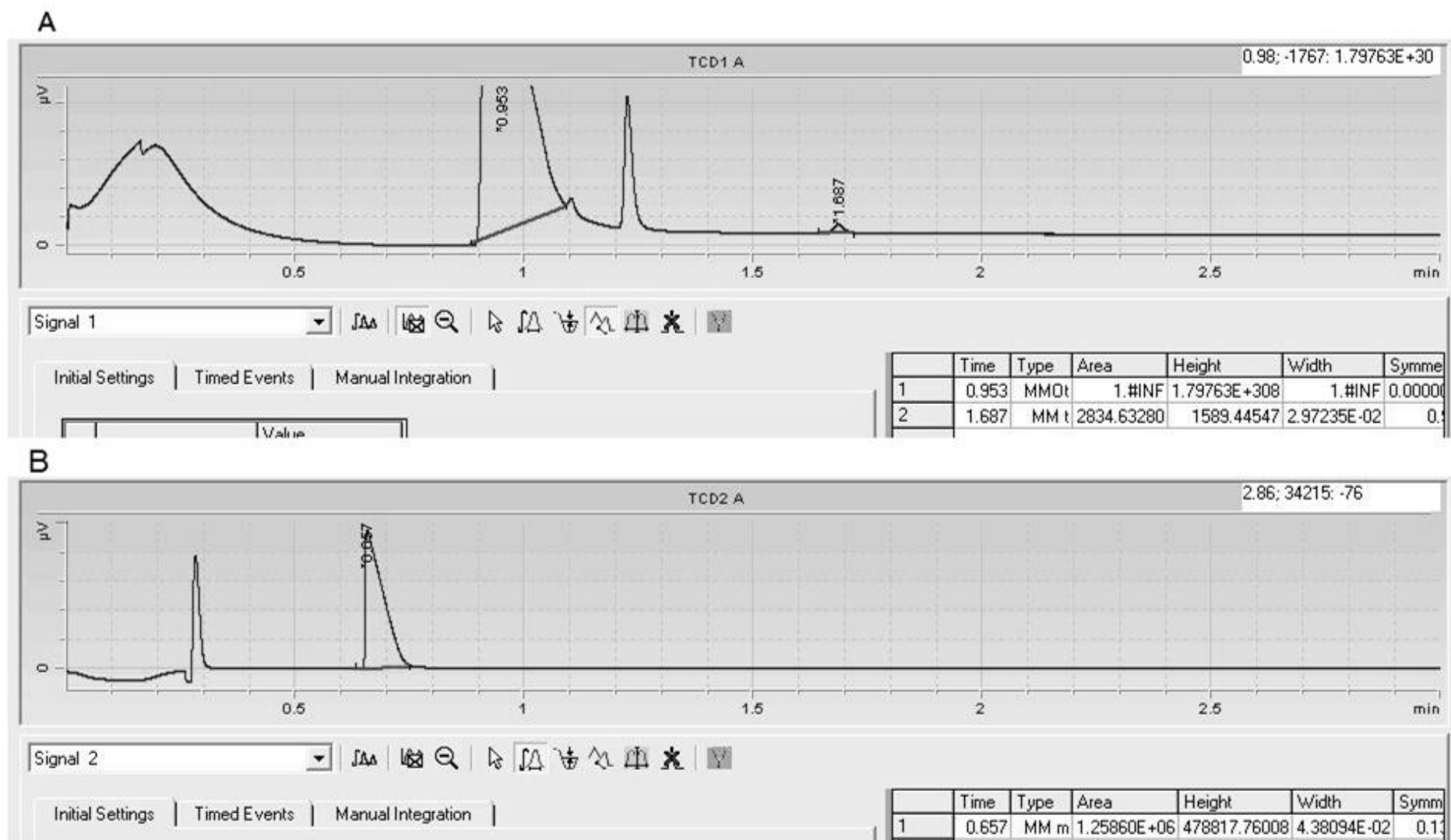
Annex 2

Figure 6.2 – GC Spectra of the reaction 3. A: Signal 1 – rt=0,953 H_2 ; rt=1,687 CH_4; B: Signal 2 – rt=0,657 CO_2.
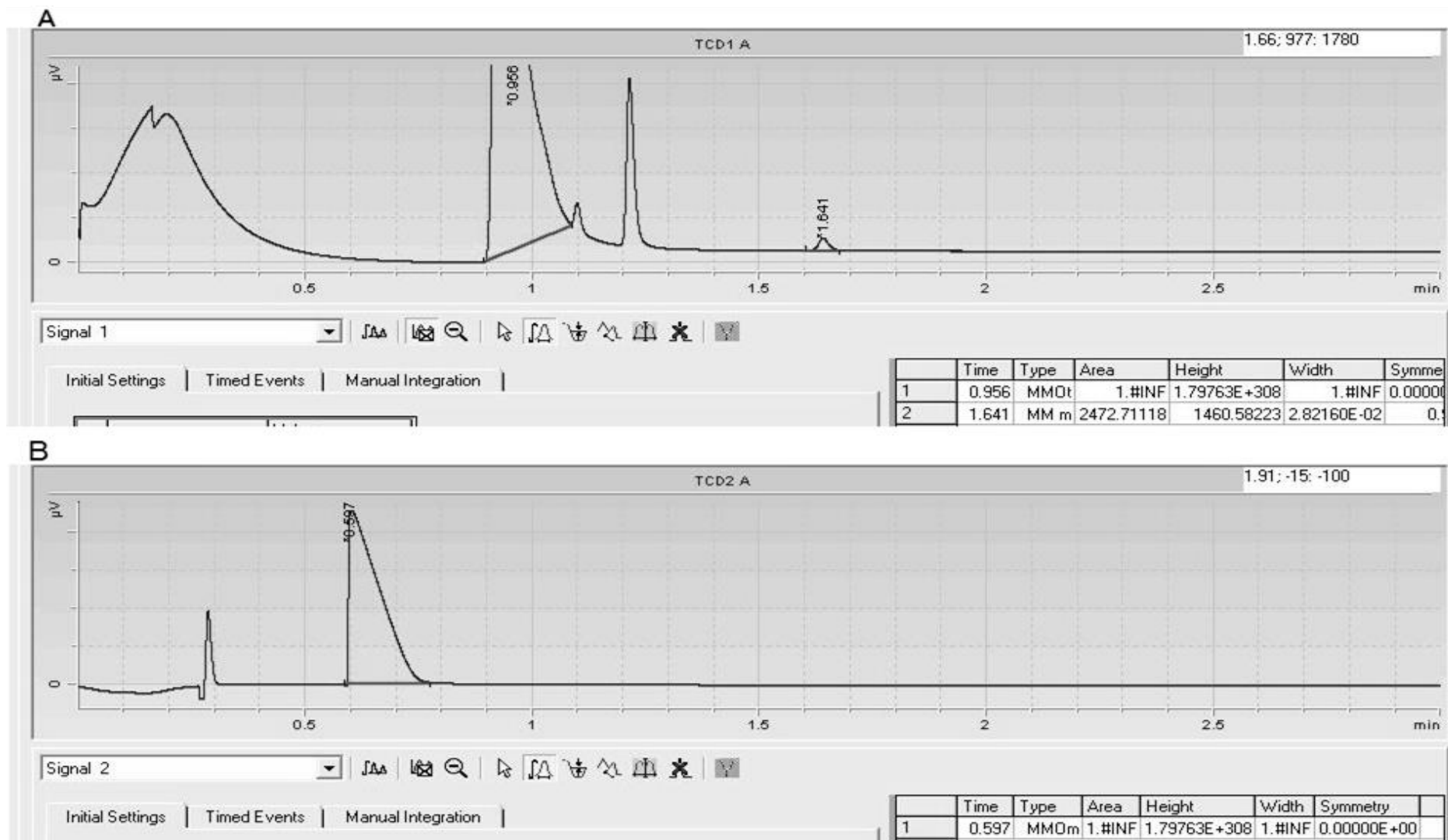
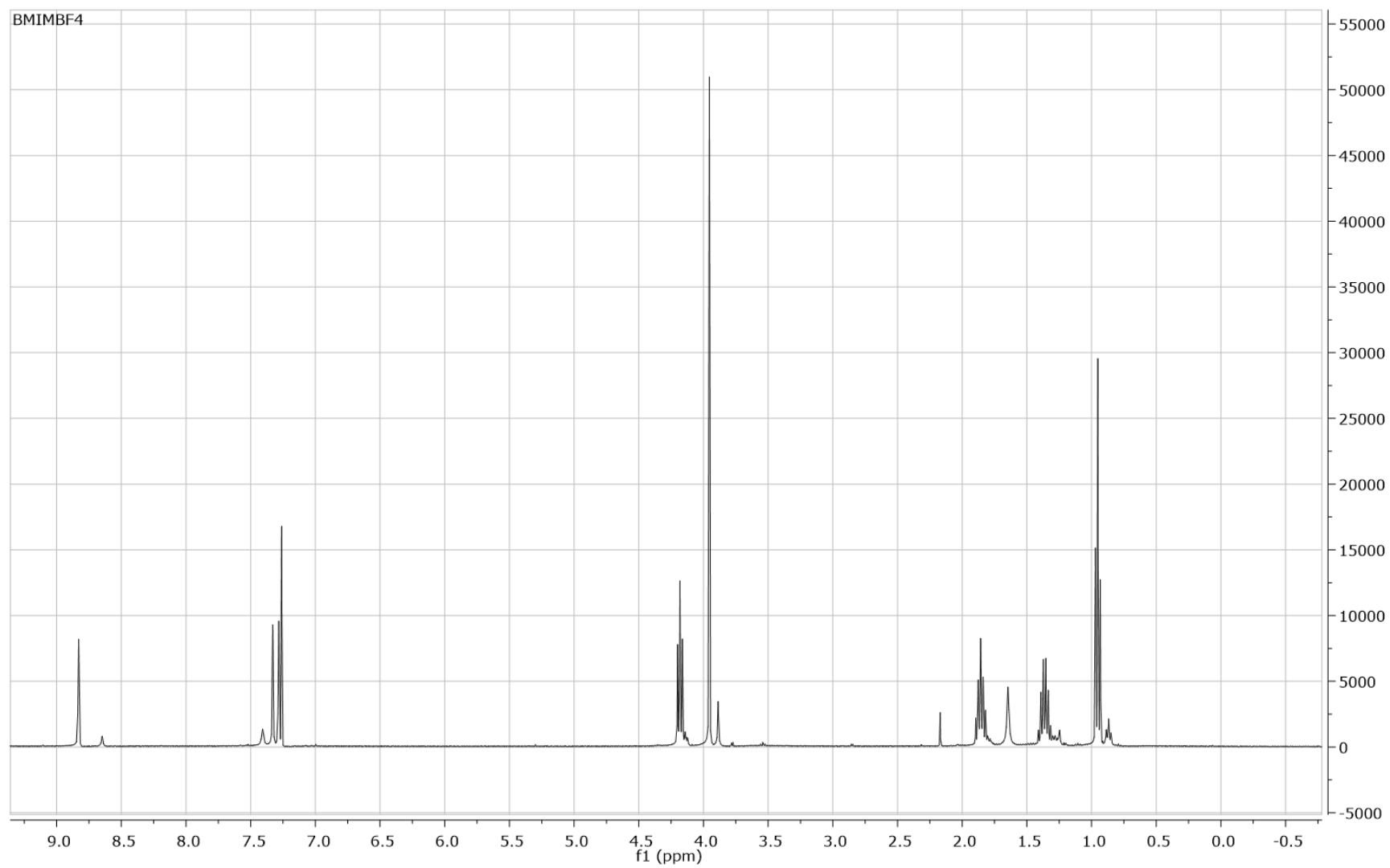**Figure 6.3 –** GC Spectra of the reaction 8. A: Signal 1 – rt=0,956 H_2 ; rt=1,641 CH_4; B: Signal 2 – rt=0,597 CO_2.

Annex 4

Figure 6.4 – Proton NMR spectrum, [bmim][BF$_4$].

Annex 5
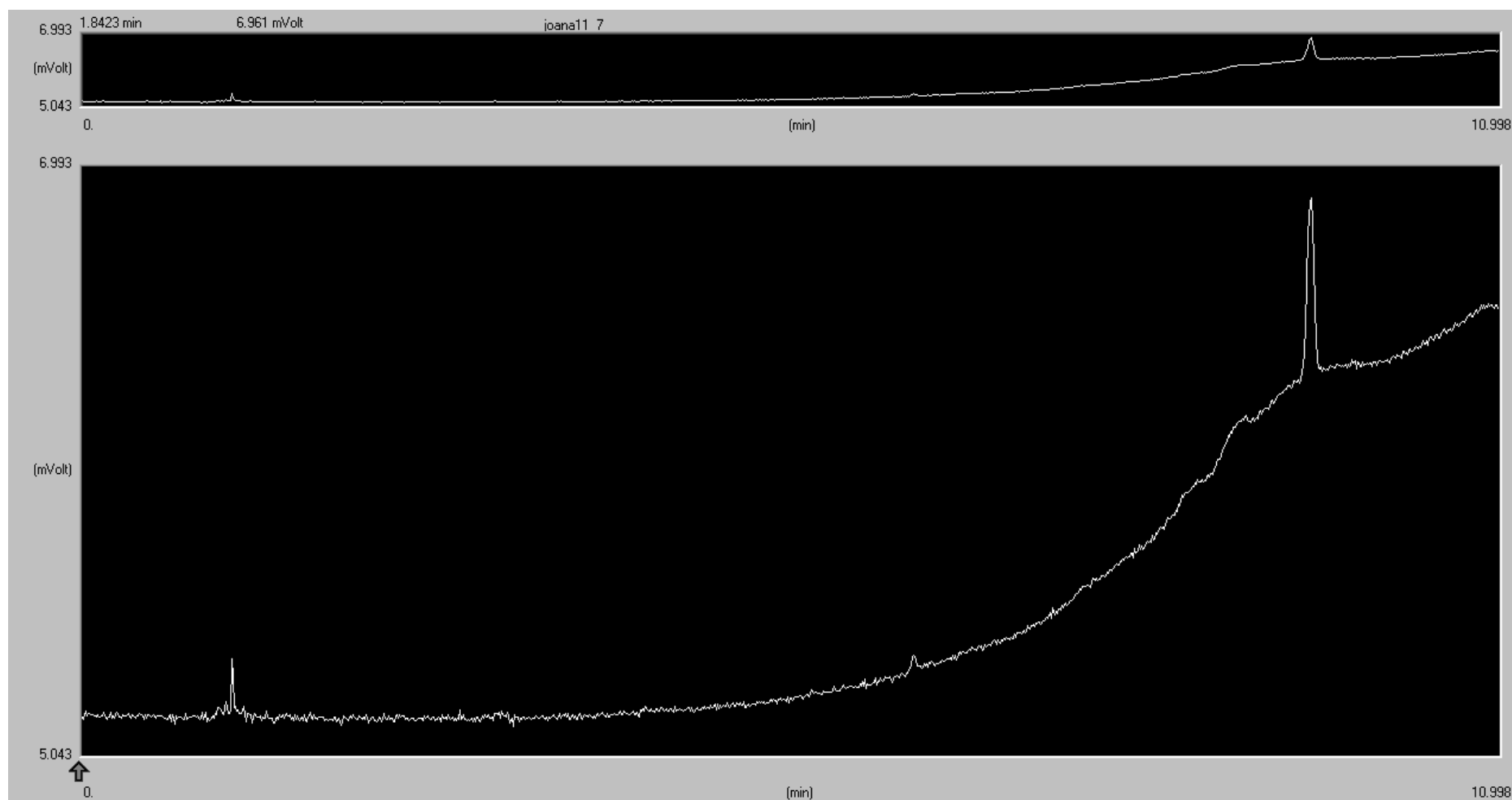
Figure 6.5 – HS-GC spectrum, reaction 9.

Annex 6
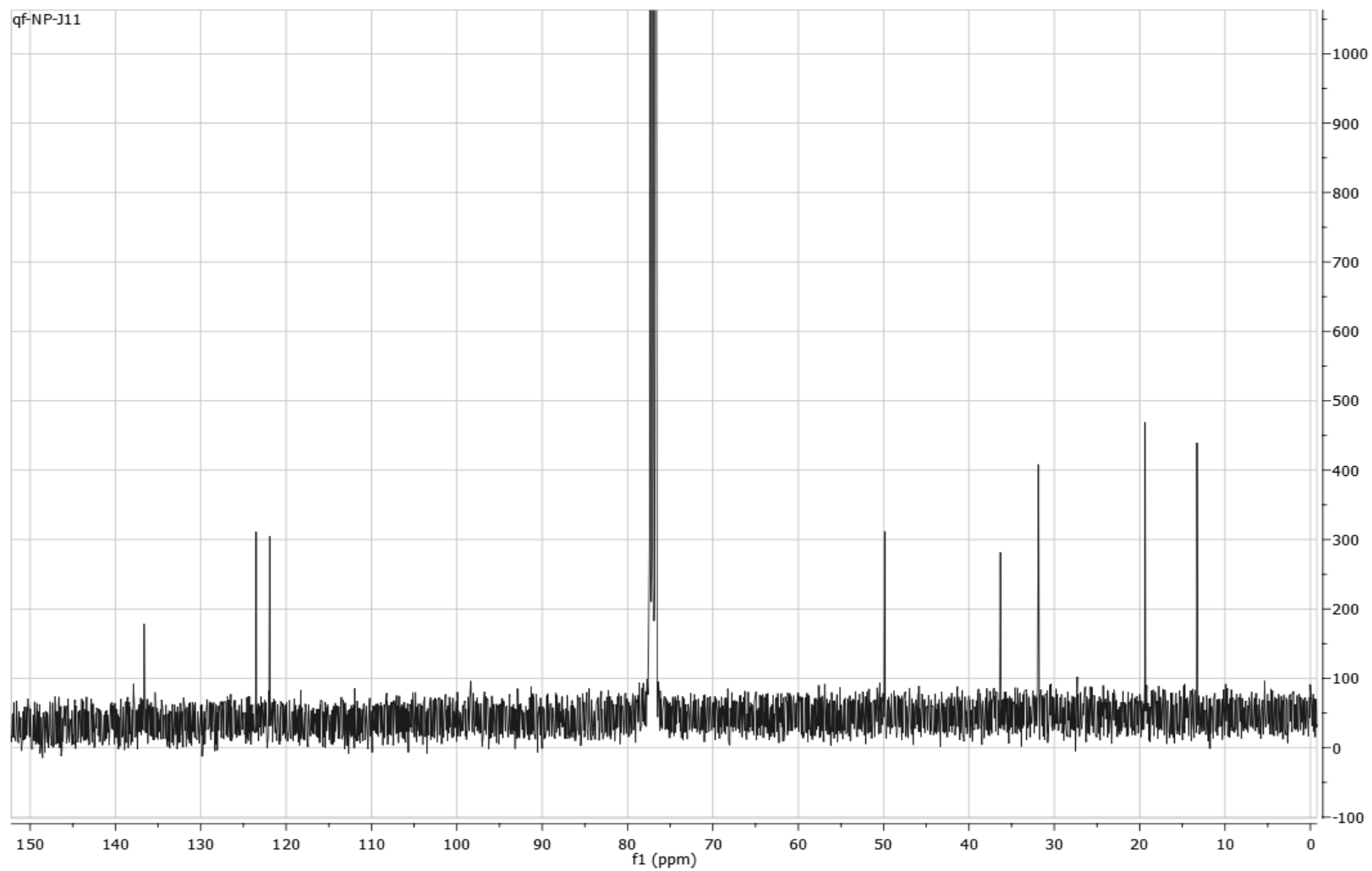
Figure 6.6 – Carbon NMR spectrum, reaction 9.

Annex 7
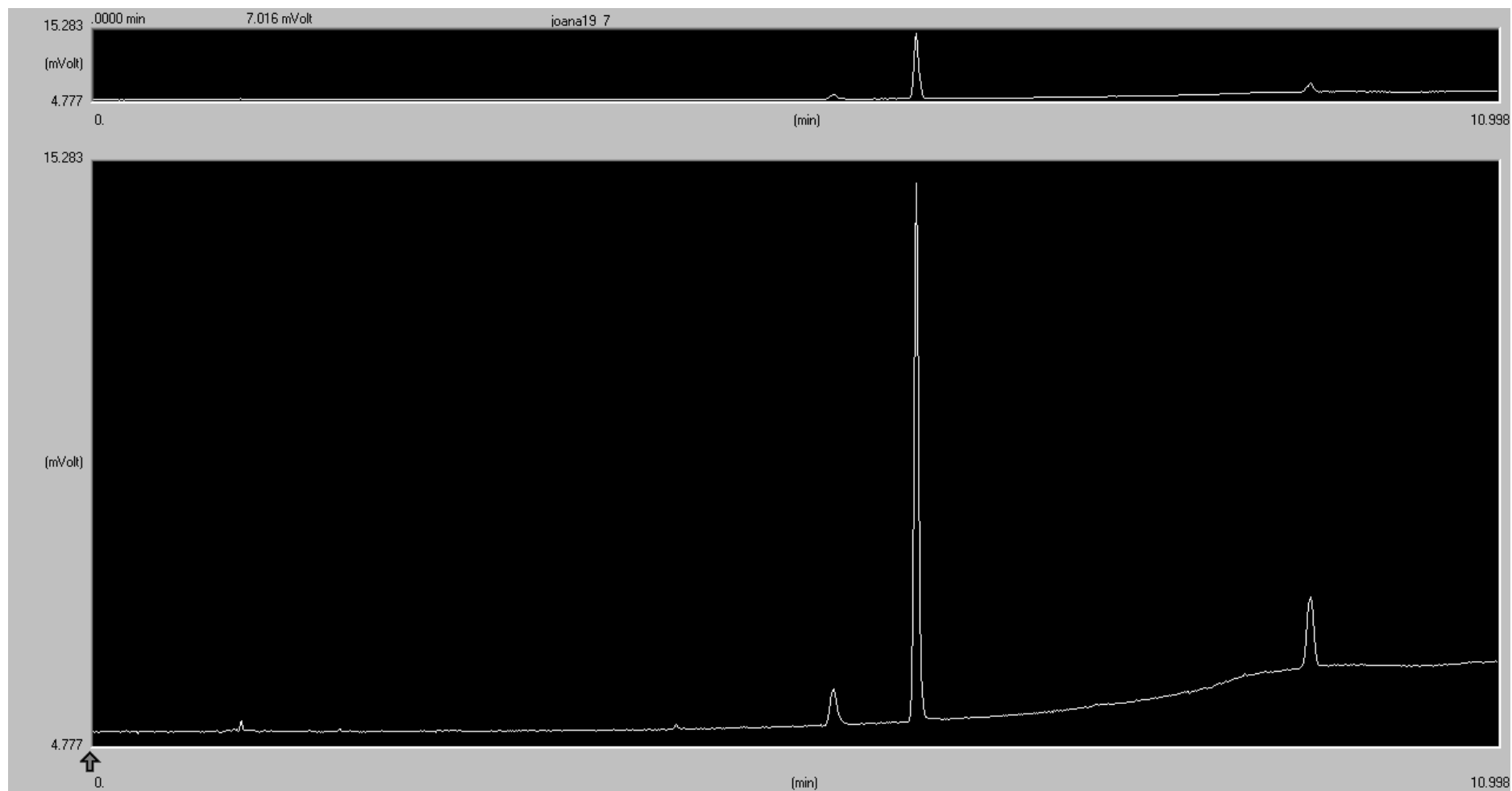
Figure 6.7 – HS-GC spectrum, reaction 10.

qf-NP-J19
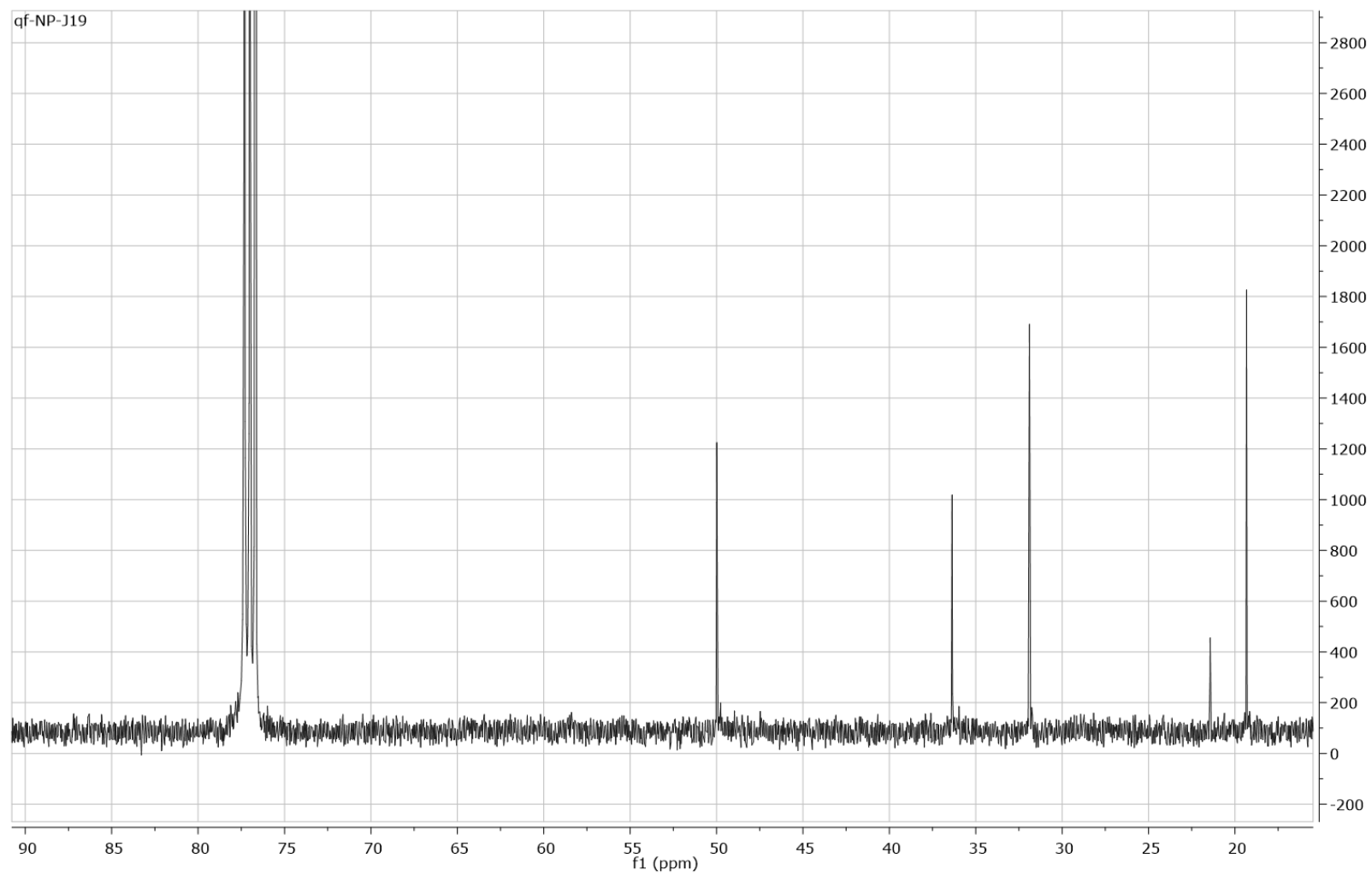
Figure 6.8 – Carbon NMR spectrum, reaction 10.

Annex 9
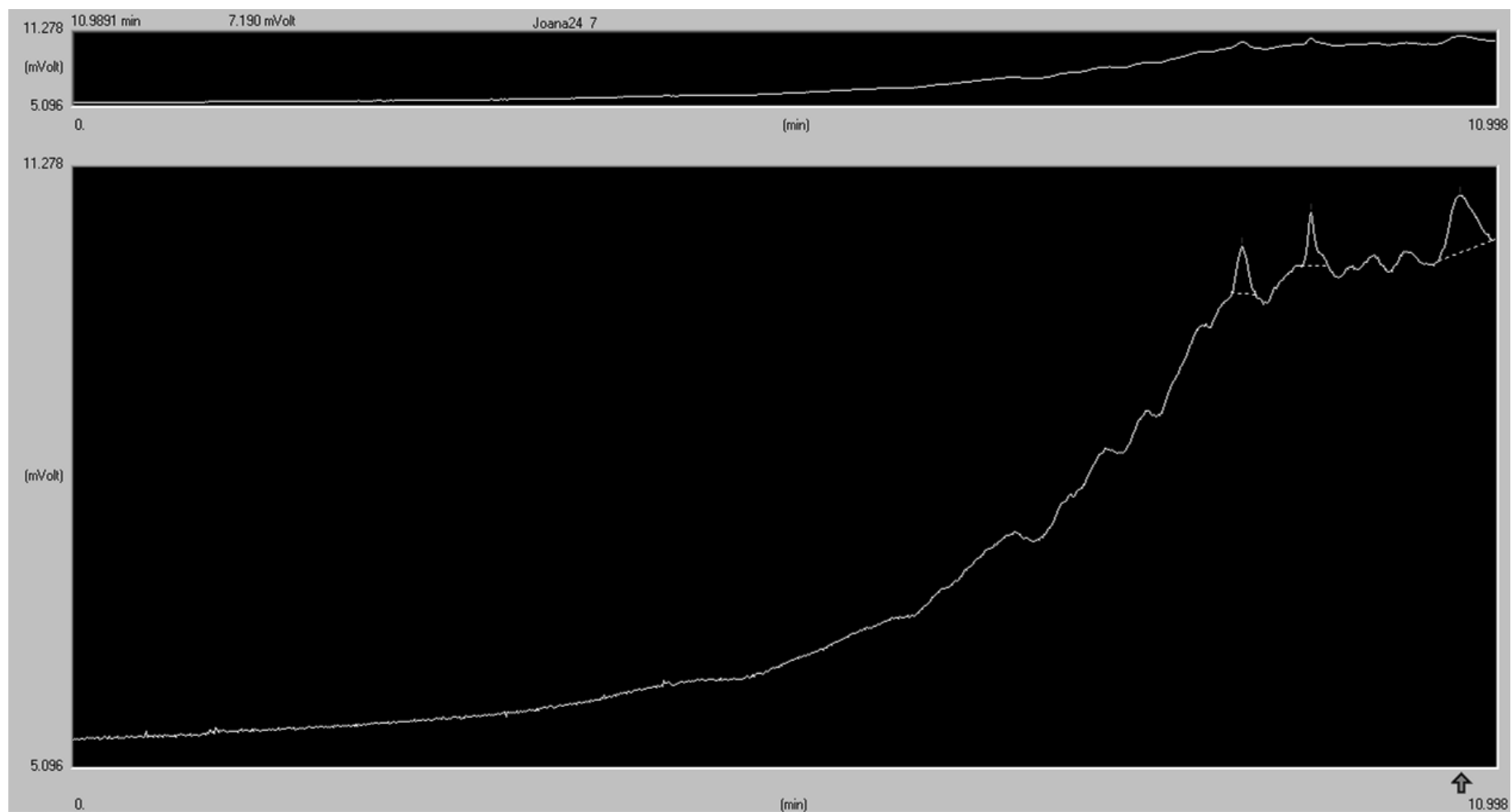
Figure 6.9 – HS-GC spectrum, reaction 11.

Annex 10
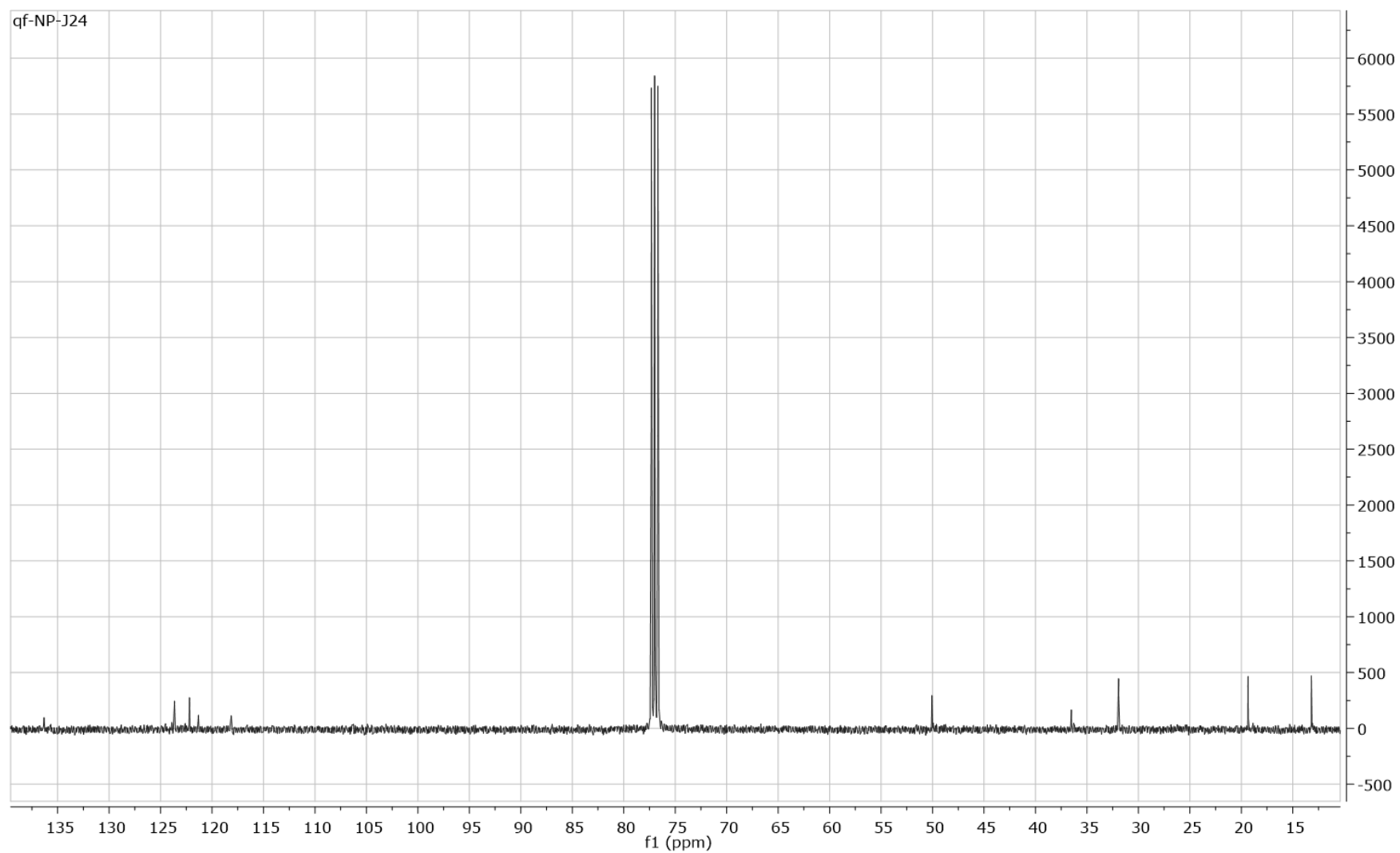
Figure 6.10 – Carbon NMR spectrum, reaction 11.

Annex 11

Figure 6.11 – Certified calibration of a mixture of hydrocarbons.