CO_2 valorization as a raw material for the chemistry industry or other ones: Analysis of opportunities in Portugal considering our industry

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December 2022

Abstract

Climate change caused by the emission of greenhouse gases of anthropogenic origin, such as CO_2, is a concern that has been promoting a collective effort at an international level to reduce the environmental impact of human activities. An option under study for the decarbonization of the industry is the recycling of carbon from CO_2, i.e., the Capture and Use of CO_2. In this way, CO_2 will no longer be considered a waste, becoming a raw material.

In this dissertation, a survey was made of the ways of recovering CO_2 that can be implemented in Portuguese industry. To this end, the main industrial installations that emit CO_2 at national level were identified and the potential users of the captured CO_2 were studied to convert it into economically attractive products. Both CO_2 sources and possible consumers were located using the QGIS software and the possible relationships between them were studied, considering the distances that separate them and the means of transport accessible on site.

It was found that the largest sources of CO_2 emissions in Portugal at the Industry level correspond to Oil Refining, Electric and Thermal Energy Production and Cement Production facilities. In this way, the possible CO_2 users around these installations were studied in greater detail.

Keywords: CCU in Portugal, Main fixed sources of CO_2 in Portugal, CO_2 Emitters, CO_2 Capture, Potential users of captured CO_2, Valuable CO_2-based products.

1. Introduction

1.1. GHGs and Climate Change

Climate change caused by human habits and activities is a concern that has been promoting a collective effort at international level to reduce the environmental impact of different activities and an increase in demand for a more sustainable planet.

It is estimated that the planet has warmed approximately 1°C in relation to pre-industrial levels and this increase could reach 2°C in the coming years if no measures are taken to mitigate the environmental impacts of human activity.

1.1.1. Portugal's Commitment and the ETS*

In 2016, at the Conference of the Parties to the United Nations Framework Convention on Climate Change, Portugal assumed the objective of achieving Carbon Neutrality until 2050 to help limit global warming to 1.5°C compared to the pre-industrial period.

To achieve carbon neutrality in 2050, as provided for in *Roteiro para a Neutralidade Carbónica 2050 (RNC 2050)*, the target for reducing GHG emissions in Portugal was set by between 85% and 90% by 2050, with an emission reduction of between 45% and 55% by 2030 and between 65% and 75% by 2040 compared to 2005 (Resolução do Conselho de Ministros n.º 107/2019).

To mitigate climate change, the reduction of GHGs in the atmosphere is being studied, reducing its emissions and increasing carbon capture in the form of CO_2.

In view of this objective of mitigating climate change, monitoring of GHG emissions is essential, being the Agência Portuguesa do Ambiente (APA) the responsible for regulating greenhouse gas emissions under the Emissions Trading Sistem (ETS). Operators of installations that carry out the activities covered by the ETS shall be enabled by *Títulos de emissão de GEE (TEGEE)*, in which the installation's activities and emissions are described.

1.2. Fossil fuels and CO_2 emissions in Portugal

According to the National Inventory Report 2022 - Portugal, for the year 2020, carbon dioxide is the gas with the highest weight in total GHG, representing about 73% of total national emissions (APA, 2022c). This event is partly due to the predominance of the use of fossil fuels, however, their dependence is still high. In 2019, fossil fuel consumption accounted for 76% of primary energy consumption in Portugal (43% oil, 24% natural gas and 6% coal) (IEA, 2021). Fossil fuels support the means of transport and various industrial sectors.

Carbon dioxide emissions by sector in 2020 are shown in Figure 1.

* *CELE - Comércio Europeu de Licenças de Emissão* in Portugal

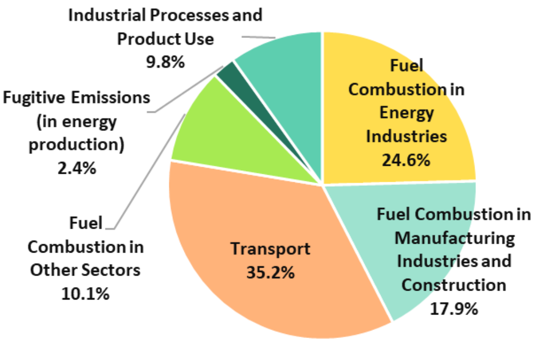

Figure 1 - Contributions from sectors to CO_2 emissions in 2020 in Portugal (graph built based on data consulted in APA, 2022d).

CO_2 emissions in Portugal result mainly from the Transports and from the Fuel Combustion in the Energy Industry, in the Manufacturing and Construction industry and in other sectors (which include the Commercial/Institutional, Residential and Agriculture/Forestry/Fishing sectors). The following is the Industry of Processes and Product Use. If we add CO_2 emissions from all industry sectors, they make up about 52% of total CO_2 emissions at national level in 2020, year in which around 22 Mt of CO_2 were emitted by industrial facilities. These values highlight the importance of looking for solutions to reduce CO_2 emissions at fixed installations, such as Carbon Capture, Utilization and Storage. In this dissertation is not studied storage, but rather the possibility of capturing CO_2 formed in the Portuguese industrial context and subsequent use as raw material in the production of economically attractive products, in order to avoid its release into the atmosphere. Carbon capture and use has the advantage of reducing GHG emissions and also prevents the depletion of fossil fuels. This process comprises the stages of capturing CO_2, compression, transport to the consumer industry and utilization.

2. Carbon Dioxide Capture and Transport

2.1. CO_2 capture systems and techniques

There are four CO_2 capture systems, being these the capture from industrial process streams, post-combustion capture, oxy-fuel combustion capture and pre-combustion capture.

2.1.1. Capture from industrial process streams

There are various industrial applications involving process streams from which it is possible to capture CO_2 in large quantity. The CO_2 capture of industrial process currents is applied in the purification of natural gas and in the production of synthesis gas. The techniques used to capture CO_2 in these cases are mostly similar to those used in the capture of pre-combustion, including the use of chemical solvents, physical solvents and membranes. There are also other industries that have process streams that are a source of CO_2, including cement and steel production and fermentation processes for food and beverage production. CO_2 can be captured from these currents using techniques common to post-combustion capture, oxy-fuel combustion capture and pre-combustion capture.

2.1.2. Post-combustion capture

CO_2 emissions from fixed sources result mainly from the fuels combustion in power plants for energy production, in mineral industry kilns, including cement production and ceramic pieces, and in furnaces in the metallurgical industry. In these processes, combustion with air is the most used technology because it is economically more viable. In this way, the capture of CO_2 from the combustion gas, i.e. post-combustion capture, is of greater relevance and importance. In this case, the combustion gas, instead of being released into the atmosphere, passes through equipment that sequesters and recovers most of the CO_2. There are several technologies for post-combustion capture, such as chemical absorption, adsorption and the use of membranes. However, CO_2 is separated from the combustion gas mostly by chemical absorbers, as these offer high efficiency and capture selectivity, lower energy consumption and lower cost when compared to other existing post-combustion capture processes. This technique is, therefore, the one that presents a higher level of development (IPCC, 2005).

2.1.3. Oxy-fuel combustion capture

In the oxy-fuel combustion capture system, combustion is carried out by approximately pure oxygen instead of air, resulting in a flue gas consisting mostly of CO_2 and H_2O. When combusting fuel with pure oxygen, the flame temperature is excessively high, but part of the CO_2 and/or H_2O rich combustion gases can be recycled to the combustor to moderate this temperature increase. In this way, combustion occurs in the presence of O_2 in high concentrations, more than 95% by volume and about 70% to 80% of the combustion gases formed and which are recycled to the boiler (Sardinha, 2010). After cooling the combustion gas to condense the water vapor, it contains about 80% to 98% CO_2. Since N_2 is removed from the air before combustion, NO_x is formed mainly due to fuel composition, however, it is formed in a smaller amount than in a normal combustion process (IPCC, 2005).
Oxy-fuel combustion thereby has the advantages of the combustion gases formed being mainly CO_2 and H_2O, which are easily separated, and also the advantage that higher combustion temperatures allow greater heat transfer and consequently smaller boilers. However, it has disadvantages, such as the high costs of producing pure oxygen, the need to convert existing boilers to the new burning conditions, the need to prevent air from entering the boiler and the need for boiler material to withstand high temperatures and corrosive conditions in the environment.

2.1.4. Pre-combustion capture

The pre-combustion capture process comprises a first reaction from which a mixture of H_2 and CO is formed. In this first step, synthesis gas composed of H_2 and CO can be obtained by two distinct routes: by making the primary fuel react with water vapor, in a process called Steam Reforming, or oxygen, in a process called Partial Oxidation (when applied to gaseous or liquid fuels) or Gasification (when applied to solid fuels) (IPCC, 2005).
Steam Reforming and Partial Oxidation/Gasification reactions correspond to Equations 1 and 2, respectively.

$$C_xH_y + xH_2O \leftrightarrow xCO + \left(x + \frac{y}{2}\right)H_2 \quad \Delta H + ve \qquad (1)$$

$$C_xH_y + \frac{x}{2}O_2 \leftrightarrow xCO + \frac{y}{2}H_2 \quad \Delta H - ve \qquad (2)$$

The gas resulting from the previous reactions is cooled in a boiler, in which the steam necessary for the reactions is generated. This is followed by the conversion of CO into CO_2 by the addition of steam in an exothermic reaction called the Water Gas Shift Reaction, given by Equation 3 (IPCC, 2005).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41\,kJ\,mol^{-1} \qquad (3)$$

Finally, CO_2 is removed and recovered from the CO_2 and H_2 mixture obtained, usually by a physical or chemical absorption process. In the separation step, the CO_2 content can be included in the value range of 15-60% (dry base) and the total pressure is typically between 2 and 7 MPa (IPCC, 2005). An advantage of this technology is the production of pure H_2, which can be used as fuel. However, pre-combustion capture technology has the great disadvantage of being mostly applicable to new installations, given the requirement of very specific equipment which makes it impossible to adapt to existing industrial units.

2.2. Transport of CO_2

After capturing CO_2 from the emitting sources, it is transported to locations for export or to industrial units where it can be used as raw material. CO_2 can be transported as solid, gas, liquid or supercritical fluid (EEA, 2011). The transport of CO_2 can be carried out by pipelines, ship, tank truck or tank train. The choice depends on the transport distance, the quantity to be transported and the geographical conditions and characteristics. For large distances and quantities, the pipeline is the solution adopted, allowing these to transport gas by land, sea, mountains and icy areas. On the other hand, maritime transport is typically used in smaller scale projects or when CO_2 is destined for a location far from the coast and in this case, ship transport may be preferable because it is cheaper (IPCC, 2005). The means of transport are identical to those responsible for transporting natural gas and must be carbon steel based to prevent corrosion in the presence of CO_2 (Sardinha, 2010). In addition, for transport in pipelines it may be necessary to dehydrate CO_2 and remove the H_2S in order to avoid corrosion (Sardinha, 2010).
Gas transported at a pressure close to atmospheric pressure occupies a lot of volume, requiring large installations. To reduce volume, CO_2 can be compressed, liquefied or solidified. Liquefied is suitable for transport by ship or in a tank (by truck and train), as is done with liquefied natural gas and liquefied petroleum gas. In this case, it is necessary to maintain pressure, cooling and thermal insulation in order to ensure that CO_2 remains only in the liquid state (Oliveira, 2016). Solidification requires much more energy than other options and transporting CO_2 in solid state is more complex in terms of safety rules. On the other hand, in pipeline transport, CO_2 is transported in the form of compressed gas (IPCC, 2005). After captured, CO_2 can be compressed up to about 150 bar, being the most common transport pressure between 10 and 80 bar (IPCC, 2005).

3. Capture and use of CO_2 in Portuguese industry

3.1. Sources of CO_2

In this work, emissions related to the industry sector are studied, not being considered the emissions related to transport, fugitive emissions, forest fires and the Residential, Commercial/Institutional and Agriculture/Forestry/Fishing sectors.
According to the 2022 APA´s data for the emissions referring to the year 2020 (APA, 2022d), CO_2 emissions in Portugal in relation to industry result mainly from the combustion of fuels in the energy industry and in the manufacturing industries and construction, corresponding to 47.0% and 34.2% of total CO_2 emissions at national industry level in 2020, respectively. Thus, fuel combustion in industry accounts for approximately 81.2% of CO_2 emissions from industrial sources. The remaining 18.8% of emissions correspond to the Industrial Processes and Product Use. The weights of the different activities of the Fuel Combustion sector in the Energy Industry are detailed in Figure 2.

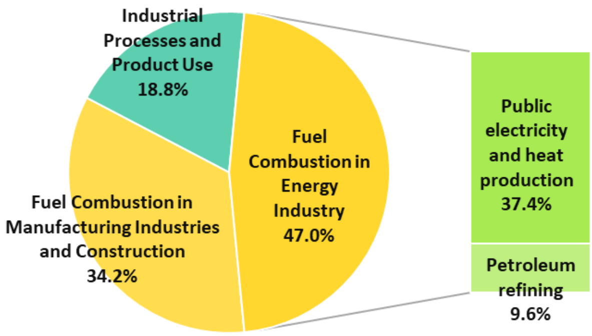

Figure 2 - Detailed distribution of the weight of the different activities responsible for fuel combustion in Energy Industry in 2020 (graph built based on data consulted in APA, 2022d).

On the other hand, the weights of the different activities of the Fuel Combustion sector in the Manufacturing Industries and Construction are detailed in Figure 3.

In the Industrial Process and Product Use, the Mineral Industry stands out with the greatest weight in CO_2 emissions by this sector, with most emissions due to cement production. Thus, the production of cement, that is, the clinker production in high-capacity furnaces, corresponds to the activity in the field of Industrial Processes and Product Use with higher weight in CO_2 emissions to the atmosphere in Portugal. The weight of the different activities of the Industrial Processes and Product Use sector is detailed in Figure 4.

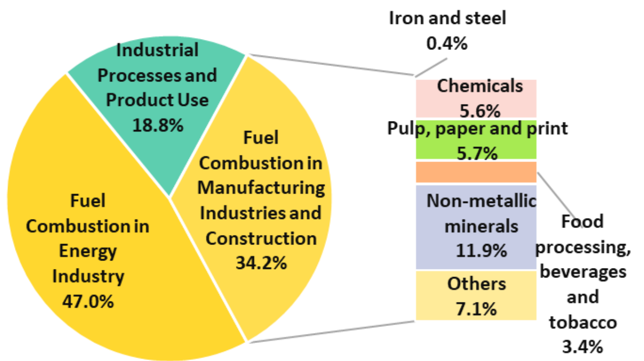

Figure 3 - Detailed distribution of the weight of the different activities responsible for fuel combustion in the Manufacturing and Construction Industry in 2020 (graph built based on data consulted in APA, 2022d).

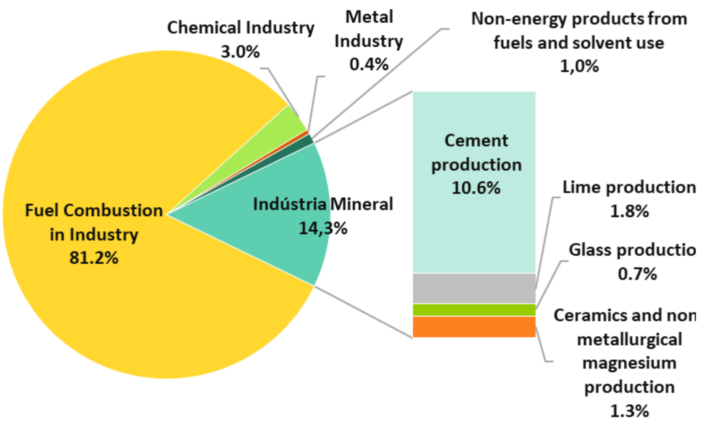

Figure 4 - Weight in CO_2 emissions from the different activities of the Industrial Processes and Product Use sector in 2020 (graph built based on data consulted in APA, 2022d).

After checking the sectors that contribute the most to CO_2 emissions in Portugal, the possibility of implementing CO_2 capture technologies in the various activities carried out is then analyzed. The CO_2 capture technologies have also associated high costs, both in the initial investment and throughout the operation and as such, these projects are preferably applicable to large installations and whose flow of CO_2 produced justifies it. In this way, the potential of the emitted sources for the application of CO_2 capture technologies depends on the volume emitted and the concentration of CO_2 in the gases to be treated, because the higher the CO_2 content, the lower the capture costs, as the capture is simpler and, consequently, requires less energy consumption. On the other hand, the more impurities are present in the gases to be treated, the greater the number of treatment and purification steps for the recovery of CO_2. In this way, certain sectors of industry will have a greater potential for the incorporation of these technologies than others.

According to the IPCC (2005), plants with emissions greater than 0.1 Mt CO_2/year are considered large stationary emitters and consequently points with greater potential for capturing CO_2.

Regarding the concentration of CO_2 in the gases to be treated, in natural gas thermoelectric plants, combustion gases are generated with concentrations of CO_2 typically between 3% and 4% by volume. In coal-fired thermoelectric plants, combustion gases are produced at atmospheric pressure with a content of approximately 14% by volume. In Portugal, the two coal-fired thermoelectric plants were deactivated in 2021, so in the report for the year 2020 in which the previously analyzed data are included (Figures 1 to 4) these two plants are still included. In refineries, produced gases can contain between 3% and 13% by volume of CO_2. In the effluents of the cement and pulp industry's calcining kilns, the CO_2 content varies between 14% and 33%. The flue gases from cement plants contain between 15% and 30% and in the combustion gases of boilers for recovery of black liquor in the production of paper pulp, the concentration varies between 18% and 20%. In the production of iron and steel the concentration of CO_2 can reach 15% in volume, in the production of hydrogen gases with a CO_2 content between 15% and 20% in volume are formed and in the process of fermentation of sugars for the production of ethanol, practically pure CO_2 is obtained. The percentages mentioned are all percentages by volume and for pressure close to atmospheric pressure (IPCC, 2005; Oliveira, 2016).

3.2. Potential CO_2 Users

CO_2 recovered through capture can be used in various processes, in the industrial unit where it is captured or in other industrial installations that have the capacity to use it as raw material.

Most CO_2 utilization processes are based on carboxylation and reduction reactions. Carboxylation occurs when the double bonds of the carbonyl group (C=O) are not completely broken, which happens in mineral carbonation and in some polymerization reactions. On the other hand, in the reduction reaction, at least one C=O double bond is broken. Despite the high energy requirement of this process, the CO_2 reduction reaction can generate various valuable products, such as methane, methanol, synthesis gas (H_2 and CO), ethanol, dimethyl ether, formic acid, among others (Costa et al., 2021).

In order to proceed with a selection of utilizations that are suitable for the Portuguese industry, an analysis was first made of several possible applications for the captured CO_2, among which the following were studied:

- Extraction using CO_2 as solvent;
- Welding;
- Pulp and Paper Industry (pH control, pulp washing and production of Precipitated Calcium Carbonate for printing paper);
- Fire extinguishers;
- Food industry (carbonation of beverages, packaging, storage and transport of food products in controlled atmosphere and also cryogenic freezing of food);
- Greenhouses enriched with CO_2 to increase and accelerate growth;
- Culture of microalgae for various purposes, such as the production of food supplements, pharmaceuticals and cosmetics and in the production of bio-oil;
- Aquaculture of bivalves;
- Water and wastewater treatment (pH adjustment and remineralization);
- Synthesis of synthetic fuels (methane and methanol);
- Polyols, isocyanates and polyurethane;
- Synthesis of polycarbonates and cyclic carbonates;
- Synthesis of glycerol carbonate;
- Synthesis of dimethyl carbonate;
- Synthesis of acids (formic acid, acetic acid, salicylic acid and acrylic acid);
- Urea synthesis.

4. Methods

In order to study the opportunities for the application of CO_2 capture technologies and subsequent utilization in Portugal, the industries responsible for CO_2 emission into the atmosphere were identified, using the list of facilities integrated into the ETS, available on the APA website in its most recent version, dated June 29, 2022 (APA, 2022b). Also in the APA website, were collected data regarding the distribution of CO_2 emissions per municipality, available in the Excel sheet "Emissões totais por Concelho em 2015, 2017 e 2019" (APA, 2022a),
being these the most current data published. Verified Emissions of CO_2 in recent years for integrated emitters in the ETS were consulted in the Excel sheet referring to CO_2 Verified Emissions most recently published on the European Commission website (European Commission, 2022). From the activities described in "Atividades do sistema Comércio Europeu de Licenças de Emissão", available in *Anexo II do Decreto-Lei nº 12/2020, de 6 de abril* and the *Classificação Portuguesa das Atividades Económicas (CAE)*, a color division was carried out to be used in the QGIS software.

Potential users for the captured CO_2 were also evaluated and located, and possible relationships and interactions between the emitting industries and potential users were studied, taking into account their geographical proximity and the means of transport available to carry out the transport of CO_2 from the emitting source to the places of consumption. Data referring to the spatial distribution of CO_2 consumption/imports per municipality were provided by the *Instituto Nacional de Estatística (INE)* on May 5, 2022, through the request for information made through the INE Portal. For the study of means of transport, the National Natural Gas Transport Network was consulted, present on the REN - Redes Energéticas Nacionais website (REN, 2022). The railways in Portugal were collected in the form of shapefile obtained in the Portal de dados abertos da Administração Pública (Portal de dados abertos da Administração Pública, 2022).
To study the geographical disposition of the CO_2 emitters and user industries and the possible interaction between them, the QGIS software by Open Source Geospatial Foundation (OSGeo) in its version 3.24.2 was used, through which all the maps analyzed were constructed.

5. Results and Discussion

To study CO_2 emissions by municipality by industrial sources, in this work, the sector called PublicPower was considered, which includes the production of electricity and heat (including municipal waste incineration and combustion of biogas with energy use) and also considered the industry sector, which includes oil refining, combustion in the manufacturing industry, industrial production: cement, lime, glass, nitric acid, other chemical industry, iron and steel, pulp and paper, food and beverage and wood processing (APA, 2022a). It was then possible to create a map with a color gradient according to each municipality's contribution to CO_2 emissions.
To facilitate the analysis of the geographical distribution of emissions in Portugal and to understand the origin of the different emission intensities, the main industrial sources of CO_2 were located, i.e. the facilities integrated in the ETS.
From the overlapping of data referring to the spatial distribution of national emissions in 2019 and the location of the facilities integrated in the ETS, mentioned above, resulted in the map that can be observed in Figure 5.

It is important to note that, as part of the measures taken for the energy transition, the Sines coal-fired Thermoelectric Power Plant was deactivated in February 2021, the Pego Thermoelectric Power Plant last operated on coal in November 2021 and the Porto Refinery stopped its activity in the first half of 2021. However, since the most recent data available in the APA website for spatial distribution of emissions refer to the year 2019, CO_2 emissions from these installations were still included in the map illustrated in Figure 5.

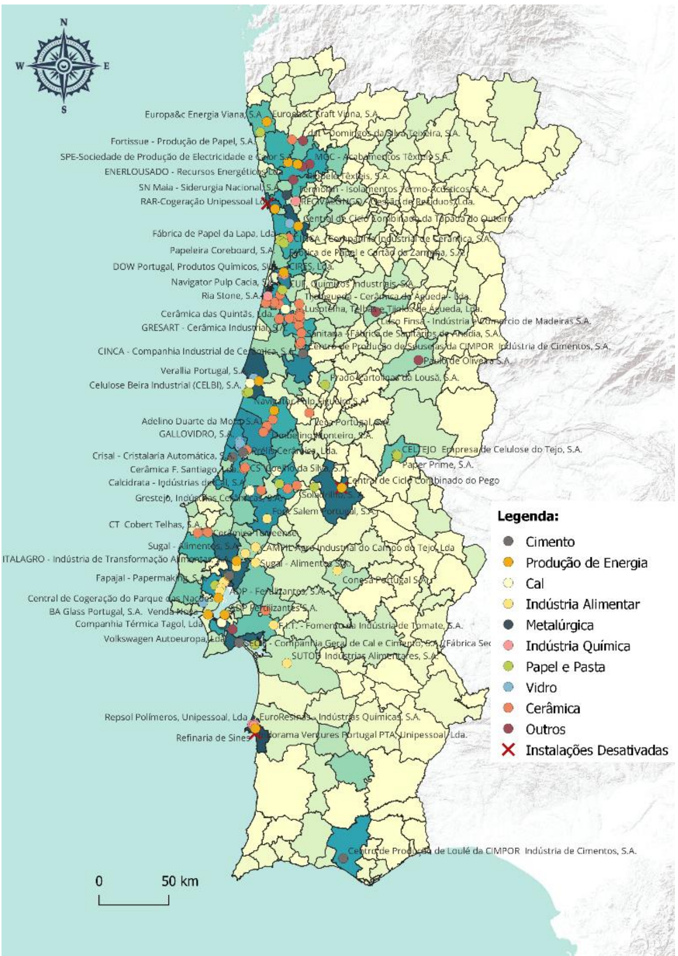

Figure 5 - Installations integrated in the ETS colored according to the industry sector and spatial distribution of CO_2 emissions in Portugal (image built based on data consulted in APA, 2022a).

As previously verified, the fossil fuels combustion in the energy industries is the largest responsible for CO_2 emissions from stationary sources, such as thermoelectric plants and refineries. This event explains the higher intensity of CO_2 emissions in the municipality of Sines, where the Petrogal Refinery in Sines is located and where in 2019 the Sines coal-based power plant was still operating. Next comes the municipality of Figueira da Foz, where is located the Combined Cycle Power Plant of Lares operated by EDP and the municipality of Gondomar, where is the Combined Cycle Power Plant of Tapada do Outeiro operated by Turbogás. Also the municipality of Abrantes has high intensity of emissions due to the Pego Thermoelectric Power Plant, which in 2019 it still operated on coal and currently is only working the Natural Gas Combined Cycle unit. In Alenquer the intensity of emissions is also one of the highest, which is partly due to the Ribatejo Thermoelectric Power Plant operated by EDP. The municipality of Matosinhos, part of the CO_2 emissions recorded in 2019 correspond to the Petrogal Refinery in Porto, which has since been deactivated.

Another sector highly responsible for the emission of CO_2 to the atmosphere is the cement industry sector, which justifies the fact that the municipalities of Vila Franca de Xira and Setúbal are characterized by a high intensity of emissions, due to the presence of the production centers of CIMPOR Alhandra and Secil-Outão, respectively. CIMPOR's production center in Souselas, Coimbra, has also gained consecutively more significance in CO_2 emissions in recent years, which justifies the high intensity of emissions in the municipality of Coimbra in 2019 and is expected to be even higher today.

By analyzing the verified emissions in each of the facilities integrated in the ETS in the year 2021 (Figure 6), it is possible to confirm the largest sources of CO_2.

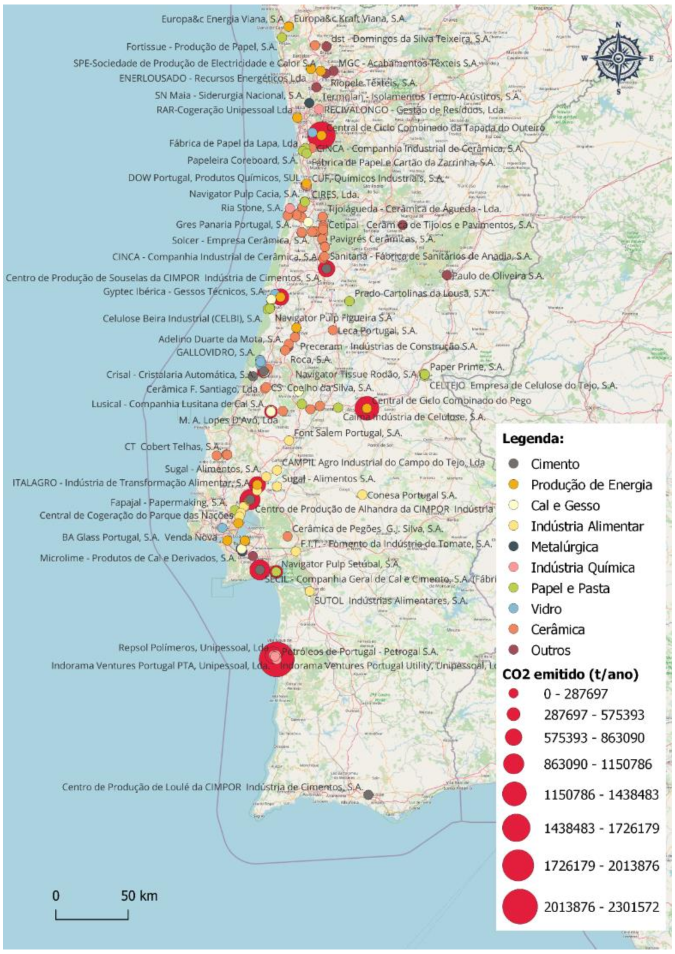

Figure 6 - CO_2 emissions verified in 2021 by the facilities integrated in the ETS (image built based on data consulted in European Commission, 2022).

After the identification of the CO_2 sources, were studied the different possibilities of application of CO_2 listed in section “3.2. Potential CO_2 Users”. For each application, a survey was carried out on the companies that work in each of these fields in the national territory and that may start to consume the captured CO_2.

First, a map was constructed with a color gradient according to the consumption/import of CO_2 per municipality, based on data provided by the National Institute of Statistics *(INE)*. The data correspond to the period from January to December 2021 (preliminary data) and the municipality of the headquarters of the companies and not of the manufacturing units. It is important to note that the data provided by the INE do not include factories whose headquarters are not in national territory. To that map was added the location of several installations which may include the captured CO_2 in its manufacturing process (Figure 7). It is important to point out that the companies mentioned here have not made any commitment to the application of capture and/or use of CO_2, being only scenarios studied in the ambit of this work.

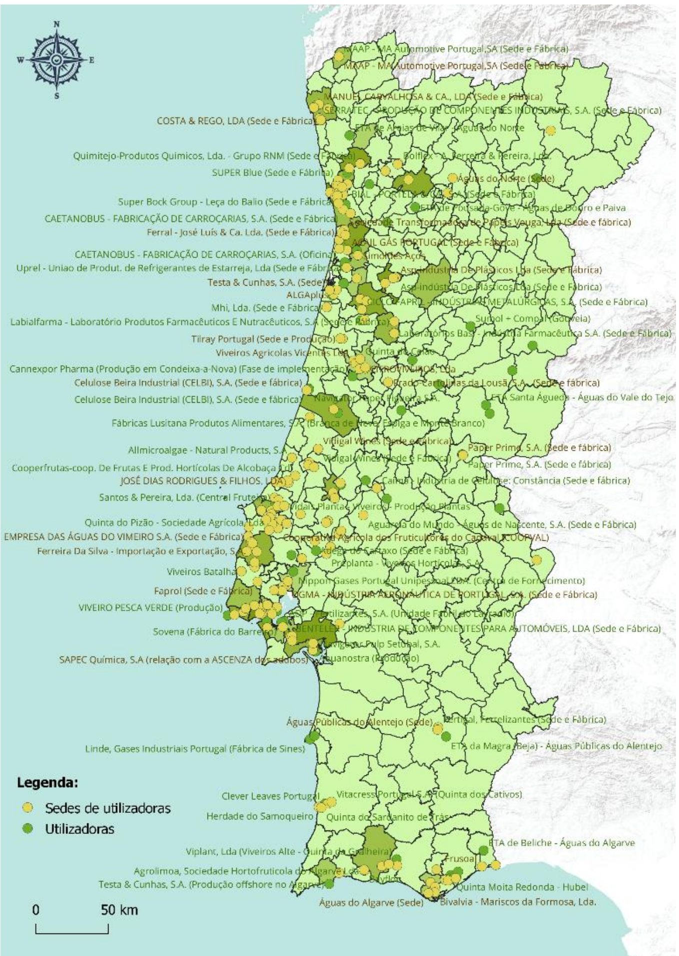

Figure 7 - Possible users. Production sites (green) and company headquarters (yellow).

Among the various facilities with potential for the consumption of captured CO_2 studied, the ones that were found in greater quantity in Portugal were the greenhouses. These allow a more direct use of gaseous effluents, avoiding costs with purification processes. There are large areas of greenhouse throughout the Portuguese territory, however, some facilities do not have identification or, instead of closed greenhouses, the crops are protected by open tunnels, making it impossible to use a modified atmosphere, in this case, enriched with CO_2. In these situations, it is necessary to adapt the culture conditions, in order to close the greenhouses and make possible the introduction of CO_2. The greenhouses are followed by the installations that carry out MAG welding. However, the CO_2 used for this purpose is included in mixtures with 18% to 25% CO_2 by volume, resulting in not very high amounts of CO_2 consumed. This is followed by the fruit storage centers in a controlled atmosphere, requiring a high degree of purity for this purpose, as they are foodstuffs.

5.1. Potential means of transport for CO_2 captured in Portugal

The best transport options for the captured CO_2 to its consumer units in national territory are the pipelines or the transport by truck/train tanker. Given the climate emergencies and the consequent need to find rapid solutions for transport in order to be able to implement CO_2 capture and use technologies as soon as possible, a solution for transport between emitters sources and consumer plants is the use of existing infrastructure in our country. These structures include roads, railways and pipelines. In addition to the advantage of facilitating and accelerating the implementation of CCU at the national level, it has the advantage of significantly reducing the costs of investment in infrastructure. The National Natural Gas Transportation Network, operated by REN - Gasodutos S.A., can be seen in Figure 8.

Figure 8 - National Natural Gas Transportation Network (image collected on REN, 2022).

As for rail transport, this was added to the maps of CO_2 emitters and consumers, in order to identify transport opportunities between them.

5.2. Analysis of the 15 largest CO_2 emitters

After surveying emitters, possible users and possible means of transport, a reasonable maximum distance for

transporting CO_2 from the source to the place of consumption of 50 km was considered.
In the dissertation, the 15 largest emitters were studied in particular, according to the values of 2021. To this end, a circular area with a radius of 50 km was defined around these 15 installations in order to analyze the potential users for the CO_2 captured in them. The emitters analyzed in greater detail can be found in Table 1. It is important to note that the 2021 values still include the Coal-fired Pego Thermoelectric Power Plant, however, as it ceased to operate at the end of 2021, it was not included in this more detailed study nor in the count of the 15 largest stations.

Table 1 - 15 largest $CO1_2$ emitters in Portugal in 2021 and their verified emissions value in that year (European Commission, 2022).

Installation	Verified Emissions (ton)
Refinaria de Sines	2 301 572
Central de Ciclo Combinado da Tapada do Outeiro	1 441 014
Central de Ciclo Combinado do Pego	1 163 308
CIMPOR de Alhandra	891 465
Secil-Outão	869 636
CIMPOR de Souselas	848 122
Central Termoelétrica do Ribatejo	785 806
Repsol Polímeros, Unipessoal, Lda	753 075
Central de Ciclo Combinado de Lares	646 705
Secil Maceira-Liz	399 743
Lusical - Companhia Lusitana de Cal S.A.	339 766
Navigator Paper Setúbal, S.A.	294 671
CIMPOR de Loulé	232 983
Indorama Ventures Portugal Utility	225 873
Europa&c Kraft Viana, S.A.	137 784

5.3. New Opportunities - Synthesis of Synthetic Fuels and Urea

In recent times, interest in the synthesis of synthetic fuels such as methane and methanol has been growing because they represent an alternative to fossil fuels and also greater independence from fuel sources outside the country. Both methane as methanol can be synthesized from captured CO_2 and H_2. For the process to be really beneficial to the environment, the H_2 used must be green, that is, produced from the electrolysis of water. Portugal presents very favorable conditions for the synthesis of these products, particularly in Sines, given their geographical location and the resources already existing on site. Sines is a coastal zone, so the water supply for the production of H_2 by electrolysis would be facilitated and has availability of various resources for the production and use of renewable energy. It is still necessary to develop technologies that allow the direct use of this water in the electrolysis process or its desalination. On the other hand, Sines is the municipality with the highest density of CO_2 emissions, integrating large emitters in the region, so the capture and use of CO_2 in this region would be an added value for the decarbonization of the industry. Furthermore, Sines is home to large consumers of H_2, such as Refineries, which will be able to make use of the H_2 produced from the electrolysis of water, instead of using the H_2 produced by the Steam Methane Reforming. Sines also has a deep-water port, allowing the export of manufactured products and has the Liquefied Natural Gas Terminal *(TGNL)* of Sines, so it has transport infrastructure, storage and connection to the Natural Gas transport network, including access to methane ships, pipelines, tank trucks and tank trains.

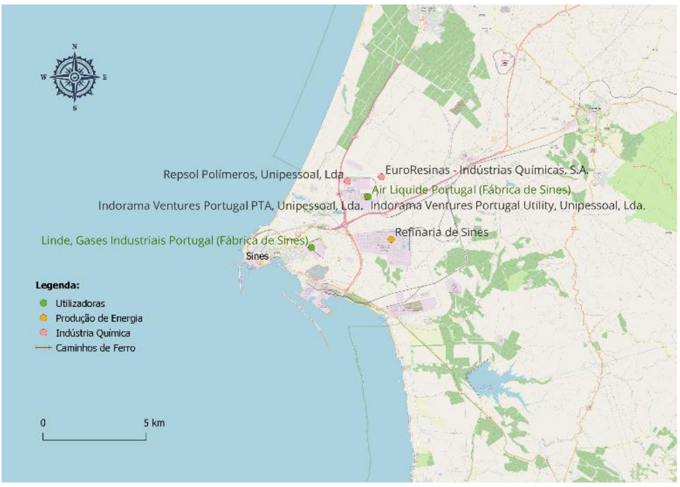

Figure 9 - Emitters integrated in the ETS and possible users of CO_2 in the municipality of Sines.

Another application for CO_2 with great potential in Portugal is urea production. Currently, there is no urea production unit in Portugal, and all urea consumed is imported. The value of imported urea was 221 864 tons in 2021 (INE, 2022). It was then studied the possibility of building an industrial unit with capacity to produce all the necessary urea, from ammonia and CO_2. All ammonia consumed nationally is imported and stored by the company Alkion Terminal Lisbon, S.A. in the Barreiro Liquid Bulk Terminal, being later distributed throughout the country. Thus, a good location for the installation of the urea production unit would be in Barreiro, where not only is space available for the construction of the factory, but also access to ammonia would be facilitated and CO_2 captured as well, given its proximity to large emitting sources. A radius of 50 km was defined around the approximate location where the urea production plant would be built, that is, next to the ammonia import and storage terminal, in order to evaluate which emitters are in this radius and which, as such, can provide CO_2 for the synthesis of urea. Access to means of transport in the region was also verified (Figure 10).

Figure 10 – Possible location for the urea production plant and study of the emitters sources and means of transport in a radius of 50 km.

It was found that inside a radius of 50 km there are several emitting industries, and those with the highest emission values in the studied area are the cement plants: CIMPOR Alhandra Production Center and Secil-Outão Factory. Transportation between Secil-Outão and Barreiro may take place by pipeline, railway line or tanker truck. On the other hand, transportation from CIMPOR Alhandra is more difficult, since the unit is on different banks of the Tejo River and can be carried out by the same means of transport, but along much longer and less direct routes. In the same situation as CIMPOR Alhandra, there is the third largest emitter in the studied area, that is, the Ribatejo Thermoelectric Power Plant. Closest to the site is the fourth largest emitter in this area, Navigator Paper Setúbal, S.A., also having the advantage of having the railway line and the natural gas pipeline network to join the two plants. There are several other installations that may be CO_2 suppliers and which, moreover, are closer than the above, however, they are all characterized by significantly lower CO_2 emission values than the previous ones.

The facilities that are closer, precisely in Barreiro, are the Fisigen Cogeneration Plant and ADP Fertilizantes S.A. ADP Fertilizantes S.A. it is itself a consumer of ammonia imported in this place and urea, also imported.

Calculating the CO_2 necessary to produce the urea imported in the year 2020, taking into account the equation of the urea production reaction, 162 547 tons CO_2 are required. Any of the four largest emitters in the region emit values higher than necessary. On the other hand, CO_2 emissions from the Fisigen Cogeneration Plant and ADP Fertilizantes S.A. in 2021, amounted to 104 779 tons CO_2, which is not enough to satisfy the country's urea need, so it is necessary to use CO_2 captured in another/s installation/s. However, it is important to study the feasibility of the capture process taking into account the characteristics of the gases to be separated, including CO_2 concentration, which could make it impossible to use these industries and give the cement or pulp and paper industry an advantage.

6. Conclusion

The CO_2 capture technologies are preferably applicable to large installations and whose CO_2 flow produced is relevant, i.e. when the gas flow rate to be treated and their concentration in CO_2 is significant, because the higher the CO_2 content, the lower the capture costs, as they require less energy consumption. Thus, certain sectors of industry will have greater potential for the incorporation of these technologies than others. The IPCC (2005) considers large stationary emitters, and consequently points with greater potential for the capture of CO_2, the industrial units that emit at least 0.1 Mton CO_2/year. In Portugal, the facilities under these conditions correspond to the twenty largest stations integrated in the ETS. Looking at these twenty, it turns out that the largest emitters correspond to energy production and cement production facilities, followed by lime, pulp and paper and glass production facilities.

Relatively to the concentration of CO_2 in the flue gases or process streams of these installations, it was found that the gases formed in cement, lime and paper pulp production facilities have a high concentration in CO_2, higher than the typical concentration in the flue gases resulting from natural gas power plants and refineries.

Regarding CO_2 emissions caused by the burning of fossil fuels measures can be taken, such as the use of alternative fuels, in order to reduce emissions. However, refineries and power plants will continue to consume significant amounts of energy and emit CO_2 in equally significant amounts. Therefore, the capture of CO_2 remains a very important measure. On the other hand, CO_2 formed in the calcination reaction carried out in the production of lime and cement and in the paper industry cannot be avoided by these measures, which makes the capture of CO_2 become an even more relevant measure for these sectors.

Several possible users for captured CO_2 were studied. CO_2 can be used in the industrial unit where it is captured or in other industrial facilities that are capable of using it as raw material.

CO_2 can be used as a way of cleaning equipment and machinery through dry ice jets, so it can be applied in several industrial units, including the emitters themselves. Also in the Pulp and Paper industry, emitted CO_2 can be used on-site in new processes, including washing pulp, adjusting the pH of waste water and producing Precipitated Calcium Carbonate for printing paper. In carbonated beverage factories, which include fermentation in their process, CO_2 can be recovered and used for carbonation of the beverages produced.

In the case where CO_2 is captured and used in other industrial units other than the source itself, it can be applied as an extraction solvent, as welding shielding gas, to remove burrs from plastic or rubber parts produced by injection molding, in CO_2 extinguishers, in the carbonation of water and soft drinks, in the storage, packaging and transport in an atmosphere enriched in CO_2, in plant greenhouses also enriched in CO_2, in the culture of microalgae and bivalves, in the treatment of water for consumption, in the synthesis of synthetic fuels and in the synthesis of other chemicals such as polyols, isocyanates, carbonates (including polycarbonates), acids (for example acetic acid, formic acid and salicylic acid) and urea.

In the future, it will be interesting to study in detail the composition of flue gases from the different sources in Portugal, in order to study the best way to capture CO_2 and which applications that CO_2 is suitable for, and also, to evaluate how advantageous is to use CO_2 in the several applications. Must also be evaluated the impact of capturing in the emitters, namely, in the performance and in the energy efficiency of the unit. It is also relevant to study the necessary changes in equipment, both in sources and in CO_2 consumers and evaluate the economic impact of it. Can be carried out a survey of the activities and facilities where is already used captured CO_2 and study these industrial units as an example to follow for the implementation of the same technologies in Portugal. In the future, can be also verified the amount of CO_2 consumed in the Production of Pulp and Paper and in the carbonation process in the Production of Beverages, in order to verify if the CO_2 captured in these facilities is sufficient to cover the internal needs and verify if even so, part of the captured CO_2 could be used by other users.

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