CHAPTER 3

PARANA SEDIMENTARY BASIN'S POTENTIAL FOR CO_2 GEOLOGICAL STORAGE

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ABSTRACT

Techniques of Carbon Capture and Storage (CCS) are important alternatives for decarbonisation, based on the world scenario aiming at net-zero emissions and energy transition. In Brazil, there is a vast potential for these technologies. The Parana Sedimentary Basin presents one of the best alternatives for CO_2 storage, considering the proximity to stationary sources of CO_2 and potential geological reservoir units, such as the significant variability of lithologies and total depth of the volcano-sedimentary succession. Also, the region comprising the basin includes the main areas of national production of biofuels. Therefore, locating CCS plants within the area can contribute to significant reductions in carbon emissions. This chapter presents an overview of the geological aspects of the Parana Sedimentary Basin, focusing on an assessment of its theoretical potential for CO_2 geological storage. This evaluation is based on data available in the literature involving geological investigations, considering saline aquifers, black shales, coal and basalts as the main potential reservoirs for CO_2 storage. The Rio Bonito, Itararé, Irati, Ponta Grossa and the Serra Geral Formations present potential geological reservoirs for CCS.

Keywords: CO_2 Geological Storage; Parana Sedimentary Basin; BECCS; Decarbonization.

1. INTRODUCTION

Brazil's southern and south-eastern regions are associated with the highest CO_2 emissions from stationary sources in the country, with local emission rates up to 14,000 kt/year (Rockett et al., 2011). According to SEEG (2018, 2019), CO_2 total emissions in these regions would sum up to 420 Mt/year. More than half of these emissions would come from power plants, together with a large share of the steel and cement production industries, which contribute to over 3,000 ktCO_2/year (SEEG, 2018, 2019).

In a global scenario looking for a reduction in emissions and striving to tackle and prevent the impacts of climate change, Carbon Capture and Storage (CCS) technologies are considered one of the most important paths to achieve the proposed goals based on the Paris Agreement. According to the International Energy Agency (IEA), these techniques could reduce a cumulative amount of around 100 GtCO_2 by 2050, representing 14% of the total reduction in CO_2 emissions by 2050 (IEA, 2019). Also, limiting the availability of CO_2 storage would increase the cost and complexity of the energy transition once this technology is part of a least-cost portfolio needed to achieve climate and energy goals (IEA, 2019).

In summary, CCS technologies allow the final disposal of CO_2 captured from sources such as combustion of fossil fuels for power generation on thermoelectric complexes and cement industries. The CO_2 produced must then be separated from other gases, dehydrated, compressed and transported to the recommended site for permanent storage. Some of the main reservoirs described in the literature for CO_2 storage are depleted oil and gas reservoirs, coal layers, saline aquifers, black shales and mafic and ultramafic rocks, such as basalts (IPCC, 2005; Busch, 2008). Geological reservoirs for CO_2 storage must meet specific criteria (Table 1) to guarantee safe and permanent storage, including: minimum depth and thickness of the layer, presence of effective seal, good porosities, and trapping mechanisms. Sedimentary basins are good prospects considering CO_2 reservoirs. They generally contain a combination of various rocks that can be combined to provide suitable potential reservoirs for CO_2 storage.

Reservoir type	Depth (m)	Thickness (m)	Permo Porosity	Main trapping mechanism	Critical factors
Oil/Gas Reservoir	> 800	> 10	Porosity >10 % Permeability	Stratigraphic and structural	Retrofit
Saline Aquifer	> 800	> 10	2Md	Sealant layer	Potability
Coal layer	> 300 < 1.000	>2	Microporosity	Sorption in organic content	Low permeability
Black-shale	> 800	> 10	Microfractures	Sorption in clay	Distance > 600m from aquifers
Basalts	> 400	-	Vesicles and fractures	Mineralisation and sealant layer	Hydro availability

Table 1. Summary of requirements for CO_2 storage of each potential reservoir type.

Source: Pelissari (2021).

According to IPCC (2005), basins suitable for CO_2 storage have structural simplicity, thick sediment accumulations, permeable rock formations and low porosity formations acting as seals. The Possible geological units with potential for CO_2 storage within the Paraná Sedimentary Basin are predictable based on the data collected from the available literature.

The Paraná Sedimentary Basin extends through the states of Mato Grosso, Goiás, São Paulo, Paraná, Santa Catarina, and the Rio Grande do Sul in Brazil. It presents potentials to store the CO_2 emitted in its region considering the proximity to source sinks and reservoir rock units with the required geological configurations to serve as CO_2 repositories. According to Lima et al. (2011), this basin presents geological formations favourable for CO_2 injection, but it has no record carbon storage activity yet.

Also, Brazil's Southern and South-Eastern regions have great potential for geological storage because they have significant CO_2 emitting sources, principally from the Energy and Industrial Sectors (Figure 1) close to the Parana Basin (Carneiro et al., 2013). Therefore, there is a demand for reducing emissions, and there are geological reservoirs available for CO_2 storage within the Paraná Sedimentary Basin. According to Ketzer et al. (2007), there is a storage capacity of 462,000 $MtCO_2$ in saline aquifers and around 200 $MtCO_2$ in coal layers of the basin.

There are also significant potentials for CO_2 storage in basalts. Pelissari (2021) also indicates a potential for carbon sequestration in the basin's coal, black shales and basalts.

This chapter aims to present a brief discussion on the potential of the Paraná Sedimentary Basin for CO_2 geological storage, considering the main aspects of emissions, geological settings of the units and a summary on the legal and economic topics.

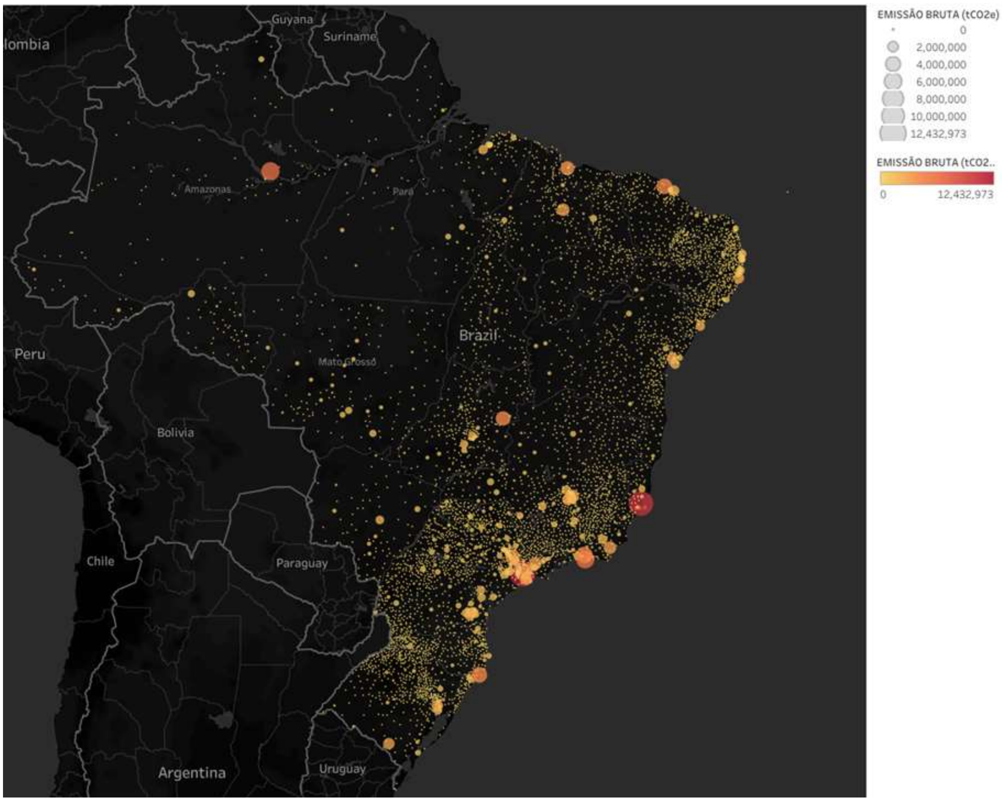

Figure 1. Brazilian gross emissions (tco2eq) by the city from the Energy and Industrial Sectors. Source: SEEG (2020)

2. GEOLOGICAL SETTINGS

As compiled in Milani et al. (1994, 2007), the Paraná Sedimentary Basin is filled by a sequence of volcano-sedimentary rocks from Ordovician to Cretaceous, with a depocenter of about seven kilometres thick, occupying an area of over one million square kilometres in the South-Central region of the Brazilian territory (Figure 2). The stratigraphic sequence includes rocks described in the literature as potential reservoirs for carbon geological storage, such as coal layers, oil and gas reservoirs, saline aquifers, black shales and basalts (IPCC, 2005).

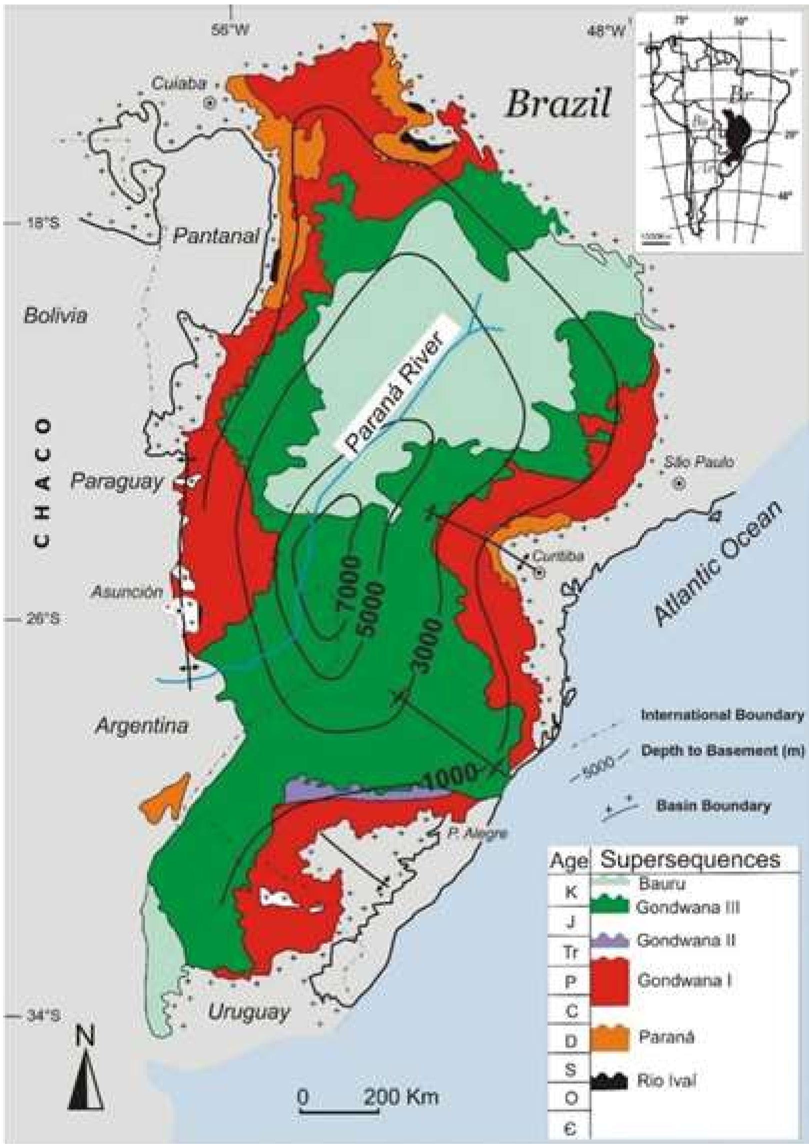

Figure 2. Geological map of the Brazilian portion of the Paraná Basin . Source: Milani et al. (1997, 2004).

The basin's stratigraphic column consists of six super-sequences correspon-ding to the Paleozoic and Mesozoic eras, including volcanic and sedimentary rocks—the Precambrian basement is composed of granite-gneiss complexes. The accommodation space for the Rio Ivaí Supersequence was created by reactivating basement weaknesses. The super-sequences include the basal sandstones of the Alto Garças Formation, diamictite layers of the Iapó Formation and Vila Maria Formation's fossiliferous shales and siltstones (Milani, 1997). Above and separated by erosive discordance is the Paraná super-sequence, which is deposited with Eodevonian sandy sediments of the Furnas Formation, gradually transitioning to marine sediments of the Ponta Grossa Formation composed of shales, siltstones and sandstones (Milani et al., 2007).

The Gondwana I super-sequence, separated by an unconformity, including the occurrence of the constituent formations of the Itararé Group, representing different environments of a fluvio-lacustrine and marine depositional systems under the influence of glaciers (Schneider et al., 1974). Covering the rocks of the Itararé Group are the rocks of the Rio Bonito and Palermo formations, which constitute the Guatá Group, with sandstones, siltstones and pelites of different depositional systems, and coal layers in the Rio Bonito formation.

The Irati, Serra Alta, Teresina, and Rio do Rastro formations constitute the Passa Dois Group, covering the Guatá Group. The rocks of the Irati Formation represent deposition in the marine environment of calm waters consisting mainly of shales and limestones (Schneider et al., 1974). The shales and siltstones of the Serra Alta Formation represent deposits of the marine environment, and the Teresina Formation comprises shallow and rough water marine silt and sandstone deposits (Schneider et al., 1974).

The Rio do Rastro Formation is at the top of the Passa Dois Group, composed of intercalations of sandstones and siltstones. The deposition of this formation is initially attributed to a shallow marine environment (supra-tidal) that transitions to coastal lowland deposits and subsequently to the establishment of fluvio-deltaic sedimentation (Schneider et al., 1974).

Above are the eolian deposits of the Botucatu Formation and the volcanic rocks of the Serra Geral Formation, from the Supersequence Gondwana III (Milani et al., 2007). The Botucatu Formation predominantly comprises sandstone facies deposited in a desert environment (Milani et al., 2007). The volcanic rocks of the Serra Geral Formation emerged from a Mesozoic fissural magmatic event and consist of a thick pile of basaltic lava and an intricate network of dikes and sills that cut through the entire sedimentary section of the Paraná Basin (Milani et al., 2007).

3. POTENTIAL RESERVOIRS FOR CARBON GEOLOGICAL STORAGE

Large urban and industrial centres are located in the area of occurrence of the Paraná Sedimentary Basin. It has significant stationary sources of CO_2, with a considerable variety of lithologic units in the stratigraphic sequence of the Basin, presenting great potentials for the application of CCS technologies. Studies such as Lima (2010), Rockett et al. (2011), Kalkreuth et al. (2013), Ketzer (2014), Diakakis (2019), San Martín Cañas (2020) and Pelissari (2020a, 2021) indicate prospective formations for CO_2 geological storage within the Basin.

Considering the potential CO_2 geological reservoirs described in the literature, at least five significant units in the Paraná Basin can be related to high regional potential for CO_2 storage: organic shales of the Irati and Ponta Grossa formations, basalts of the Serra Geral Formation, sandstones of the Itararé Group and sandstones, and coal of the Rio Bonito Formation. Each formation has its specific characteristics and requirements to fit as safe reservoirs and guarantees an effective abatement of CO_2 along the time, as summarised in Table 1. In this way, the five mentioned potential reservoirs should fit the minimum requirements for carbon sequestration on a local scale.

3.1. Coal Layers

The occurrences of coal in the Parana Sedimentary Basin are related to the bottom portion of the Rio Bonito Formation, the Barro Branco and Bonito Members, with depths varying up to 4,000m and average thicknesses up to 100m (Vilela & Cardoso, 2018). The Rio Bonito formation is also composed of cyclic Permian successions of sandstones and conglomerates, shales, clayey and carbonate siltstones, with the main structures consisting of parallel and cross stratifications (Schneider et al., 1974). The coal layers have an average cumulative thickness of 10 m and 40 km of horizontal continuity (Holz et al., 2000).

The coals are volatile bituminous coal with major maturation in areas close to the basic igneous intrusions, where they get up to anthracites (Kalkreuth et al., 2008, 2010). Almeida (2019) categorised the coals according to the ISO 111760:2005 classification as Bituminous C, with variable Vitrinite and high ashes content. Once the coal presents great affinity to CO_2, with preferential adsorption of CO_2 on the macerals, carbon storage has a huge capacity, mainly on its micro porosities (Rodrigues et al., 2015). Besides, the stratigraphically superior formation is the Palermo Formation, which contains shales, siltstones and claystone, with low permeabilities, which presents potential for capping rocks, guaranteeing safety for the CO_2 storage.

According to Weniger et al. (2010), the volumetric ratios of adsorption of CO_2 versus CH_4 are around 2:1 to 7:1, indicating a great potential for CO_2 enhanced-coalbed methane. In this way, considering that the coals of the formation achieved the generation window of gas, mainly CH_4 (Costa et al., 2014; Kalkreuth et al., 2020), it becomes an attractive aspect for the CO_2 injection and storage in the formation, with associated CH_4 production.

Considering that the main coal deposits occur in the southern portion of the Basin, within the State of Rio Grande do Sul, there would be a significant potential for carbon storage in this region, as already assessed by studies like Kalkreuth et al. (2013). However, there would also be a considerable potential on the south-eastern portion of the State of Santa Catarina, where there is a considerable thermoelectric activity, and the coal occurrences also satisfy the minimum criteria for carbon geological storage, as studied by Pelissari (2021).

Thus, coal layers of the Rio Bonito Formation, occurring under 300m of depth, present significant potential for carbon storage in the Parana Basin. The potential of these coal layers for carbon storage was also assessed and confirmed by Rockett et al. (2010), Ketzer et al. (2014), Holz (2010) and Kalkreuth, et al., (2013) and Pelissari (2021).

3.2. Saline aquifers

Saline aquifers are one of the most used reservoirs for carbon storage around the world. Considering the minimal criteria for CO_2 storage, such as capping rocks, depths higher than 800m and minimum porosities and permeabilities, at least two possible formations within the Parana basin present significant potentials; the sandstones of the Rio Bonito Formation and Itararé Group. The sandstones of the Rio Bonito Formation occur at depths up to 4,000m, being typically coarse and associated with porosities of around 20 % (Milani et al., 2007). Above the Rio Bonito Formation are the Palermo and Irati formations, composed of low permeability rocks such as claystones, siltstones and shales, serving as capping rocks (Lima et al., 2011).

In this way, these rocks present significant potentials for CO_2 storage, which is even major due to their associations with the coals of the Rio Bonito Formation, which offers excellent potential for carbon adsorption, increasing the storage capacity of the formation. Thus, in places with depths higher than 800 m, it would be possible to store CO_2 on the saline aquifers of this unit if the other minimum safety criteria are fit.

The Itararé Group is the bottom unit of the Parana Basin, and it is divided into four Formations: Lagoa Azul, Aquidauana, Campo Mourão and Taciba. It consists of rocks related to glacial marine and fluvio-lacustrine environments (Schneider et al., 1974), which hosts the Ponta Grossa-Itarare Oil System reservoirs. The total thickness of the formation is up to 1,500m, mainly composed of coarse sandstones interbedded with diamictites, conglomerates and claystones (Milani, 1997).

The porosities vary from 1 to 20% on the sandstones (França & Potter, 1991), favourable for CO_2 storage. The unit is covered by rocks of the Guatá Group, including sandstones, claystones, siltstones, coal and conglomerates, which do not guarantee a satisfactory capping aspect due to relatively high permeabilities and porosities. Although both the Rio Bonito and the Itararé units host hydrocarbon reservoirs, presenting better potentials for carbon sequestration.

Hence, above the depths of 800 m, if the capping units present suitable thickness, continuity and integrity, besides low permeabilities, these units can be potential saline aquifer reservoirs for carbon sequestration once they meet the theoretical and geological minimum criteria.

3.3. Black Shales

The basin has two main geological formations that contain black shales: the Irati and the Ponta Grossa Formations. The Ponta Grossa formation comprises Devonian shales, with total organic carbon contents ranging from 1.5 to 2.5% of organic matter type II (Zalán et al., 1990). These are the source rocks of the Ponta Grossa-Itararé Oil System (Zalan et al., 1990).

The rocks of the formation occur at depths up to 4,500 m and with thicknesses up to 600m along the basin (Zalán et al., 1990; Candido, 2007), sealed by low permeability rocks, such as the Itararé Group's clayey and siltstones and the formation shale layers themselves, serving as internal sealants (Zalán et al., 1990; Milani, 2007). The black shales have considerable contents of phyllosilicates in their composition, reaching about 60% of the total components (Weniger et al., 2010), which is favourable for carbon storage, once CO_2 is adsorbed by clay minerals and organic matter (IPCC, 2005; Bush et al., 2008).

In this way, the Ponta Grossa Formation presents a considerable potential for CO_2 storage, just as concluded by Ketzer et al. (2007). According to the depths and thickness maps by Zalan et al. (1990) and Ferreira et al. (2010), considering that for CO_2 storage in shales, the reservoirs should have minimum depths of 800m, the most prospective areas for carbon storage on the unit would be in the western-central region of the Paraná Basin.

The Irati Formation consists mainly of black shales and Permian carbonates (Hachiro, 1996), with 8 to 13% organic content, peaks up to 24%, and type I-II organic matter (Zalán et al. al., 1990). These black shales are source rocks of the Irati-Pirambóia Oil System, with potential for generating hydrocarbons due to thermal activities from the basic igneous intrusions in the basin (Milani et al., 1990, Milani & Zalán, 1999; Milani et al., 2007; Rocha, 2021).

Their thickness varies along the basin, up to 150 m, with depths of up to 3,500 m (Zalan et al., 1990), being sealed by internal sealing rocks (shales and carbonates with low permeabilities), as well as shales from the overlying Serra Alta Formation and carbonates from the Teresina Formation (Rohn, 1994). Also, the clay content reaches up to 70 % of the total components (Holanda et al., 2018; Abreu, 2004), favourable for carbon storage once CO_2 is adsorbed by clay minerals and organic matter (IPCC, 2005; Bush et al., 2008). In this way, the Irati Formation presents a potential for CO_2 storage, accordingly to San Martín Cañas (2020). The areas of the formation with higher prospects for CO_2 storage are the western part of the state of São Paulo, where the depths are > 800m.

The portion also has favourable thickness and logistics conditions considering the proximity to stationary sources of CO_2, hence, reducing costs of transportation (San-Martin Cañas, 2020). Besides, according to Weniger et al. (2010), the volumetric sorption capacity ratios are between CO_2 / CH_4 for shales of Irati, and Ponta Grossa formations range from 1.5: 1 to 4.5: 1, with maximum CO_2 sorption capacities of 3.2 to 12.2 m³/t, varying mainly with mineralogical composition. Preferential sorption of CO_2 in shales leads to CH_4 desorption, presenting an attractive aspect for CCS projects once the injection of CO_2 could be coupled to shale gas production.

3.4. Basalts

Another potential unit for CO_2 storage is the Serra Geral Formation, associated with successive Cretaceous volcanic spills, consisting essentially of tholeiitic affiliation basalts (Melfi et al., 1988), with thicknesses up to 1,700m (Milani et al., 2007). The high degree of fracture of the unit described by Lastoria (2002) defines the unit as a fissured aquifer with calcic waters (Machado e Freitas, 2005; Lisboa, 1996; Reginato et al., 2013).

Basalts are good prospects for carbon storage due to their susceptibility to react with CO_2 in the presence of water and to form carbonate minerals from a continued reaction, which guarantees permanent and effective imprisonment of the gas (Bachu, 2007; Matter et al., 2016). The calcic waters of the Serra Geral

Aquifer also favour this process, helping with the availability of ions for mineralisation reactions. Thus, the Serra Geral Formation presents good potential for CO_2 storage, according to Carneiro et al. (2013), which indicates potential storage of about 270 $MtCO_2$ / year in this formation. However, the author stresses that large-scale CO_2 storage in volcanic rocks is still in the demonstration phase, as in Matter et al. (2016) and Von Strandmann et al. (2019).

4. BECCUS

Coupled with biofuels facilities, such as bioethanol or biodiesel production, CCS can lead to negative emissions, considering BECCS (Bio-Energy Carbon Capture and Storage). Once biomass captures CO_2 through photosynthesis, it leads to a net-negative carbon cycle if the generated CO_2 from biomass fermentation is captured and stored. Or it can be related to a carbon neutral cycle (i. e. when CO_2 is captured from the atmosphere by biomass and then returned to the atmosphere after biofuel combustion) (IEA Bioenergy, 2020). In this way, BECCS technologies should be strongly encouraged and implemented to achieve more significant reductions in carbon emissions.

The production of biofuels is divided into four different generations, according to the feedstock type: saccharine and starch (first generation); lignocellulosic biomass (second generation); micro/macroalgae biomass (third generation) and genetically modified cyanobacteria (fourth generation) (De Souza Abud & Silva, 2019). The primary industrial route for bioethanol production is the microbiological process from alcoholic or ethanolic fermentation (Silva et al., 2005). Sugars from different feedstocks, such as sugarcane and corn, are converted into ethanol, CO_2 and other byproducts by yeast cells (Monceaux, 2009). Brazil is the second biggest world producer of bioethanol, mainly from first-generation production from sugarcane fermentation, with a production increase of around 5% in 2019, achieving 33 billion litres (Conab, 2019) and emissions of approximately 24 million tons of CO_2/year (Garcia and Sperling, 2010). The sugarcane culture is concentrated mainly in the Northeast and South-Center regions (Vieira, 2008; novaCana, 2020).

Considering that the South-Center region of Brazil contains the Paraná Sedimentary Basin, the bioethanol-CCS combination may present a good possibility for BECCS projects (Pelissari et al., 2020b). The gas effluent from sugar fermentation for ethanol production is 99% pure CO_2, which is much more concentrated than the gas effluents from thermoelectric plants and refineries, giving it a very competitive character among others on the capture aspect (Smeets and Faaij 2010).

5. INFRASTRUCTURE

Some of the essential requisites for CCS projects are: satisfy geological conditions to guarantee safe and permanent storage; innovative technologies to capture and separate CO_2 at minimum costs; the proximity of the emitting source of CO_2 to the reservoir to reduce expenses with transportation; the existence of robust legislation to regulate all the steps of the CCS process and to guarantee continuous monitoring of the reservoir units, mainly after the end of the injection. Other factors include financial and economic incentives from both the governmental and private sectors, coupled with a consolidated carbon credit market to make CCS projects feasible, and the public acceptance of the technology (Kheshgi et al., 2012).

The necessary infrastructure for CCS projects consists mainly of the CO_2 capture and compression plant, transportation and injection facilities. The transportation can be done by different possibilities, according to the distances and conditions involved. Pipelines are generally the most economical and safe way to deliver CO_2 to storage sites, but ships and roads are alternatives for longer and shorter distances.

On the economic side, according to literature, the carbon capture phase is the most expensive one, representing up to 75% of CCS costs (Plasynski et al., 2009). Besides, new technologies are being developed with time and may bring down these elevated costs. It is crucial to consider the importance of incentives for developing CCS technologies and their implementation from both governmental and private sectors. Thus, fiscal incentives, a carbon market and carbon taxes are alternatives to be used for that.

On the legal aspect, the regimentation of CCS activities is essential to guarantee its correct implementation, safety, and efficiency. It includes monitoring CO_2 behaviour in the underground reservoir after the end of the injection phase. In this way, defining the correct procedures, pointing out the responsibilities and presenting a robust regulatory framework that foresees the obligations and penalties for all the phases of the CCS project is of extreme importance.

In Brazil, there is still no such regulatory framework, but some academic and governmental institutions are working on this topic to provide possibilities for the development of CCS activities. In this scenario, the European framework for CCS could be used, the 2009/31/CE Directive from the European Parliament on carbon geological storage, from 23/04/2009, once it is currently the world reference on the topic. This directive is adaptable to the Brazilian reality to define correct management for CCS activities.

At last, the public acceptance of CCS technologies is also of great relevance, considering that the projects are to be implemented offshore and onshore and may impact the local populations. In this way, it is recommended that marketing and social consciousness be developed so that the community understands the possible benefits and impacts of the project to be implemented and accepts its consequences, if any (Abreu Netto et al., 2020).

6. FINAL REMARKS

The Paraná Sedimentary Basin can develop Carbon Capture and Storage facilities due to its geological favourability and proximity to stationary emitting sources of CO_2. There is currently no operating CCS plant in the area of occurrence of the basin, and regulatory and economic developments are crucial to bringing commercial feasibility for such.

On the geological aspect, considering the main reservoir types for carbon sequestration described in the literature, there are at least five main geological formations that present the potential for CO_2 storage on the basin:

- Coal and saline aquifers on sandstones of the Rio Bonito Formation and Itarare Group
- Black shales of the Irati and Ponta Grossa Formations
- Basalts of the Serra Geral Formation

Other units could also present the potential for CO_2 storage, mainly considering local occurrences and possible structural and stratigraphic traps that could guarantee permanent and safe carbon abatement.

Since there is an essential activity of the biofuels sector in the occurrence area of the Paraná Sedimentary Basin, there is also a potential for the installation of CCS plants coupled with the generation of biofuels like bioethanol, creating BECCS facilities that could deliver neutral or negative emissions.

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