Potential of different industries in Brazil to produce syngas

ProQR
COMBUSTÍVEIS ALTERNATIVOS
SEM IMPACTOS CLIMÁTICOS

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This study was prepared in connection with the project Climate Neutral Alternative Fuels (ProQR) realized through the German-Brazilian Technical Cooperation for Sustainable Development in partnership with the Ministry of Science, Technology, Innovation and Communications (MCTIC) and the Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH. This project is part of the International Climate Initiative (IKI). The Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) supports this initiative based on a decision adopted by the German Bundestag.

The ProQR project has the objective of creating an international reference model for alternative fuels without climate impact for air transport and other sectors without electromobility potential.

Abstract

With the increasing demand for air transport services and the consequential growth of global air traffic registered each year, greenhouse gas (GHG) emissions will most likely rise quickly in the long term. In order to meet the international climate targets set by the Paris Agreement of 2015, the aviation sector set ambitious GHG emissions reduction goals towards carbon neutrality. A promising solution to decarbonise the aviation sector and to reach both the international and national commitments is the use of Sustainable Aviation Fuels (SAF), such as Power-to-Liquid (PtL) kerosene. To reduce aviation emissions in Brazil, the Deutsch Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH and the Brazilian Ministry of Science, Technology and Innovation (MCTI), on behalf of the German Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU), launched the project Climate Neutral Alternative Fuels, also called ProQR, in 2017.

This study addresses the potential of different Brazilian industries to produce syngas with a view to estimating the potential production of PtL SAF through the Fischer-Tropsch (FT) process. A detailed overview of different industries and their suitable feedstock sources for syngas production is also presented, particularly the soybean, biodiesel, sugarcane, ethanol, corn, rice, steel, cement, and pulp industries.

The selected industries were analysed in terms of their production processes in Brazil and the suitable residues and low-value by-products to determine their annual potential for syngas production through a conversion process. It was found that the soybean, corn, and sugarcane industries have the greatest potential for syngas production, followed by the steel, pulp, cement, ethanol, rice, and biodiesel segments. The potentials were then mapped by region and state using a geographic information system which enabled the identification of potential localities for SAF plants. The Central-West region of Brazil, specially Mato Grosso state, and the Southeast region, mainly the states of São Paulo and Minas Gerais, were found to have the greatest potential for syngas production and the most suitable localities for SAF plants.

This study shows that the Brazilian annual production of SAF could potentially reach 193 million tons if we consider the potential syngas production of all industry segments. The geographical location of Brazil, which favours the use of renewable energy sources, combined with the findings regarding the potential production of SAF by the country per year, appears to support the establishment of the extensive role of PtL kerosene in the Brazilian aviation sector.

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List of Acronyms

ABCP	Brazilian Association of Portland Cement *Associação Brasileira de Cimento Portland*
Abiarroz	Brazilian Association of Rice Industry *Associação Brasileira da Indústria do Arroz*
AEL	Alkaline Electrolysis
ANAC	National Civil Aviation Agency *Agência Nacional de Aviação Civil*
ANP	National Agency of Petroleum, Natural Gas and Biofuels *Agência Nacional do Petróleo, Gás Natural e Biocombustíveis*
AR	Availability of the residue
ASTM	American Society for Testing and Materials
BEN	National Energy Balance *Balanço Energético Nacional*
BF-BOF	Integrated blast furnace-basic oxygen furnace
BMU	German Ministry for the Environment, Nature Conservation and Nuclear Safety *Bundesministerium für Umwelt, Naturschutz und nukleare Sicherheit*
BNDES	National Bank for Economic and Social Development *Banco Nacional de Desenvolvimento Econômico e Social*
$CaCO_3$	Calcium carbonate
CaO	Lime (calcium oxide)
CCS	Carbon capture and storage
CCU	Carbon capture and utilization
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
COP	Conference of Parties
CORSIA	Carbon Offsetting and Reduction Scheme for International Aviation
DAC	Direct air capture
DDGS	Distiller's dried grans and solubles
DLR	German Aerospace Center *Deutsches Zentrum für Luft- und Raumfahrt*
DME	Dimethyl ether
EAF	Electric Arc Furnace
EOF	Energy optimizing furnace
EPE	Energy Research Office *Empresa de Pesquisa Energética*
FAO	Food and Agriculture Organization of the United Nations
Fe_2O_3	Iron oxide

Fe_3O_4	Iron ore
FINEP	Financier of Studies and Projects *Financiadora de Estudos e Projetos*
FT	Fischer-Tropsch
GHG	Greenhouse Gases
GIZ	Deutsch Gesellschaft für Internationale Zusammenarbeit
H_2	Hydrogen
H2O	Water
HEFA	Hydroprocessed Esters and Fatty Acids
IABr	Brazilian Steel Institute *Instituto Aço Brasil*
IATA	International Air Transport Association
IBÁ	Brazilian Tree Industry *Indústria Brasileira de Árvores*
IBGE	Brazilian Institute of Geography and Statistics *Instituto Brasileiro de Geografia e Estatística*
ICAO	International Civil Aviation Organization
IEA	International Energy Agency
IGCC	Integrated gasification combined cycle
IPCC	Intergovernmental Panel on Climate Change
KIT	Karlsruhe Institute of Technology
LHV	Lower heating value
LSPA	Statistics of Agricultural Production *Levantamento Sistemático da Produção Agrícola*
MCTI	Ministry of Science, Technology and Innovation *Ministério da Ciência, Tecnologia e Inovações*
MEA	Monoethanolamine technology
MMA	Ministry of the Environment *Ministério do Meio Ambiente*
MME	Ministry of Mines and Energy *Ministério de Minas e Energia*
MSW	Municipal Solid Wastes
PEM	Proton Exchange Membrane
PNPB	Brazilian National Biodiesel Production and Use Program *Programa Nacional de Produção e Uso do Biodiesel*
Proálcool	National Alcohol Program *Programa Nacional do Álcool*
ProQR	Project Climate Neutral Alternative Fuels
PtL	Power-to-Liquid
PtX	Power-to-X
QGIS	Quantum Geographic Information System

RWGS	Reverse Water-Gas Shift reaction
SAC	Civil Aviation Secretary *Secretaria de Aviação Civil*
SAF	Sustainable Aviation Fuels
SEEG	Greenhouse Gas Emission and Removal Estimating System *Sistema de Estimativas de Emissões e Remoções de Gases de Efeito Estufa*
SNIC	National Cement Industry Union *Sindicato Nacional da Indústria do Cimento*
SNG	Synthetic Natural Gas
SOEC	Solid oxide electrolysis cell
TGRBF	Top Gas Recycling Blast Furnace *Reciclagem de Gases de Altos-fornos*
TRL	Technology Readiness Level
UFRJ	Federal University of Rio de Janeiro *Universidade Federal do Rio de Janeiro*
UnB	University of Brasília *Universidade de Brasília*

1. Introduction

On behalf of the German Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU), the Deutsch Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH and the Brazilian Ministry of Science, Technology and Innovation (MCTI) set up the project Climate Neutral Alternative Fuels, also called ProQR, in 2017. ProQR has the objective to reduce GHG emissions from aviation by using alternative fuels, also referred to as Power-to-Liquid Sustainable Aviation Fuels (PtL SAF). Moreover, the project aims to create an international reference model for the application of climate neutral alternative fuels in air transport sectors without potential for electromobility development. To reach this objective, the project includes four components: Demonstration Plants, General Framework, Human Capacity Development and Dissemination (GIZ, 2020).

The key element of the ProQR project will be a pilot plant in Brazil, which produces SAF based on the Fischer-Tropsch (FT) process. The MCTI and the National Agency of Petroleum, Natural Gas and Biofuels (ANP) are the implementation partners on the Brazilian side. The most important partners from the Brazilian public sector are the MCTI, the Financier of Studies and Projects (FINEP), and the Ministry of Mines and Energy (MME), together with the ANP, the Energy Research Office (EPE), the Ministry of the Environment (MMA), the National Civil Aviation Agency (ANAC), and the Civil Aviation Secretary (SAC). On the German side, the German Aerospace Centre (DLR) is substantially contributing to the project. There are also close partners in the academic field, such as the University of Brasilia (UnB) and other stakeholders.

1.1. Motivation

With the current global trend of economic and population growth, the increase of both energy and material demand in the near future is inevitable. As society is built upon a major reliance on fossil-based energy, fuels, chemicals, and materials, the world will soon be facing huge challenges not only as a direct consequence of the extensive consumption but also as a result of the energy security issue. The production of enormous quantities of waste and the continuous increase of anthropogenic GHG emissions are some of these challenges.

To address this issue, 187 countries set themselves a common goal at the United Nations Framework Convention on Climate Change in 2015 (COP21): to keep the rise in global average temperature well below 2°C by 2050 compared to pre-industrial levels (IPCC, 2019). According to the Intergovernmental Panel on Climate Change (IPCC), the immediate adoption of new technologies and innovative solutions, such as carbon-neutral energy and efficient waste management systems, is indispensable to meet the 2°C target (DENA, 2019b; IPCC, 2019). Therefore, a strong decarbonisation process and the adoption of sustainable concepts, such as circular economy, are indispensable in different sectors (DENA, 2019a; Garcia et al., 2019). This study focuses on the data and potentialities related to the aviation sector.

In 2017, the aviation sector accounted for 3% of the global GHG emissions: a total of 859 million tons of CO_2 (DENA, 2019a). With the increasing demand for air transport services and the yearly growth of the global air traffic of approximately 5%, the GHG emissions worldwide will most likely rise rapidly in the long term (DENA, 2019b). Considering this scenario, the International Air Transport Association (IATA) presented a climate protection plan: to increase fuel efficiency by about 1.5% every year, to achieve carbon-neutrality in air travel by 2020, and to halve net CO_2 emissions by 2050 in comparison to 2005 (IATA, 2021).

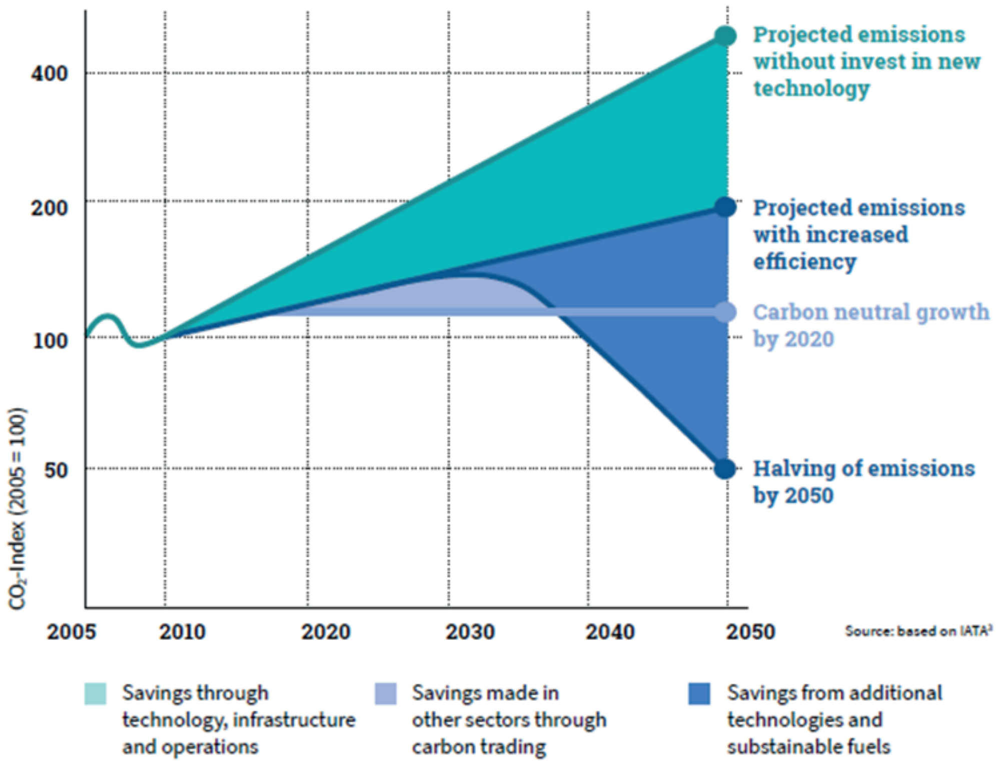

Figure 1: Greenhouse Gas (GHG) emission reduction targets of the aviation sector. Source: DENA (2019b)

This agenda could be achieved by increased efficiency, but this increase would not be enough to halve the emissions by 2050, as can be seen in Figure 1. Efforts and actions related to the use of new technologies and, especially, alternative fuels have proved to be crucial and necessary in the long term (DENA, 2019b). In order to achieve carbon-neutral growth by 2020, the International Civil Aviation Organization (ICAO) implemented the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA), which aimed to stabilize CO_2 emissions from international aviation until effects of the new technologies adopted could be noticed and analysed. From 2021 to 2026, only volunteering countries will be subject to CORSIA offsetting requirements, whereas from 2027 on, carbon compensation projects will be mandatory for all international flights (DENA, 2019a).

In the long term, carbon neutrality can only be reached if new technologies are adopted, together with the substitution of fossil-based aviation fuel (jet fuel) by alternative and sustainable fuels. Alternative fuels are synthetic fuels obtained from renewable energy, water, and carbon dioxide. Solutions like hydrogen or battery-electric approaches are being researched and developed, but it is still unlikely that these technologies can fully replace the existing infrastructure. Due to the high requirements regarding security and safety in the aviation sector and the high investment costs and long lifespan of aeroplanes, SAF is needed to reduce CO_2 emissions by the current generation of fleets (DENA, 2019b).

The most attractive solution to decarbonize the aviation sector and the key factor to reach the climate targets is the use of Power-to-X (PtX) fuels (Carvalho et al., 2019; DVWG, 2018)[1]. The production of synthetic fuel through FT synthesis, using synthesis gas (or syngas) as the main intermediate, stands as a promising option as it is already certified to be blended with the conventional jet fuel and, therefore, does not demand new infrastructure investments. It will be possible to use the existing infrastructure, keeping the capacity to meet the ever-growing demand in the aviation sector (DENA, 2019b). The decarbonisation of this sector not only reduces impacts and consequences on the climate change matter but also ensures profitability for air companies, considering they could be charged through CORSIA for their carbon emissions in the future.

In Brazil, the demand for aviation fuels is already increasing greatly. According to the EPE, this increase will range from 7,2 million tons in 2018 to 14,8 million tons in 2050 (Araujo, 2019). As the demand for aviation fuels in 2050 more than doubles, the production stays nearly constant, which results in growth in aviation fuel imports. Besides this trend, Brazil has the highest aviation fuel costs worldwide, especially due to its remote regions such as Amazonas state (GIZ & MCTIC, 2019). ProQR project was launched considering this particularity and the carbon-neutral growth of the aviation sector.

Brazil is considered a suitable country to produce PtL mainly due to its overall favourable geographical situation regarding renewable sources. The potential for photovoltaic energy generation across the whole country, the constant wind in the Northeast region, and the wide availability of resources give Brazil the chance to be the first distributor of PtL fuels around the world. Also, Brazil's extensive experience in bioenergy and biofuels makes it an important potential player to produce PtL for the aviation sector. The fuel produced in Brazil could be used first to supply the national demand and replace fuel imports. Locally produced fuel could then be exported to countries willing to pay for the carbon-neutral fuel, such as countries in Europe. Figure 2 shows the map of Brazil with an overview of its 5 main regions, its 26 states and the Federal District.

1. PtX fuels can be defined as synthetic fuels produced with renewable electricity. They can be divided into Power-to-Gas (PtG) and Power-to-Liquid (PtL) fuels (DVWG, 2018).

Figure 2: Map of Brazil divided into regions and states. Source: own elaboration

It is important to know which feedstock to use to produce PtL fuels sustainably. In order to contribute to the reduction of GHG emissions, the generation of CO_2 should be avoided in the production of PtL fuels (DENA, 2019b). Therefore, the feedstock should be carbon-neutral itself or unavoidable waste, such as industrial by-products and residues. The utilization of suitable by-products and residues from the industry sector to produce SAF encourages the biorefinery concept and a cooperative relationship between companies and industries known as industrial symbiosis (Aberg, 2014; Patricio et al., 2017). Industrial by-products and residues are converted into high value-added products which, on top of increasing the overall economics and industry efficiency, also ensures the transition into a circular economy (Garcia et al., 2019).

In this study, the potential of different Brazilian industry segments to produce syngas is investigated to further estimate the theoretical potential to generate PtL SAF in the country. Syngas is the initial intermediate in the FT synthesis and can be obtained through the conversion of different feedstock sources. This project aims to generate PtL fuel sustainably by using low-value by-products and residues from the Brazilian industry sector, a solution that does not require changes in the conventional industrial processes. To determine the potential of different Brazilian industry segments, a methodology was developed which is detailed in the next section.

1.2. Methodology

The methodology developed for this study is shown in Figure 3. It has three main steps (in blue) followed by two additional steps (in grey), which lead to additional information regarding the potential of Brazil to produce PtL fuels at national and regional levels.

In the first step, the industries able to produce syngas in Brazil were identified and selected. A waterfall methodology was developed to identify stationary sources for direct and indirect syngas conversion on a national level based on literature review (Figure 4). After that, an evaluation matrix was applied to help select the industries covered in this study.

In the second step, every industry was analysed individually regarding their conventional industrial processes, and the suitable by-products and residues were defined.

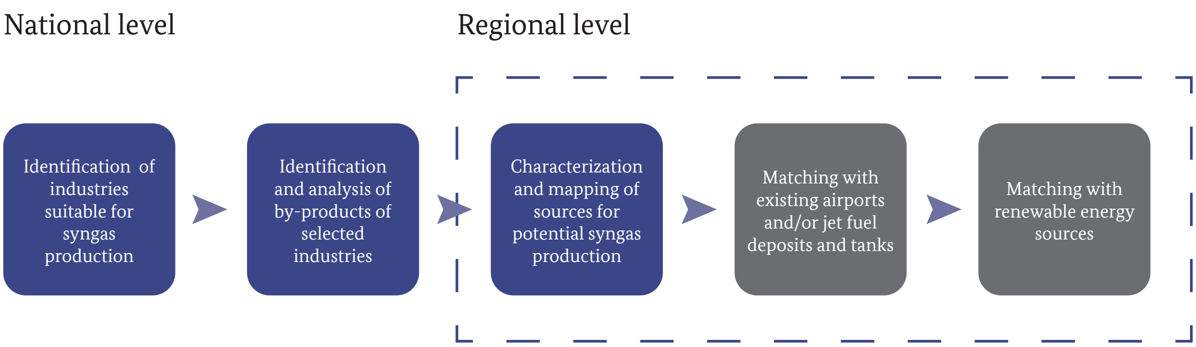

Figure 3: Five-step methodology divided into national and regional levels. Source: own elaboration

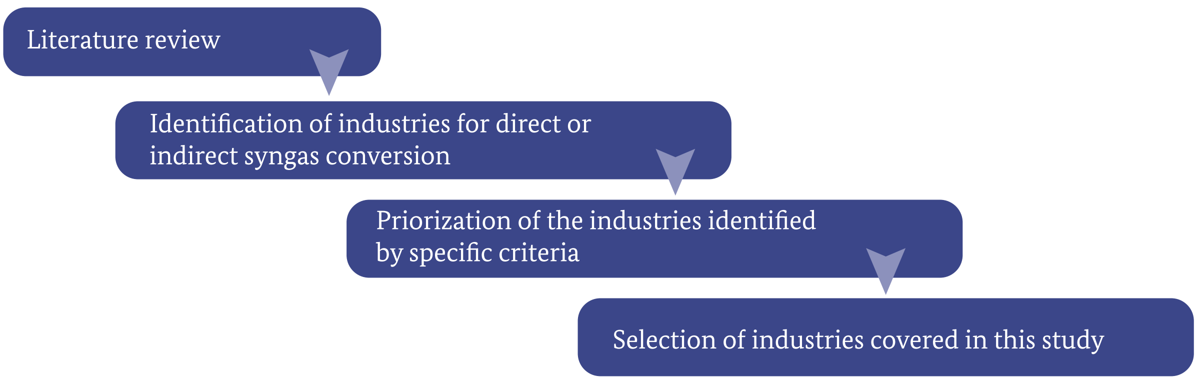

Figure 4: Methodology for the identification and selection of industries for syngas production. Source: own elaboration

In the third step, the potential syngas production of every industry was mapped on a regional level. An evaluation by region and state was performed as shown in Figure 5. Firstly, the by-products and residues selected were determined or estimated by region and state with the support of the EPE database or additional factors identified in the literature. After that, their potential syngas production was calculated by using a reference conversion process. Also, information about requirements, energy demand and the localisation of the industrial plants was collected. With this information, the potential syngas production could be mapped by region and state using a geographic information system (QGIS).

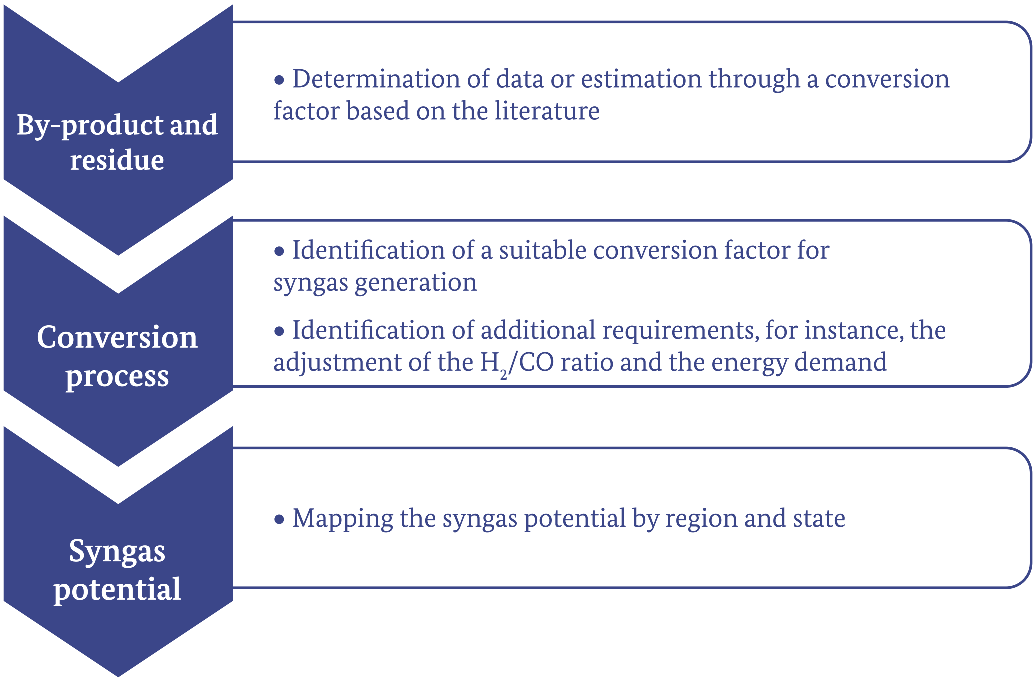

Figure 5: Methodology for the determination and mapping of the potential syngas production. Source: own elaboration

This study is divided into four chapters. In chapter 2, the FT synthesis route is explained in more detail as ProQR is presented. Syngas is examined as a versatile intermediate, its requirements for the FT route are given, and the direct and indirect syngas generation processes are introduced. In this chapter, the conversion processes used to determine the potential syngas production and their energy demands are also presented.

In chapter 3, the direct and indirect feedstock sources identified in Brazil are listed, and the industries are prioritized and selected through an evaluation matrix focusing on a decarbonized future. The industries selected are then studied in more detail by analysing their main processes and suitable by-products and residues for syngas production.

In chapter 4, the potential syngas production is determined after estimating the by-products and residues for every industry by region and state. After this mapping, the industries are compared, and possible locations for the production of aviation fuel by some industries are identified and presented.

In the end, a general conclusion about the topic is given, together with an outline for future studies.

2. State of the art

In this chapter, we present alternative fuels for the aviation sector and explain the FT production route applied within the project ProQR. Followingly, synthesis gas, one of the most important intermediates of the FT production route, is introduced and its requirements for this route are given. The different processes for syngas generation are described, and the conversion processes used in this study are explained.

2.1. Alternative fuels for the aviation sector

Aviation fuels must meet strict international standards. In Brazil, the organization responsible for the regulations for aviation fuels is the ANP. Table 1 presents the main routes for the production of alternative aviation fuels already certified by the American Society for Testing and Materials (ASTM). It also shows the maximum approved blends with conventional jet fuel (Jet A-1).

Table 1: Jet fuel production pathways approved by the ASTM. Source: adapted from Carvalho et al. (2019) and Ebner (2018)

Pathway	Max. Blending	ASTM certification	Approved by ASTM since
Fischer-Tropsch with Aromat(FT-SPK/A)	50%	D 7566 Annex IV	2015
Fischer-Tropsch (FT-SPK)	50%	D 7566 Annex I	2009
Hydroprocessed Esters and Fatty Acids HEFA)	50%	D 7566 Annex II	2011
Alcohol to Jet (ATJ)	50%	D 7566 Annex V	2018
Hydroprocessed Fermented Sugars (SIP)	10%	D 7566 Annex III	2014

The technological pathway applied in ProQR is based on the FT route, which yields high quality synthetic sulphur-free products with a high cetane number and insignificant content of nitrogen, nickel, vanadium, asphaltenes, and aromatics (Resolution 778 of the ANP). While there is a handful of alternative jet fuel production plants on a commercial scale, which mostly follow the HEFA pathway (Carvalho et al., 2019), Brazil could be one of the first countries in the world to produce PtL jet fuel with the FT route. As shown in Table 1, according to directive ASTM D7566-Annex I & IV and Resolution 778 of the ANP, the synthetic fuel produced by the FT route can already be blended up to 50% with conventional Jet-A1 as drop-in fuel.

In DENA (2019b), it is shown that the PtL jet fuel from the FT route needs much less water than other technologies. It is also more favourable than the other technological routes in terms of land use and, therefore, more sustainable. A more detailed description and comparison of the production pathways and aviation fuel certification can be found in Ebner (2018).

Figure 6 shows the main steps of the technological pathway used in ProQR. The Technology Readiness Level (TRL) – which represents the maturity of a technology on a scale from 1 to 9, with 9 being the most mature – of the FT synthesis is 8, and this is often regarded as a key technology for the production of transportation fuels and other liquid products (DENA, 2019b; Ebner, 2018). The technological pathway chosen in the ProQR project uses mainly water (H_2O), carbon dioxide (CO_2), and electricity from renewable energy sources to produce PtL jet fuel. In the decentralized approach shown in Figure 6, CO_2 is captured from ambient air by a Direct Air Capture (DAC) system, and hydrogen (H_2) is obtained from water electrolysis to generate syngas. The processed syngas, which is the main intermediate of the FT pathway, enters the FT reactor, resulting in syncrude. The resulting hydrocarbons are virtually free of impurities, such as sulphur, nickel, nitrogen, vanadium, and asphaltenes (Carvalho et al., 2019). Then, the very long and heavy hydrocarbon chains are cracked into shorter and lighter ones. The resulting substances include gases and liquid hydrocarbons such as diesel, gasoline, and kerosene, which is the focus of ProQR.

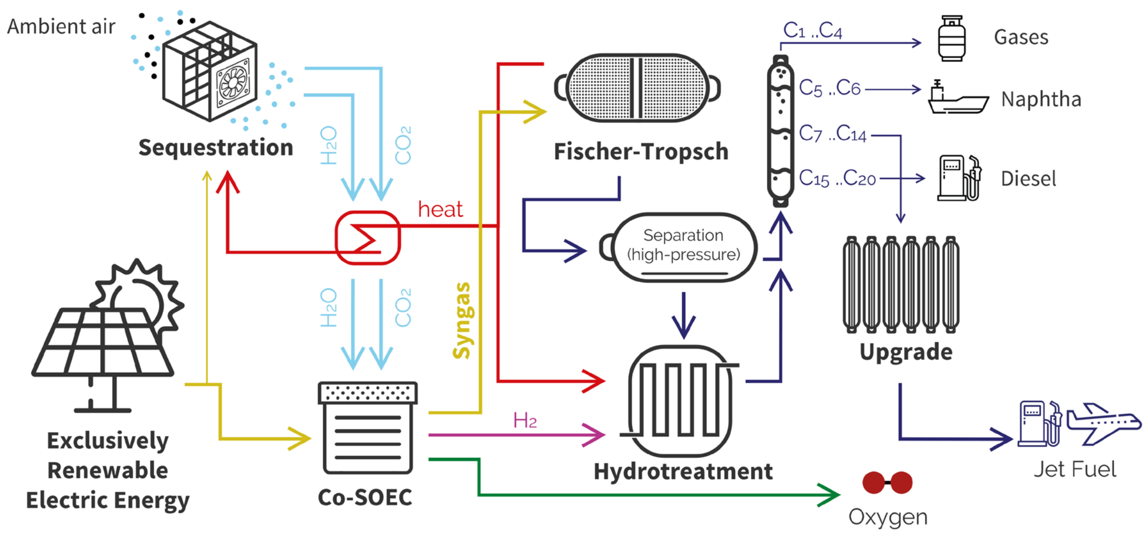

Figure 6: Decentralized approach for the production of SAF by ProQR. Source: GIZ (2020)

Syngas is a versatile intermediate in the process and plays an important role in the production of synthetic fuels, especially in the FT route. Therefore, this study focuses on the potential production of this important intermediate in Brazil. Besides the feedstock and the production pathway shown above, there are other sources and ways to generate syngas. In the following section, syngas and its production pathways suitable for utilization in FT synthesis are described in more detail.

2.2. Syngas production

Syngas generally refers to a gaseous mixture mainly consisting of H_2 and CO, as well as less desired components, such as CO_2, H_2O and CH_4 (Aberg, 2014). It offers many commercial benefits (Figure 7) and can be used not only for power generation, iron and steel manufacturing and synthetic natural gas (SNG) production but also for the production of valuable chemicals, petrochemicals and fuels such as fertilizers/methanol, dimethyl ether (DME), ethylene, hydrogen and ammonia. Moreover, it is used to create FT products, which includes synthetic aviation fuel.

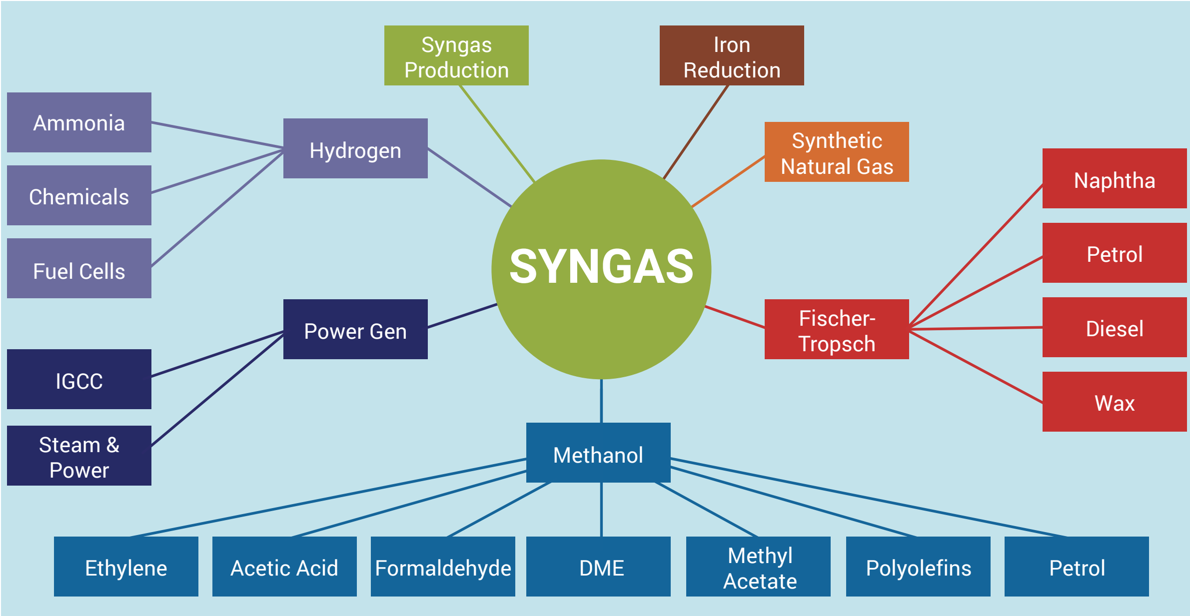

Figure 7: End-products of syngas. Source: Aberg (2014)

Syngas can be generated from a wide variety of carbon-containing raw materials and feedstocks. Feedstock can be fossil-based, such as natural gas, coal, lignite, petroleum, or pet coke, or lignocellulosic biomass, such as woody energy crops, oil crops, organic wastes, forestry and agro-residues and other by-products of agro-industrial processes, and wastes (Aberg, 2014; Carvalho et al., 2019). For carbon-neutral PtL fuels, the feedstock source plays an important role and must be either carbon-neutral by itself or a by-product and/or residue. This study focuses on industrial low-value by-products and industrial unavoidable residues.

Table 2: List of end-products from chemical synthesis of syngas and their requirements for the H_2/CO ratio. Source: adapted from Aberg (2014)

Product	H_2/CO ratio
Methanol	≈2
Ammonia	∞
DME	1
SNG	1.5-3
FT fuels	2
Hydrogen	∞
Alcohols	1-1.5

The exact composition of syngas is hard to predict and depends on several factors, such as the primary feedstock and the conversion process used for its production (Chen et al., 2018). The products derived from syngas have different requirements regarding syngas composition, particularly the H_2/CO ratio and the tolerance for impurities (Aberg, 2014). In Table 2, a list of common end-products from the chemical synthesis of syngas and their required H_2/CO ratio is shown. The optimum H_2/CO ratio of the syngas composition for the FT synthesis in this project is 2/1.

Clean syngas is the basis for the production of various fuels and chemicals. The FT process is a catalyst-driven reaction and has specific requirements on the purity and quality of the syngas produced (see Table 3). It is necessary to remove sulphur and chlorine from syngas to avoid catalyst poisoning. Also, purification steps are often required to prevent catalyst deactivation caused by particles, alkali metals, CO_2 and some catalyst inert gases (Aberg, 2014). The syngas generated must be cleaned and conditioned, if necessary, to remove impurities and adjust the H_2/CO ratio to 2/1.

Table 3: Syngas requirements for the FT process. Source: adapted from Allegue and Hinge (2012)

Impurity	Tolerance level
$H_2S + COS + CS_2$	1 ppmv 0.2 ppm 60 ppb
NH_3 + HCN	1 ppm
HCL + HBr + HF	10 ppb
Alkali metals (Na and K)	10 ppb
Solids (soot, dust, ash)	Essentially completely free
Organic compounds	Below dew point
Hetero-aromatics	1 ppm
Nitrogen and sulphur level	minimized

ppm= parts per million; ppmv= parts per million by volume; ppb= parts per billion

There are various processes for syngas generation from a number of feedstocks. In this study, different syngas production pathways suitable for the FT synthesis from the literature are examined, which are further used to calculate the potential syngas production in Chapter 4. The focus is the generation of H_2 and CO, which can be achieved either separately (indirect syngas production) or combined in one process (direct syngas production). The following section explains these two methods.

2.2.1. Indirect syngas production

In indirect syngas production, H_2 and CO are generated separately and combined in a final conversion process. The reaction $CO_2+H_2 \rightleftharpoons CO+H_2O$, called Reverse Water-Gas Shift (RWGS), is one of the main ways to accomplish this conversion. The efficient conversion of CO_2 into CO depends on the use of catalysts that make the process more selective, i.e., avoid a significant generation of products other than CO. One of those unwanted products is methane (CH_4), which is produced in the methanation reaction that may occur concomitant to the RWGS reaction.

In the following, we present the processes for the generation of H_2 through water electrolysis and CO from CO_2 sources and, after that, we describe in more detail the conversion process for syngas production utilized in this study.

2.2.1.1. Production of carbon dioxide

CO is one of the main compounds of syngas and is converted into hydrocarbons by the FT synthesis (Gonçalves et al., 2017). It can be produced by the conversion of CO_2, which is obtained in two primary ways (DENA, 2019b): DAC and carbon capture from concentrated sources. The purity of the CO_2 obtained is an important requirement for the further conversion process.

It should be mentioned again that in order to contribute to the reduction of GHG emissions and to create carbon-neutral products, no CO_2 should be formed in the generation of synthetic products, such as aviation fuel.

The two primary ways to obtain CO_2 for syngas production are described subsequently.

2.2.1.1.1. Direct air capture

CO_2 can be captured and filtered directly from ambient air. Though ambient air consists mainly of nitrogen and oxygen, its concentration of CO_2 has reached 414 ppm and is increasing. The direct removal of CO_2 helps to achieve the globally desired negative and zero emissions. The capture of CO_2 from the environment is a relatively new technology with a TRL of 6 (DENA, 2019b). Swiss Climeworks (n.d.), the company that developed the first commercial carbon removal technology, is working closely with ProQR, especially regarding the decentral approach (see Figure 6 in Chapter 1).

During the air capture process (Figure 8), the air is drawn into the plant and the CO_2 within the air is chemically bound to the filter. Once the filter is saturated with CO_2, after approximately three hours, it is heated (using mainly low-grade heat as the source of energy) to around 100°C to release the CO_2 from the filter. The CO_2 released is then concentrated and meets the requirements for the following electrolysis with a purity of about 99,9% (Climeworks, n.d.). According to Climeworks, the plant has an energy demand varying between 1500 to 2000 kWh_{th} and 200 to 300 kWh_{el}, and 5 tons of CO_2 can be collected per day with their DAC-36 plant.

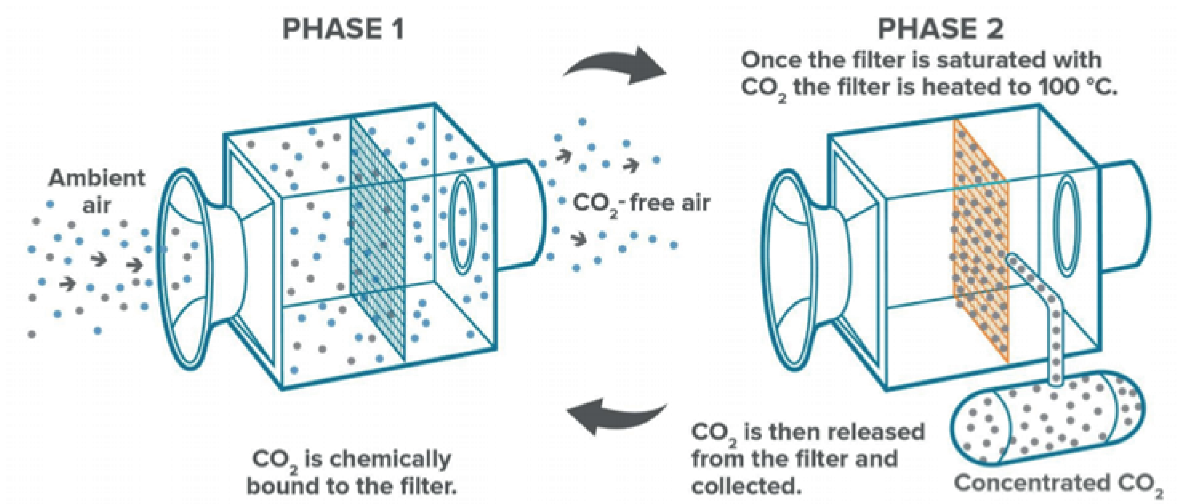

Figure 8: Simplified direct air capture system from Climeworks (n.d.)

2.2.1.1.2. Carbon capture from concentrated sources

CO_2 can also be captured from stationary emission streams. The industrial sector represents a possible carbon source for syngas production. The utilization of unavoidable CO_2 generated by the industrial sector not only contributes to the reduction of GHG emissions but also gives opportunities for industrial symbiosis and biorefinery concepts to develop high value-added products, such as synthetic aviation fuel through syngas. The CO_2 captured from stationary sources must be purified to meet the requirements for the conversion.

There are four main processes to capture CO_2 from concentrated sources: postcombustion, precombustion, oxyfuel combustion, and industrial processes separation (IOGP, 2019). They are described below and illustrated in Figure 9.

In *postcombustion capture*, CO_2 is separated at industrial installations or power plants from the flue gas after the burning of fossil fuels or biomass in the presence of air. Nowadays, the capture of CO_2 by amine-based absorption systems, such as the monoethanolamine technology (MEA), is recognized as a reference technology and is commercially available (IEAGHG, 2017; IOGP, 2019). After being absorbed by the amines, the CO_2 molecules are released by heating or drastic pressure reduction to result in CO_2 with high purity. Postcombustion is among the most used and mature technologies for CO_2 capture from stationary sources and is successfully utilized at an industrial scale (Ketzer et al., 2014).

In *precombustion capture*, CO_2 is separated before the combustion of fossil fuels or biomass. It is a three-stage process. First, the fuel is gasified, which already results in syngas. This is followed by a shift conversion of CO to CO_2 to yield more hydrogen. Finally, the CO_2 is separated to be treated further, and the hydrogen serves as an energy carrier (IEAGHG, 2017). Compared to postcombustion, precombustion capture is not easily upgradable at the existing stationary sources. It has been used mostly in the Integrated Gasification Combined Cycle (IGCC) technology as a clean coal technology.

In *oxyfuel combustion*, pure oxygen is used for the combustion of the fuel instead of air. The flue gas that results from this combustion is CO_2 rich but contains other compounds that require the CO_2 stream to be purified before further utilization (IEAGHG, 2017). In comparison to the postcombustion technology, the oxyfuel technology is still at a precommercial stage.

Several types of *industrial processes* generate CO_2 that can be separated using the capture technologies outlined above or less complex methods in the case of biogenic sources. For biogenic sources of CO_2, also known as high-purity CO_2 sources, the need for purification tends to be smaller if compared to other industrial sources. In this case, the CO_2 only goes through compression steps (IEAGHG, 2017; Restrepo-Valencia & Walter, 2019).

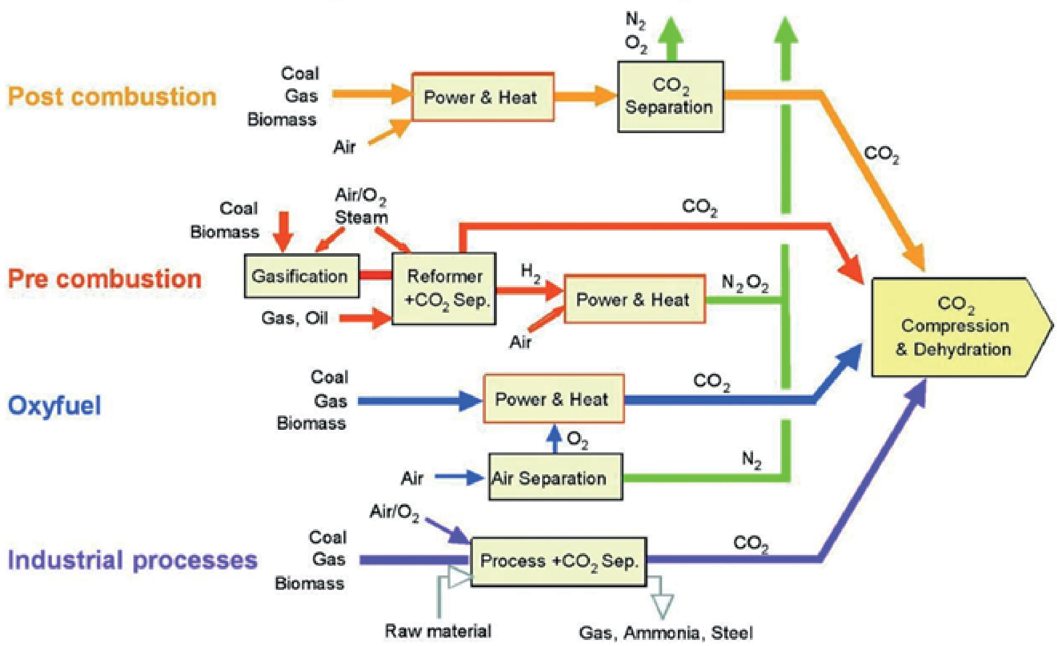

Figure 9: Main CO_2 capture systems. Source: IPCC (2015) and Ketzer et al. (2014).

In this study, amine-based post-combustion is the technology applied for the capture of CO_2 from industrial sources. In comparison to other systems, post-combustion capture is a proven and mature technology that is commercially available and can be easily qualified to be used in existing plants (Kuparinen et al., 2019). According to literature, a conventional MEA capture process can be considered the reference capture method. It has a capture rate of 80% to 90% with a CO_2 purity of about 99%. The energy demand for sorbent regeneration is between 3 to 4 Megajoules (MJ) per kg CO_2 (DVWG, 2018; Kuparinen et al., 2019). For the calculations, this study considers an energy demand of 3.7 MJ per kg CO_2 and a capture rate of 90%.

2.2.1.2. Production of hydrogen

Hydrogen is one of the most ideal energy carriers and has a huge potential for the conception and production of future fuels. However, several difficulties must be faced when establishing its production processes, most of them related to infrastructure – including storage and transport –, which slows down the path of its commercial use. Therefore, synthetic fuels generated through the FT route represent a good alternative not only because of its possibility to benefit from the existing infrastructure in the production process but also due to the opportunity to improve and enlarge its storability (Wang et al., 2016). Hydrogen is one of the main raw materials in the FT synthesis, along with CO. It can be obtained from a wide range of sources, such as natural gas, biomass, and water. Also, it can be a by-product of the industrial production of chlorine, cyanide, and styrene, for instance (IEAGHG, 2017). Due to its deep-seated high value, though, it will not be considered as a possible feedstock source further in this study.

To produce a climate neutral fuel, the hydrogen used must result from water electrolysis powered by renewable energy sources. Currently, alkaline electrolysis (AEL), proton-exchange membrane (PEM) electrolysis and solid oxide electrolysis cell (SOEC) are the three main technologies for the production of hydrogen (DENA, 2019b). During the electrolysis, water splits into hydrogen and oxygen by electrical energy, as shown in the following equation.

$$2\,H_2O \rightarrow 2\,H_2 + O_2$$

The AEL and the PEM electrolysis are low-temperature conversion processes and account for the most common industrial applied technology since both are already used in commercial scales (DVWG, 2018). A more recently developed technology is SOEC, a high-temperature conversion process that holds the promise of greater efficiency and lower energy consumption (DENA, 2019b). This technology has been demonstrated only on a pilot plant scale by companies like Sunfire GmbH in Germany, which is working closely with the ProQR project. SOEC is currently still a less mature technology and demands higher investment costs if compared to the AEL and PEM electrolysis. However, the investment cost of water electrolysis is estimated to fall within the next decades, especially by using SOEC technology. This might happen due to the economics of scale, which goes in hand with a scale-up of plant size and the utilization rate of the conversion plants (DENA, 2019b). In Table 4, the TRL, the efficiency and the energy consumption of the three technologies mentioned are presented. The electrolysis method used in this study is based on SOEC and is described in more detail below.

Table 4: Energy consumption, efficiency and TRL of water electrolysis technologies. Source: adapted from DENA (2019b) and DVWG (2018)

	AEL/PEM	SOEC
(TRL)	9/8	6
Efficiency (%)	41–69	65–95
Energy consumption (MJ/m³)	16.6	15.7

2.2.1.3. Production of syngas by co-SOEC electrolysis

The H_2O and the captured CO_2 must be further converted to form syngas, which can be generated by a separate conversion of CO_2 and H_2O and then mixed, together or simultaneously. During the separate conversion pathway, the H_2O is converted to hydrogen by water electrolysis and the CO_2 is converted to CO through RWGS reaction, as shown below. This reaction uses the hydrogen from water electrolysis to convert the CO_2 into steam and CO (DVWG, 2018). After the separate conversion, the CO and the H_2 are mixed to form syngas.

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{2}$$

CO_2 and H_2O are converted simultaneously into syngas by a solid oxide co-electrolysis (co-SOEC). Besides the hydrogen produced by SOEC, this electrolysis process also converts CO_2 into CO at the same time. The working principle of co-SOEC electrolysis for syngas production is illustrated in Figure 10. The CO_2 and H_2O enter the cell and receive electrons at the cathode, which are supplied from an external renewable power source. This procedure produces syngas, as well as oxygen anions, which are transported across the electrolyte to the anode, resulting in oxygen as a by-product (Wang et al., 2016).

$$\begin{gathered} CO_2 + 2e^- \rightarrow CO + O^{2-} \\ H_2O + 2e^- \rightarrow H_2 + O^{2-} \end{gathered} \tag{3}$$

In addition to the electrochemical reaction at the cathode, the RWGS chemical reaction takes place which reduces the total electrical consumption (Wang et al., 2016).

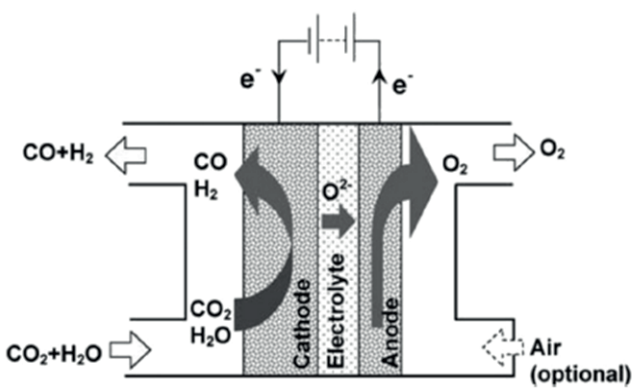

Figure 10: Working principle of co-SOEC electrolysis. Source: Wang et al. (2016)

According to Wang et al. (2016), high-temperature co-SOEC electrolysis is a highly efficient technology for syngas production with low cost and enhanced durability comparatively. To achieve these outcomes, co-SOEC electrolysis requires the previous purification of the CO_2. Once high-purity CO_2 is used, no extra gas cleaning steps are required after the conversion. In this study, due to the advantages of co-SOEC electrolysis, this technology is considered as the conversion process for syngas production. It is presented on Löchle (2019) and Fu et al. (2010) and results in 0,84 kg syngas per kg CO_2. The resulting syngas follows the requirements for the FT synthesis, such as purity or the H_2/CO ratio of 2/1, and generally does not demand further adjustments. The H_2O required in the electrolysis for H_2 production is assumed to be available by then.

As previously mentioned, co-SOEC electrolysis currently entails high investment costs and significant energy demand, but these costs are expected to decrease in the next decades. This technology shows an energy demand of 1,9 kWh_{th} and 5,1 kWh_{el} for each kg of syngas produced (DVWG, 2018).

2.2.2. Direct syngas production

The direct production of syngas means the simultaneous generation of H_2 and CO through a conversion process of feedstock sources. Reforming, pyrolysis, gasification, and co-gasification processes are examples of conversion technologies. According to a literature search regarding the direct production of syngas for the FT synthesis, gasification of biomass and reforming of natural gas or biogas are among the most studied ones so far (Amin et al., 2015; Carvalho et al., 2019; DVWG, 2018; Garcia et al., 2019; Isaksson, 2015; Resolution 778 of the ANP). The gasification and reforming processes are described in more detail in the following sections, and promising conversion processes according to the literature are applied in the calculations related to the syngas potential to be treated in Chapter 4.

2.2.2.1. Gasification of biomass

Gasification is a thermochemical conversion process whereby the partial oxidation of carbon-containing solid or liquid feedstocks by the introduction of either oxygen or steam results in H_2, CO rich syngas (Garcia et al., 2019). Due to its partial oxidation, most of the energy content of the feedstock remains present in the syngas. As a technology, gasification has been known for several centuries and has been used for fuel production through FT synthesis, primarily using coal as feedstock. Today the gasification technology has a TRL of 9 and is a promising process in synthetic fuel production also regarding the conversion of biomass and wastes (Carvalho et al., 2019; Garcia et al., 2019). As this project aims to generate PtL fuel sustainably, only biomass from industrial residues and by-products with low value are considered for syngas production through gasification in this study.

Gasification is only one of several steps to produce syngas for synthesis. The pretreatment of the feedstock (drying, grinding etc.) and the treatment of syngas from impurities are also usually necessary. In Figure 11, a schematic of the gasification technology with a biomass residue stream as feedstock is shown. The pretreatment of biomass feedstock steps, such as drying and torrefaction, are considered of great importance to maximize the conversion efficiency and the fuel characteristics (Garcia et al., 2019). The raw syngas derived from biomass gasification is often polluted by tar, ashes, and other particulate emissions such as nitrogen and sulphur (DVWG, 2018), which must be filtered to meet the requirements for the FT synthesis. Besides this cleaning step, the syngas undergoes a conditioning step to remove CO_2 and other impurities, and the H_2/CO ratio is adjusted (Carvalho et al., 2019). There are different adsorption solutions and technologies for membrane CO_2 removal from syngas, such as the MEA amine adsorption. A summary of CO_2 removal technologies can be found in Allegue and Hinge (2012).

Because supply chain development, waste pretreatment and the treatment of syngas are challenging and energy-intensive, they are usually pointed out as the main barriers to overcome (Garcia et al., 2019).

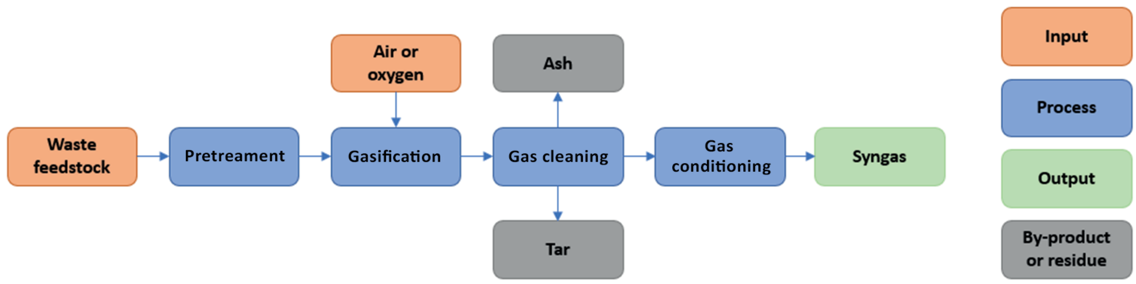

Figure 11: Steps of biomass gasification. Source: adapted from Garcia et al. (2019) and Carvalho et al. (2019)

There are a variety of gasification technologies available and in use, such as fixed bed, fluidized bed, entrained flow, and plasma gasifier. According to the literature, the fluidized bed and the entrained flow gasifiers are the most suitable technologies for the production of synthetic fuel (Carvalho et al., 2019; DVWG, 2018; Resolution 778 of the ANP). In the following, these technologies are briefly described, and the approach adopted in this study for suitable gasification of different feedstocks is presented.

Fluidized bed gasification: the fluidization process occurs when a fluid passes upward through a bed of solid particles and, due to the velocity of this fluid, the particles become suspended in the fluid and behave like a dense fluid (McCabe et al., 1993). The fluidized bed gasifier is a mature technology regarding coal gasification and already commercially available in the case of biomass (Garcia et al., 2019). Fluidized bed gasifiers are a high-efficiency process for the gasification of biomass (Aberg, 2014; DVWG, 2018). Due to the good mixing of the feedstock and oxidant in the bottom part of the bed, this gasification creates an even temperature distribution and has excellent heat and mass transfer (Aberg, 2014). The gasification process usually operates under temperatures between 800°C and

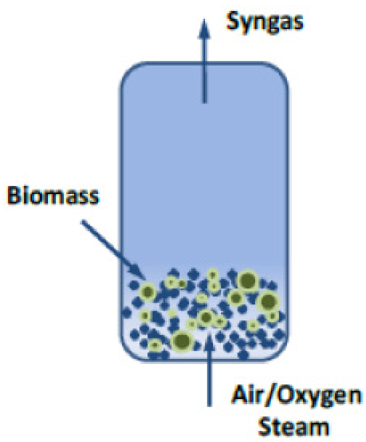

Figure 12: Simplified fluidized bed gasifier. Source: Chhiti & Kemiha (2013).

1000°C and a pressure range between 0 bar and 70 bar. The most common fluidized bed reactors are the bubbling fluidized bed and the circulating fluidized bed (Chhiti & Kemiha, 2013). The low temperatures during the gasification compared to the entrained flow gasification result in quite high tar concentrations, which makes a cleaning step unavoidable (DVWG, 2018). In Figure 12, a schematic of the fluidized bed gasifier is shown. In this kind of reactor, the fluid used is air, steam, or oxygen. Biomass reduced to particle size is inserted and an inert or a catalytic bed material is used to transport heat and mass through the reactor (Chhiti & Kemiha, 2013).

Entrained flow gasification: in this process, the biomass enters in dust form together with air concurrently and they react in a dense cloud of particles at high temperature (Chhiti & Kemiha, 2013). The entrained flow gasifier is commercially operating as a large-scale coal gasification technology (Aberg, 2014); however, there is little experience in such systems in the case of biomass (Chhiti & Kemiha, 2013). The entrained flow gasification with waste biomass only exists in test facilities such as the large-scale pilot plant from the bioliq project at Karlsruhe Institute of Technology (KIT) in Germany (DVWG, 2018; KIT, 2020). For economic reasons, it is necessary to build entrained flow gasifiers only on large scale, which makes it interesting to produce synthetic fuels in large quantities. Figure 13 shows a schematic of the entrained flow gasifier. In comparison to the fluidized bed gasifier, the entrained flow gasifier operates at more severe conditions, such as very high temperatures, between 1200°C and 1500°C, and pressures from 20 bar to 80 bar, which results in syngas almost free of tar and ash melt (Chhiti & Kemiha, 2013; DVWG, 2018). These by-products are collected at the bottom of the reactor in the form of slag. Although an entrained flow gasifier does not require the same cleaning process as a fluidized bed gasifier, it does require pretreatment either by pyrolysis or torrefaction (Allegue & Hinge, 2012).

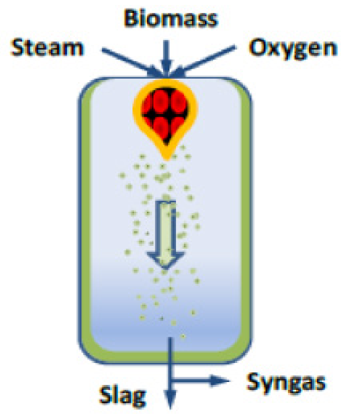

Figure 13: Simplified entrained flow gasifier. Source: Chhiti & Kemiha (2013).

The exact composition of syngas is hard to predict and can vary depending on the biomass feedstocks and the gasification technology used (Chiche et al., 2013). The resulting raw syngas depends fundamentally on gasification conditions, such as operating temperature and pressure, heating rate, type of gasifier, choice of gasifying agent, and feedstock composition (Resolution 778 of the ANP). Several studies have investigated the gasification of biomass waste and residues, but these were mostly done under laboratory conditions.

The two gasification processes presented in DVWG (2018) are used as a reference to achieve a representative comparison between the feedstocks analysed. In Table 5, the parameters of the fluidized bed and the entrained flow gasifier are given.

Table 5: Parameters of the fluidized bed and entrained flow gasifiers. Source: adapted from DVWG (2018)

Parameter	Fluidized bed gasifier	Entrained flow gasifier (bioliq)
Operating temperature (°C)	800–1000	1200–1500
Efficiency (%)	57–96	60.2
Energy demand (kJ/kJ)	0.04	0.29
Syngas composition (%) H_2 CO CO_2 CH_4	 39 29 17 11	 36 53 36 0
H_2/CO ratio	1.34	0.67

For the fluidized bed gasifier, the mean value of 76.5% is considered as the efficiency whereas the entrained flow gasifier from bioliq has an efficiency of 60.2%. The efficiencies given for the processes are related to the heating value. This value itself represents the heat released when the chemical compound is combusted stoichiometrically. With the efficiency of the gasification process and the lower heating values (LHV) of the biomass and the resulting syngas, the amount of syngas generated by every residue is estimated as follows:

$$\eta_{Gasifier} = \frac{LHV_{Syngas} * X_{kgSyngas}}{LHV_{Biomass} * X_{kgBiomass}} \tag{4}$$

The LHVs for the considered biomass are taken from the literature. For the LHV of syngas, which is not available for every biomass, we consider the mean value resulting from biomass waste gasification in other studies (Briesemeister, 2014; Costa et al., 2014; Kosov et al., 2015; Larson, 2004). Therefore, this study assumes an LHV of 9.1 MJ/kg for syngas.

The energy demand shown in Table 5 is related to the output syngas, which results in approximately 0.12 kWh and 0.74 kWh per Nm3 of syngas produced through the fluidized bed and entrained flow gasifiers. A drying process is assumed for the pretreatment whereby for every kg of moisture, a minimum of 2260 kJ is needed to vaporize the water (Adhikari, 2013). With a generally assumed 50% moisture content in the biomass, this results in the energy demand of 0.31 kWh. For the conditioning and adjustment of the H_2/CO ratio, both gasification processes need more H_2 to meet the requirements. This can be done by a water-gas shift reaction or water electrolysis such as PEM (see Table 4).

Besides its advantages regarding low production of pollutants and high CO concentrations in its composition, the entrained flow gasifier is more suitable for large-scale production of synthetic fuel (DVWG, 2018), which is also of interest. Either way, due to that, the fluidized bed gasifier is a mature and already commercially available technology considered for the calculations presented in Chapter 4.

2.2.2.2. *Reforming of methane*

Another method for syngas production besides the gasification of biomass is the reforming of methane, which has been considered as one of the industrially important processes for decades (Amin et al., 2015). Syngas production from natural gas corresponds to the largest market share of the total volume of globally produced syngas (Aberg, 2014).

Three major reforming processes dominate the commercial production of syngas: catalytic steam reforming, which is currently the most used process, followed by partial oxidation and the newer technology of CO_2 reforming. In Table 6, their syngas reactions and corresponding enthalpies are shown (Aberg, 2014).

Table 6: Main methane reforming processes with their syngas reactions and enthalpy. Source: adapted from Aberg (2014)

Reforming process	Enthalpy (kJ/mol)
Steam reforming $CH_4 + H_2O \rightarrow CO + 3H_2$	205.9
Partial oxidation $CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	-35.9
CO_2 reforming $CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247.1

Catalyst steam reforming is carried out in the gas phase and has a high conversion rate (95%), but the reaction is very endothermic and operates at high temperature and pressure, which makes it energy and material-intensive (Aberg, 2014). There are possibilities to cover this heat with the help of the FT synthesis, which is an exothermic reaction. The resulting H_2/CO ratio is often too high for the FT synthesis and must be adjusted (Aberg, 2014). The partial oxidation process takes place in the presence of oxygen and requires a high process temperature. This reforming may operate either with or without a catalyst and produce syngas with a preferable H_2/CO ratio of around 2.

Dry reforming or CO_2 reforming is another process, which provides environmental benefits due to the use of CO_2. For this, the CO_2 must be separated and purified by a carbon capture technology. The catalysts used are greatly affected by carbon deposit, which leads to deactivation and a short life span. The resulting H_2/CO ratio is about 1 and needs further adjustment for the FT synthesis.

Newer approaches have overcome the drawbacks of the reforming processes mentioned above. The tri-reforming process of methane is a combination of the steam, dry and partial oxidation of methane that uses flue gas directly. In this process, the desired H_2/CO ratio can be achieved with lower energy demand (Amin et al., 2015).

The reforming of methane is a mature technology regarding direct syngas production and results in a clean and highly efficient conversion, but is more energy-intensive compared to the gasification process (Rostrup-Nielsen, 2000). Due to that, methane is a high-value product. Since this project aims to generate PtL fuel sustainably in the first place, only biogas as a by-product from industrial processes should be considered for syngas production. Besides methane, other feedstocks can be used to produce syngas, such as the industrial by-product glycerol. In the following section, the conversion of glycerol through reforming and gasification is described.

2.2.2.3. Gasification and reforming of glycerol

Extensive research on the conversion of glycerol into syngas using different gasification and reforming processes has been reported. Glycerol ($C_3H_8O_3$) is a low-value by-product of biodiesel production which will be described in more detail in Chapter 3. The composition of the glycerol generated changes according to different conditions, and the percentage of glycerol content varies for different biodiesel plants.

Glycerol can be converted directly into syngas or used as an additive for syngas production. Glycerol conversion methods applied for syngas production are steam reforming, aqueous phase reforming, partial oxidation, gasification, and supercritical water gasification; besides, more recently developed and adopted methods include dry reforming, pyrolysis, thermal arc plasma or microwave plasma gasification, and co-gasification (He, 2017; Nda-Umar et al., 2019; Plácido & Capareda, 2016; Tomosiunas et al., 2019). In Table 7, recent studies are shown for which the thermochemical process used, the glycerol content, the experimental conditions, and the H_2/CO ratio of the syngas produced are given.

Table 7: Conversion processes of glycerol.

Process	Glycerol content	Conditions	H_2/CO ratio	Source
Catalytic reaction	30%	850°C–1000°C	1.3–1.83	Soares et al. (2006)
Air/O2 gasification	60%	950°C–1500°C Air ratio = 0.4	1.02	Yoon et al. (2010)
Co-gasification with olive kernel	49%	750°C Air ratio = 0.2	1.42	Skoulou & Zabaniotou (2013)
Co-gasification with Hardwood chips	20%	850°C Air ratio = 0.293	0.98	Wei et al. (2011)
Co-gasification with physic nut waste (pnw) or palm shell waste (psw)	30%	700°C–900°C Air ratio = 0–0.6	0.59 (pnw) 0.39 (psw)	Sricharoenchaikul & Atong (2012)
Microwave plasma gasification	100%	Air ratio = 0–0.4 2 kW microwave generator	1.63	Yoon et al. (2013)
Thermal arc plasma gasification	85%	Water vapour 83% Air 17%	2.07	Tomosiunas et al. (2019)

As it can be seen, the H_2/CO ratio varies under different conditions, such as the conversion method used, the glycerol content, and the temperature. Therefore, requirements for the FT synthesis are normally not given, and the syngas needs further product upgrading before being used as raw material. A number of side reactions might also affect the methods to convert glycerol into syngas (Tomosiunas et al., 2019).

Due to the cleaner conversion provided by the reforming process in comparison to the gasification, a steam reforming process of glycerol was adopted in this study. The catalytic steam reformer for the glycerol conversion is taken from Soares et al. (2006) and analysed in Löchle (2019) regarding its potential syngas production suitable for the project ProQR. The reforming process is an endothermic reaction, as shown below:

$$C_3H_8O_3 \rightarrow \; +3CO + \; 4H_2 \qquad \qquad \Delta H = 350 \; kJ/mol \tag{5}$$

Under experimental conditions, the reforming of glycerol with a 30% glycerol content takes place under temperatures of 300°C to 445°C. This reforming process results in 0.43 kg of syngas per kg of glycerol and has an H_2/CO ratio between 1.31 and 1.83, which is shifted to 2/1 by a PEM electrolysis. The energy demand for the conversion of glycerol is about 2.43 kWh per kg of syngas produced in which the ratio is adjusted through a PEM electrolysis, which has an energy demand of 0.54 kWh per kg of syngas produced (Löchle, 2019).

3. Potential feedstocks for syngas production in Brazil

In this chapter, sectors and industries that can serve as sources of feedstock for syngas production are identified through a literature review. Then, the industries are prioritized and selected taking into consideration the Brazilian scenario. An evaluation matrix is used for the selection with a focus on a decarbonized future. Finally, the conventional processes of the industries selected are analysed to identify the by-products and residues suitable for syngas production.

3.1. Sources of feedstock for direct syngas production

In Table 8, potential feedstock sources with their possible conversion processes are shown. The list is a result of a literature review with a focus on stationary sources whose industrial by-products and residues can be converted directly into syngas. All feedstock sources listed are available in Brazil. Although only industrial by-products of low-value and residues are considered in this study, thus excluding fossil fuels, plant biomass, and biogas, the other industries are also mentioned.

Table 8: Sources of feedstock for the direct conversion of syngas and their conversion processes. Source: own elaboration

Source	Conversion process
Fossil fuels	
• Coal, pet coke, petroleum...	• Gasification
• Natural gas	• Natural gas reforming
Plant biomass	Gasification of lignocellulose
Agro-industry	
• Agricultural and animal wastes	• Gasification of biomass
• Bioethanol	• Gasification of bagasse
• Biodiesel	• Reforming or gasification of glycerol
• Biogas	• Reforming of methane
• Forest residues	• Gasification of biomass
Municipal waste	
• Municipal solid wastes	• Gasification
• Wastewater treatment	• Reforming of methane
Pulp and paper industry	Gasification of bark and black liquor

3.2. Sources of feedstock for indirect syngas production

The CO_2 sources for the indirect production of syngas were identified based both on the literature and specific criteria. One criterion is that they should be stationary sites that emit concentrated CO_2 during their industrial processes. According to the IPCC (2005), there are large stationary sources (>0.1 Mt CO_2 per year) and small stationary sources (<0.1 Mt CO_2 per year). As for small stationary sources, this study identified only industries considered as high-purity sources with a CO_2 concentration of 30%-100% (Patricio et al., 2017).

The CO_2 emitted by the industries must be captured by a carbon capture technology to be used to produce syngas (see also Chapter 2). The industries in Table 9 were found in the literature and represent stationary industries that are suitable for Carbon Capture and Storage and Utilization (CCS and CCU). The table also shows the source of emission and the concentration of CO_2 in the flue gas. Small stationary sources like biogas or bioethanol with high purity of CO_2 are included due to the higher partial pressure of CO_2, which makes capturing easier, and their higher commercial maturity of capture technologies (IEAGHG, 2017; Patricio et al., 2017). Except for the DAC, all the industries listed exist nowadays in Brazil but of different importance and size.

Table 9: Sources of feedstock for the indirect conversion of syngas and their sources of emission. Source: own elaboration

Industry	Source of emission	CO_2 Concentration	Source
Agro-industry			
Biogas production	Purification process	99%	IPCC (2005); Patricio et al. (2017)
Bioethanol production	Fermentation process	100%	IEAGHG (2017); IPCC (2005) Patricio et al. (2017); Psarras et al. (2017); von der Assen et al. (2016)
Energy generation from fossil fuels	Gas turbines	3%–4%	IPCC (2005); Patricio et al. (2017)
	Natural gas-fired boilers	7%–10%	IPCC (2005); Patricio et al. (2017); von der Assen et al. (2016)
	Oil fired boilers	11%–13%	IPCC (2005); Patricio et al. (2017)
	Coal-fired	11%–15%	IPCC (2005); Patricio et al. (2017); von der Assen et al. (2016) Psarras et al. (2017)
	IGCC before/after combustion	1%/40%	IPCC (2005); Patricio et al. (2017); von der Assen et al. (2016)
Energy generation from biomass	Gas turbines	3%–4%	IPCC (2005); Patricio et al. (2017)
Waste treatment or incineration	Incineration of waste	10%	Patricio et al. (2017)
Mineral products			
Cement industry	Cement kilns	13%–33%	IEAGHG (2017); IPCC (2005); Patricio et al. (2017)
Lime production	Lime kilns	24%–32%	Psarras et al. (2017); von der Assen et al. (2016)
Glass industry	Various components + heat → CO_2 + glass	7%–12%	Patricio et al. (2017); Psarras et al. (2017)

Metal production Iron and steel industry	Blast furnace/oxygen steel furnace Top Gas Recycling Blast Furnace (TGRBF) Corex	17%–28%	IEAGHG (2017); IPCC (2005); Patricio et al. (2017)
Aluminium production	Hall-Heroult process	3%–10%	Patricio et al. (2017); Psarras et al. (2017)
Ferroalloys	FeMn/FeSl/FeCr	8%–10%	Psarras et al. (2017)
Magnesium	$2MgO + C \rightarrow 2Mg + CO_2$	15%	Psarras et al. (2017)
Zinc	Zinc smelting $ZnO + CO \rightarrow Zn + CO_2$	15%	Psarras et al. (2017)
Chemical industry Ammonia production	Haber-Bosch process	30%–100%	IEAGHG (2017); IPCC (2005); Patricio et al. (2017) Psarras et al. (2017); von der Assen et al. (2016)
Ethylene production		12%	IEAGHG (2017); IPCC (2005)
Ethylene oxide		30%–100%	IEAGHG (2017); IPCC (2005); Patricio et al. (2017) von der Assen et al. (2016)
Hydrogen production	Gas sweetening – refineries	100%	IEAGHG (2017); IPCC (2005); Patricio et al. (2017) von der Assen et al. (2016)
Natural gas processing		100%	IEAGHG (2017); IPCC (2005); Patricio et al. (2017) von der Assen et al. (2016); Psarras et al. (2017)
Carbon black manufacturing		2%–5%	Patricio et al. (2017); Psarras et al. (2017)
Oil refineries onshore/offshore	Boiler/Process furnace	8%–24%	IEAGHG (2017); Patricio et al. (2017); von der Assen et al. (2016)
	Cracker	3%–13%	IEAGHG (2017); Patricio et al. (2017); von der Assen et al. (2016)
Pulp and paper industry	Recovery boiler	7%–20%	IEAGHG (2017); Patricio et al. (2017); von der Assen et al. (2016)
	Energy production	13,3%	IEAGHG (2017); Patricio et al. (2017); von der Assen et al. (2016)
Textile industry	Heating energy Drying process	9%	Patricio et al. (2017)
Beer and wine production	Fermentation process	100%	Patricio et al. (2017)
Air	DAC	400ppm	Climeworks (s.d.); von der Assen et al. (2016)

3.3. Prioritization and selection of industries for syngas production

After being identified as possible sources for the direct and indirect production of syngas, the industries were examined to select those that will be covered in this study. An evaluation matrix was used with three criteria:

- adequate by-products or residues for syngas production;
- existence in a decarbonized future;
- share of industrial production in Brazil and/or the world.

As explained before, the feedstock sources must have suitable residues and/or low-value by-products. Besides, one important criterion in this study results from the question, "Which of the industries will still exist in a decarbonized future?" This future is assumed to be above mid-century. These criteria are used to eliminate industries that have a high chance to be replaced completely in a decarbonized energy system or to change their carbon-based processes, such as the iron and steel industry, which will be able to use hydrogen (Agora Energiewende, 2019). It must be mentioned that this evaluation was conducted to limit the number of possible industries for syngas production in this study. All the industries listed in Tables 8 and 9 are suitable for syngas production and can be further investigated.

The industries identified were categorized according to the question above, as illustrated in Figure 14.

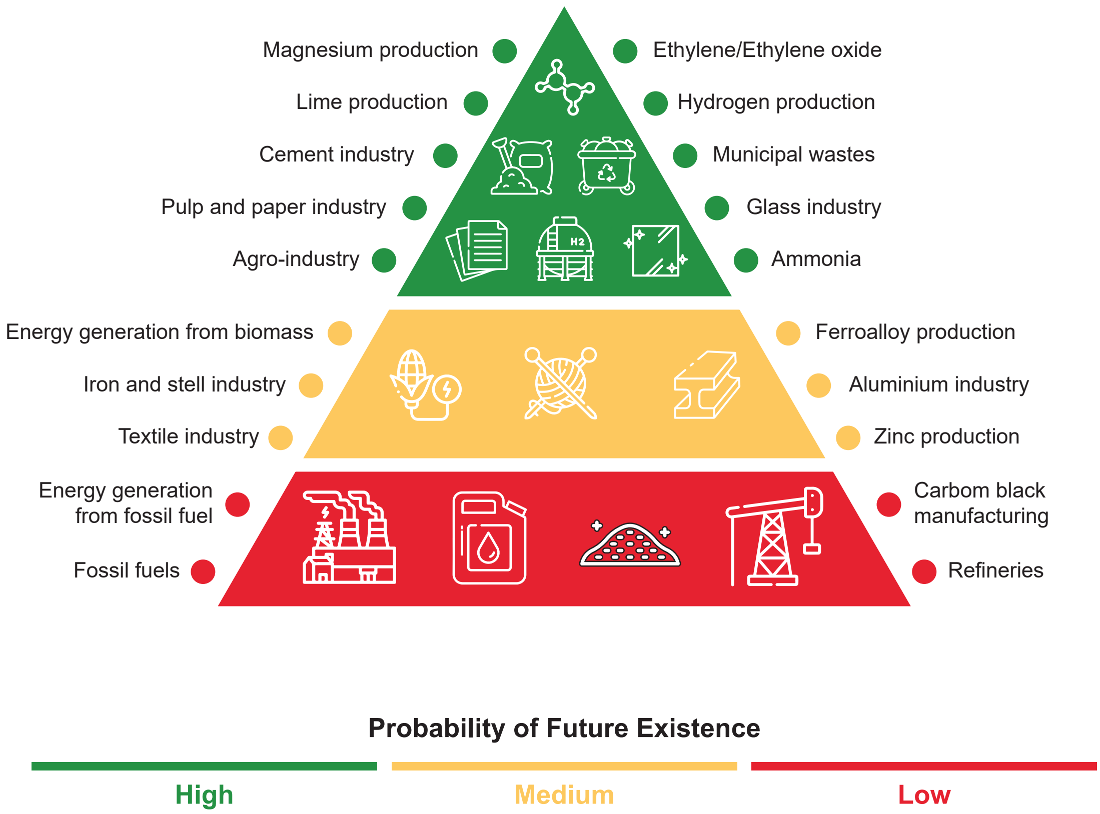

Figure 14: Evaluation of the industries regarding their existence in a decarbonized future. Source: own elaboration

The third criterion is based on the idea that the industrial production process goes along with the possible syngas production. This means that a high production probably generates more residues and therefore implies a higher syngas potential. This last criterion refers to industries which, according to the literature, have suitable by-products and residues for direct or indirect syngas production and are suitable for biorefinery concepts and industrial symbiosis.

Due to the lack of information and literature for some of the industries identified in Brazil regarding the criteria, the indirect sources (see Table 9) are restricted to the stationary industries identified by the *Brazilian Atlas of CO_2 Capture and Geological Storage* (Ketzer et al., 2014). These sources belong to the sectors of energy generation (fossil and biomass), cement, steel, oil refining, ethanol, ethylene, and ammonia, which represent highly suitable industries for carbon capture in Brazil (Ketzer et al., 2014). The production of ferroalloy and aluminium from the metal sector and the pulp industry, which is already represented in the direct generation of syngas, was also evaluated.

Every industry was rated individually by an expert team and their assumptions based on the literature on a scale from 1 to 10, 1 being the least and 10 being the highest. The criteria regarding a decarbonized future were double-weighted in comparison to the other criteria. The results of the evaluation matrix are shown in Table 10.

Table 10: Evaluation matrix for the selection of industries suitable for this study. Source: own elaboration

Industry \ Criterion	Existent in a decarbonized future*	Industrial production share	Suitable by-products and residues	Total
Pulp and paper	10	9	10	9.75
Municipal residues	9	10	9	9.25
Agro-industrial residues				
• Sugarcane, soybean, corn, and rice	10	10	9	9.75
• Bovine, poultry, and swine	10	10	9	9.75
• Forest residues	10	10	9	9.75
Energy generation				
• Fossil fuel	0	6	8	3.5
• Biomass	6	7	8	6.75
Refineries	2	8	9	5.25
Cement	10	9	9	9.25
Iron and steel	8	10	10	9
Ferroalloys (FeMn, FeSi, FeCr)	10	7	10	9.25
Aluminium	9	6	9	8.25
Ethylene and ethylene oxide	9	7	10	8.75
Ammonia	9	5	10	8.25

*In this evaluation, the criteria related to a decarbonized future are double-weighted.

Most of the industries were rated between 8 and 10 in the evaluation matrix except for the energy generation sector and the refineries, which were the lowest rated. This evaluation does not deny the potential of the low-rated industries; however, this study focused on industries that will exist in a decarbonized future, when they could get a lower rating.

In this study, only the industries rated from 9 to 10 were considered. The pulp and paper industry and the agro-industry sector were the highest ranked, followed by the municipal residues, the cement industry, the ferroalloy production, and the steel industry. As for the agro-industry, we took into consideration sugarcane crop, soybean, corn and rice, as well as poultry, bovine and swine, whose residues have the highest potentials to be used according to the literature (Forster-Carneiro et al., 2013). The biodiesel, bioethanol, and biogas production industries were also considered.

Municipal wastes include municipal solid wastes (MSW), waste incineration or biogas from wastewater treatment, which are all potential sources for syngas production. This industry and its potential to produce syngas will be treated by another project in the GIZ and therefore are not further analysed in this study. The potential for animal wastes and the related biogas production, the forest residues, and the ferroalloy production were not included due to lack of information from the industry and/or time. The industries which were analysed in more detail in this study are the following: cement, iron and steel, pulp and paper, sugarcane, bioethanol, soybean, biodiesel, corn, and rice.

3.4. Analysis of the industries selected

Every industry selected was analysed considering the Brazilian context. The suitable by-products and residues for syngas production were defined and a mass flow of the industrial process was determined. In this section, the industries are briefly introduced and their by-products and residues are identified.

3.4.1. Cement industry

Cement as a binder is an essential ingredient for concrete, which is one of the most used manufactured substances on the planet in terms of volume (IEA, 2018). Concrete is used in the construction industry and in infrastructure development to provide clean water, sanitation, and energy. The Brazilian cement industry, organized mainly by the Brazilian Association of Portland Cement (*Associação Brasileira de Cimento Portland*, ABCP) and the National Cement Industry Union (*Sindicato Nacional da Indústria do Cimento*, SNIC), was responsible for 2% of the global cement production in 2014 (IEA, 2018). Since then, the production decreased by nearly 30% as a result of the political-economic crisis (CNI, 2018). Currently, there are 100 cement production plants installed in Brazil with a nominal capacity to produce 100 million tons per year (Visedo & Pecchio, 2019). In 2018, 53.55 million tons of cement was produced, basically 50% of the nominal capacity (Penna, 2019).

Rising global population, urbanisation, and infrastructure development will stimulate the demand for concrete and therefore cement especially in developing countries, like Brazil (IEA, 2018), where this demand has been increasing steadily since 2016 (Penna, 2019). According to the *Technological Roadmap of Cement* published in 2019 by the ABPC and SNIC, the Brazilian cement production is expected to increase in the medium to long-term by 60%–120% in 2050 compared to 2014 due to the high housing and infrastructure deficit in the country and the population growth (Visedo & Pecchio, 2019).

The cement sector is the third-largest industrial energy consumer, with 7% of the global industrial energy use in 2018 (IEA, 2018), and generates by-products and residues which could lead to environmental concern. The main by-product of the cement production process is CO_2 as part of the flue gas. Brazil will increase its cement production for the development of the country but, at the same time, seeks for solutions to improve the efficiency of this production (Visedo & Pecchio, 2019).

However, switching to alternative fuels like biomass or wastes—the current Brazilian substitution level is 15% (REN21, 2019)—and increasing the efficiency still will result in unavoidable GHG emissions through the production process. The use of this by-product could increase the overall economics and the efficiency of cement production and industry. In the following, the production process of cement is analysed to identify by-products that can be used to create value-added products, especially syngas.

3.4.1.1. Cement production process and its by-products and residues

Cement is a non-metallic mineral product of an energy-intensive process. Cement manufacturing is a three-stage process: preparation of raw material, clinker production, and clinker grinding with other components. Cement can be produced either directly at the kiln site with the grinding and blending steps integrated, or at separate grinding and blending plants. There are two basic production routes: the wet or the dry route.

In Brazil, 99% of the cement production plants use the dry route, which consumes less energy compared to the wet process (IEA, 2018; Visedo & Pecchio, 2019). Figure 15 shows a simplified conventional cement production process, divided into its central energy-intensive steps. In the following, the steps on cement production are presented as described by the International Energy Agency (IEA, 2018).

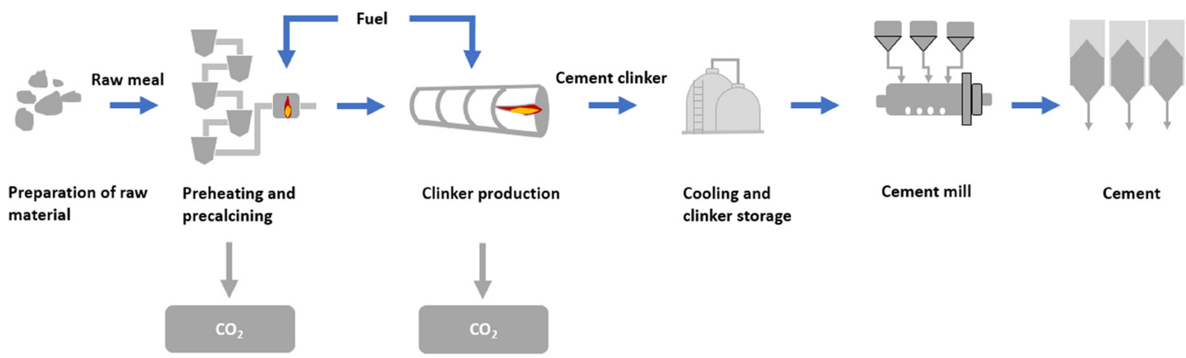

Figure 15: Conventional industrial process of an integrated cement production plant. Source: own elaboration

Calcium carbonate ($CaCO_3$) is the key ingredient in cement production and is provided by natural deposits, such as limestone, clay, or chalk. These raw materials are extracted from quarries often located close to the cement plant. Small amounts of other materials, such as iron ore, clay, or sand may also be excavated to meet the process and product requirements. The mixture of raw materials then gets crushed and homogenized to output a fine powder called raw meal (Oliveira et al., 2016).

The raw meal is passed through a preheater, which is a series of vertical cyclones, up to 900°C by hot flue gas. The preheated raw meal then enters the precalciner, a combustion chamber located at the end of the preheater, where more than 90% of the limestone is chemically decomposed into lime (CaO) and CO_2. The chemical reaction for limestone calcination is shown below:

$$CaCO_3 + heat \rightarrow CaCO + CO_2 \tag{6}$$

The CO_2 emitted in this step can be divided into emissions due to calcination (typically for 60%-70% of the total CO_2 emissions in the cement production) and emissions due to fuel combustion, which in Brazil are mainly fossil fuels such as petroleum coke, diesel, or liquefied petroleum gas. Both source streams are commingled in the off-gas.

In the next step, the precalcined raw meal enters the rotary kiln where fuel is fired directly to reach temperatures of up to 1450°C. The material slides toward the hotter zone and produces the clinker. In the kiln, the remaining calcination is completed, together with process emissions and emissions from the fuel combustion. A by-product of this process is the cement kiln dust, which is composed of micron-sized particles collected from electrostatic precipitators during the production of cement clinker (Mohammad & Hilal, 2010).

The clinker produced in the rotary kiln is cooled down rapidly by a cooler, which blows incoming combustion air into the clinker. The cooled clinker then normally is stored at the plant. From here on, the clinker can be processed further in integrated plants or transported to one of the 38 separate blending and grinding plants in Brazil. The clinker is mixed and blended with gypsum and other materials such as ash or steel slag to form a grey powder known as Portland cement.

In Brazilian cement production, the emissions through fuel combustion represent 36% of the total emissions, while the emissions from calcination have a share of 63% (Visedo & Pecchio, 2019). The remaining 1% emissions are caused indirectly by electricity use, which is relatively low with respect to the renewable share in the electricity mix of the country (Visedo & Pecchio, 2019). According to Visedo and Pecchio (2019), the Brazilian cement industry emits 0.56 ton of CO_2 per ton of cement produced, which is lower compared to the emission factor in most places on the planet. The actual carbon intensity and the direct CO_2 emissions of the Brazilian cement production result from the shares shown in Table 11.

Table 11: Share of CO_2 emissions in the cement production steps. Source: adapted from Visedo and Pecchio (2019)

CO_2 emissions / Process step	Calcination (tCO_2/tcement)	Fuel combustion (tCO_2/tcement)
Precalcining	0.317	0.124
Clinker production	0.035	0.076

3.4.1.2. Mass flow of industrial cement production with suitable by-products and residues

The Brazilian cement industry plays an important role in the development of the country. According to the roadmap elaborated by the ABCP and SNIC in 2019, Brazil is trying to increase the efficiency of its cement industry, especially regarding CO_2 emissions. The capture of the CO_2 emitted and its utilization is also part of the roadmap. The use of CO_2 and the development of value-added products through syngas could increase the product output of the industry and its efficiency. Figure 16 shows the mass flow to produce 1 ton of conventional Portland cement from limestone and small amounts of other materials. The CO_2 emissions of the process are shown at the top, and the mass flow is taken from Wang et al. (2014) and Visedo and Pecchio (2019).

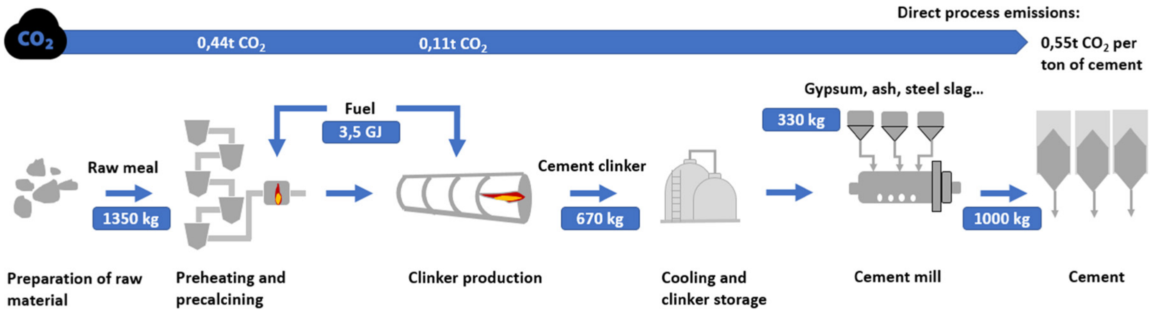

Figure 16: Mass flow of an industrial integrated cement production process. Source: own elaboration

3.4.2. Iron and steel industry

Iron and steel are versatile metallic materials produced in the same process (CNI, 2017, 2018) and applied in sectors such as construction, infrastructure, and the automotive industry. They are used to manufacture different products, equipment, and technologies. The Brazilian Steel Institute (*Instituto Aço Brasil*, IABr) represents all steel production companies in the country. In 2018, Brazil was the world's 9th largest steel producer with a 2% share of the global crude steel output. Currently, there are 32 production units in Brazil, with a nominal capacity of about 51.5 million tons of crude steel per year produced by 12 companies (IABr, 2019). Brazilian crude steel production reached 35.4 million tons in 2018, which represents an increase of 1.7% over the previous years (IABr, 2019).

The iron and steel industry is an energy-intensive sector that accounts for a handful of by-products and residues that are gaining more importance due to the increase in steel consumption and demand in Brazil since 2016 (IABr, 2019). The sustainability of this industry, the optimization of process efficiency, and the recycling of steel and its by-products are goals of the IABr (CNI, 2017). Besides the CO_2 emitted during the production process, wastewater, coke and coal dust, slag, iron powder, sludge and scrap are by-products and residues of the production of iron and steel that raise environmental concern if not managed properly (CNI, 2017; Sarkar & Mazumder, 2015). The use of these by-products and residues increases the overall economics and the efficiency of the production process. In the following section, the steel production process is analysed to identify by-products suitable for the manufacturing of value-added products, especially syngas.

3.4.2.1. Steel production process and its by-products and residues

There are two main routes of steel production: the integrated and the semi-integrated route. The difference between them is that the integrated route has a reduction step of raw materials in a blast furnace. In Brazil, 17 production units are based on the integrated route, with a share of 84.9% of the total crude steel production in 2018, and the other 15 units are semi-integrated (or minimills), using recycled steel with a production share of 15.1% (IABr, 2019). Steel is produced mainly by two different processes in Brazil: the integrated blast furnace-basic oxygen furnace (BF-BOF) or the electric arc furnace (EAF), in case of manufacturing from steel scrap in the semi-integrated route. In Table 12, the existing steelmaking processes and their share in the Brazilian output of crude steel in 2018 are shown.

Table 12: Steelmaking processes utilized in Brazil in 2018. Source: IABr (2019).

Steelmaking process	Crude steel production (tons)	Share (%)
Blast furnace-basic oxygen furnace (BF-BOF)	27,076,000	76.5
Electric arc furnace (EAF)	7,820,000	22.1
Energy optimizing furnace (EOF)	511,000	1.4

In Figure 17, the production process with the highest share in Brazil, that is, the conventional integrated blast furnace process is shown. It consists of three main steps: preparation of raw material, ironmaking, and steelmaking.

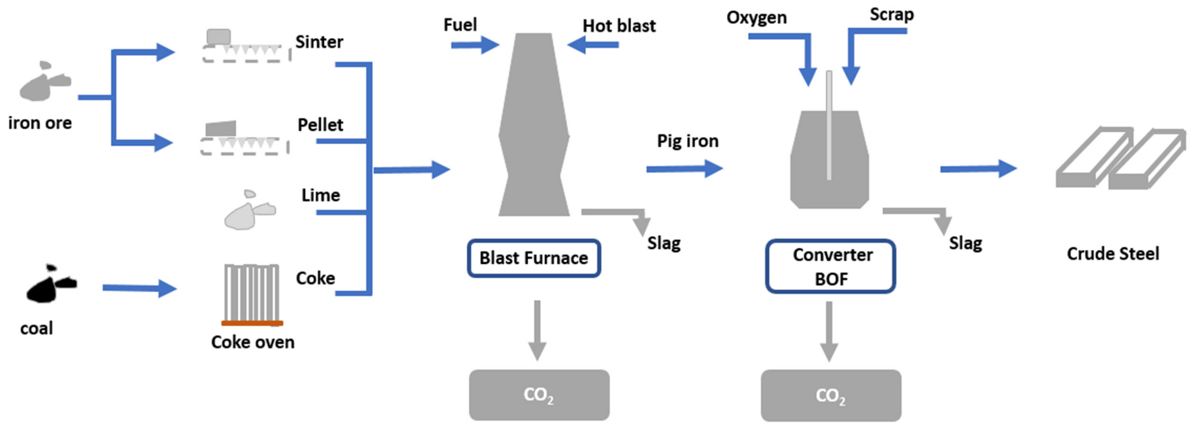

Figure 17: Conventional integrated blast furnace process for steel production in Brazil. Source: own elaboration

Examples of raw materials predominantly used in the integrated BF-BOF processes are iron ore (lump and fine ore), charcoal, limestone, and recycled steel. The first step includes the preparation of the raw material by using pelletiser, sinter plants and a coke oven, which are pollutant and generate solid wastes (Almansa & Kroon, 2016). In a sinter plant, mineral particles are melt, originating an agglomerated porous mass by combustion of a fuel (Ispatguru, 2015). The coke oven is used to produce coke, a solid fuel material required in the smelting process, from coal (American Coke and Coal Chemicals Institute, n.d.). Sinter is especially used to improve the reduction process in the blast furnace. In sinter processing, a mixture of fine ores, coal/coke and lime is ignited by a series of burners in a tunnel bed. The process results in CO_2 emissions and sludge as main by-products (Agora Energiewende, 2019; Sarkar & Mazumder, 2015). Pelletisation is the process of converting iron ore to uniformly-sized iron pellets, which are dried in a rotary kiln by firing (GIZ, 2018). As the fuel and reduction agent in the blast furnace, coke is processed during the carbonization of coal in an oxygen-deficient atmosphere and high temperatures up to 1100°C.

This process results also in CO_2 emissions and solid wastes such as coke and coal dust, sludge, and refractory wastes (Sarkar & Mazumder, 2015). According to Agora Energiewende (2019), the preparation of raw material step is responsible for 0.1 ton of CO_2 per ton of crude steel produced during the whole process. The iron-making process step takes place in the blast furnace unit, where the iron ores (Fe_2O_3 and Fe_3O_4) are reduced to iron in the presence of coke and high temperatures up to 2200°C (Agora Energiewende, 2019). The blast furnaces use primary coal and coke as fuel (IPCC, 2005). The chemical reactions in the blast furnace are shown below. The product of the reaction is called hot metal or pig iron (Almansa & Kroon, 2016).

$$\begin{gathered} 2C + O_2 \rightarrow 2CO \\ 3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2 \end{gathered} \tag{7}$$

The main by-product of this process is CO_2, which accounts for the largest share of CO_2 emissions of the whole production process. Besides the CO_2 in the blast furnace, there is also a big share of CO, which is normally used in the process itself and results again in CO_2 emissions (Agora Energiewende, 2019). The solid wastes generated are slag, flue dust, sludge, and refractory wastes (Sarkar & Mazumder, 2015). The slag produced in the BF represents nearly half of the share of the by-products generated during the whole process (CNI, 2017).

After ironmaking, the iron is converted into crude steel in the BOF. Steelmaking is exothermic and the least consumer of energy in the production process. The BOF reduces the hot metal and, if available, scrap by blowing oxygen at high pressure (GIZ, 2018). During the reduction, CO_2 is emitted and, according to Agora Energiewende (2019), its share is 12% of the total CO_2 emissions in the process. The iron industry is trying to raise its energy efficiency, and most of its by-products are already being recycled and utilized both for the generation of value-added products and as raw materials in other industries.

Currently, nearly 87% of the solid wastes produced are reused either in the process itself or by a third party, like the cement industry or other industries (CNI, 2017). Also, the liquid effluents are reused by up to 95% and result in approximately 5.8 m^3 of effluents per ton of crude steel (CNI, 2017). The CO_2 emitted during the process is the main by-product but is generally not used and released into the atmosphere. However, it can be used as raw material and converted indirectly into syngas.

The emission factor to produce crude steel in Brazil is 1.9 ton of CO_2 per ton of crude steel produced (CNI, 2017). The share of the CO_2 emissions in each step of the process, calculated according to the emission shares in Agora Energiewende (2019), is shown in Figure 18. Especially the steps of the BF and BOF account for the main emissions and are suitable CO_2 capture sources. Besides the integrated blast furnace process, the EAF route accounts for 22.1% of the Brazilian steel production. The minimill in which steel is made by melting scrap steel or scrap substitutes using the EAF route accounts for about 0.3 ton of CO_2 per ton of crude steel produced (Agora Energiewende, 2019), and its electricity is mainly renewable-based (CNI, 2017). Due to its share compared to the blast furnace process, we consider just the BF process for the generation of syngas by the steel industry. The potential syngas production and the regional distribution of the Brazilian steel industry are given in Chapter 4.

3.4.2.2. Mass flow of industrial steel production with suitable by-products and residues

The Brazilian iron and steel industry plays an important role in the development of the country. Brazil is trying to increase the efficiency of the steel production process and is already on its way to a circular economy. The goals of this industry are especially the further use and recycling of its by-products and the reduction of its CO_2 emissions (IABr, 2019). The capture and use of the CO_2 and the conversion to value-added products through syngas could increase the output and efficiency of the industry. To produce 1 ton of crude steel, the integrated route uses 1,400 kg of iron ore, 800 kg of coal, 300 kg of limestone, and 120 kg of recycled steel (Worldsteel Association, 2016). In Figure 18, the mass flow to produce 1 ton of crude steel is shown.

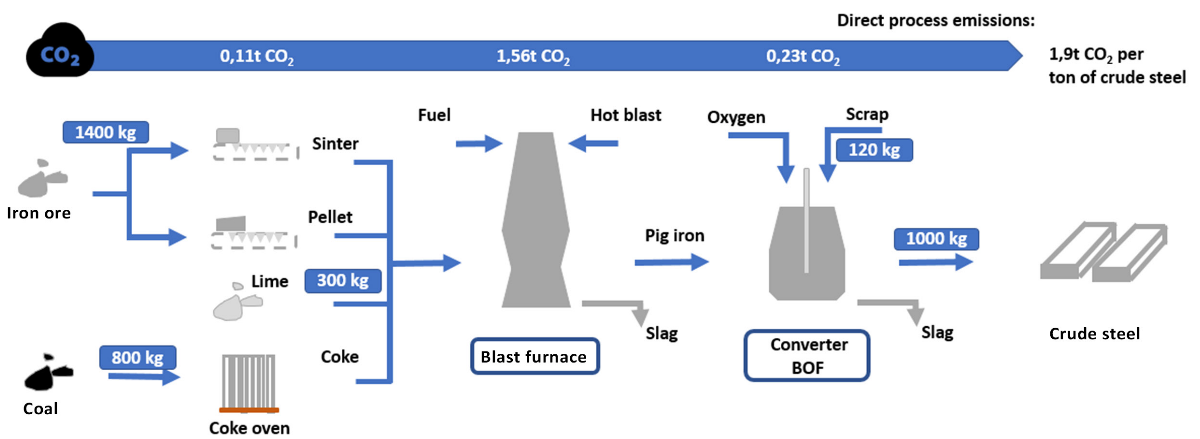

Figure 18: Mass flow of a conventional blast furnace steelmaking process in Brazil. Source: own elaboration

3.4.3. Pulp and paper industry

The pulp and paper industry produces pulp, paper, paperboard, and other cellulose-based products. These products are used in a variety of everyday applications, from paper for writing to paperboard as packaging material. The main material for paper and paperboard is different forms of pulp, which in turn are bio-based and made principally from wood or other raw materials containing cellulose fibres (Roth et al., 2016). In Brazil, nearly 96% of the raw materials used are tree-based. Of the total 7.83 million hectares of trees planted in Brazil in 2018, 36% belonged to the companies in the pulp and paper industry (IBÁ, 2019).

The Brazilian pulp and paper industry is represented by the Brazilian Tree Industry (*Indústria Brasileira de Árvores*, IBÁ). According to IBÁ (2019), Brazil is the second-biggest producer of cellulose pulp and stands out in global trade as the largest exporter worldwide. In 2018, Brazil produced a total amount of 21.1 million tons of high yield pulp, equivalent to an 8% increase over the previous year. From 2012 to 2018, Brazilian pulp production increased by 7.1 million tons, which represents an annual growth rate of 7.1%, mainly due to the expansion of exports to China and European countries (IBÁ, 2019). Brazil ranks eighth among global paper manufacturers with a production of 10.4 million tons in 2018, which represents a slight drop of 0.4% compared to 2017. Paper production, which is mainly for the domestic market, increased 2% between 2012 and 2018 (IBÁ, 2019).

Pulp and paper is one of the most energy-intensive industries in Brazil, with a share of 4.8% of the total energy consumption in the country in 2016 (EPE, 2018). Pulp and paper are internationally used essential commodities, and their production is growing in Brazil especially due to rising export numbers and the favourable climate conditions for the raw materials (DEPEC, 2019; IBÁ, 2019). Brazil is highly efficient and competitive especially in the production of cellulose pulp (Hora, 2017; Hora et al., 2017). To maintain this competitiveness, the Brazilian pulp and paper industry must reposition itself in the market, especially by developing bioproducts in pulp mills (Hora et al., 2017).

The production process of the pulp and paper industry results in the formation of wastewater, waste gases and solid wastes, which lead to environmental concern if not managed properly (Mladenov & Pelovski, 2010). Some of the most significant by-products and residues of the pulp and paper industry are black liquor, sludge, bark, waste chips, boiler ash, and waste emissions, such as CO_2 (CEPI, 2003). Although the residues from the industry have decreased, complete elimination is not feasible (CEPI, 2003). Their use as raw materials in other industries and in a biorefinery concept could increase the overall economics, sustainability, and efficiency of the process to reposition pulp and paper industries in the market (Hora, 2017; Hora et al., 2017). In the next section, the conventional industrial process is analysed to identify the by-products and residues suitable for the manufacturing of value-added products, especially syngas.

3.4.3.1. Pulp production process and its by-products and residues

Pulp and paper mills can either be integrated, producing the pulp and paper on-site, or separated, in which case the pulp is dried and pressed into bales before being transported to paper mills (Roth et al., 2016). The industrial pulp and paper production process can be divided into the following main steps: preparation of wood, pulping, and papermaking.

Preparation of wood: the trees used as raw material in the Brazilian pulp and paper industry are mainly eucalyptus (short fibre), with a consumption of 77 million tons, followed by pines (genus Pinus, long fibre), with 15 million tons. The consumption of eucalyptus and pines represented 98% of the total amount consumed in 2018 (IBÁ, 2019). The trees are cut down from the planted area to wood logs and transported to the production sites. The forest residues are generally left behind to contribute to the soil as nutrients (EPE, 2018). Then the wood logs are debarked, chipped, and shredded to a uniform size suitable for the pulping process. The bark of the logs and the smaller chips, not suitable for pulp production, become by-products and residues. They are reused as biofuel for electricity and heat generation in a biomass boiler by some pulp and paper production mills (EPE, 2018; Kuparinen et al., 2019). Since these by-products are derived from wood and bio-based, they could be thermochemically converted into syngas (Kuparinen & Vakkilainen, 2017; Onarheim et al., 2018).

Pulping: this is the initial stage and the source of most of the by-products generated by the pulp and paper industry. The wood used to make pulp contains cellulosic fibres, lignin, and hemicelluloses. The purpose of pulping is to break down the structure of the fibre feedstock into the constituent fibres. Chemical and mechanical processes are the main steps to separate the cellulose fibres to produce the pulp (EPE, 2018). The chemical process is by far the dominating pulping method globally and represents 95% of the Brazilian production (DEPEC, 2019; IBÁ, 2019). Figure 19 shows a simplified kraft pulp and paper production process, with a focus on chemical pulping.

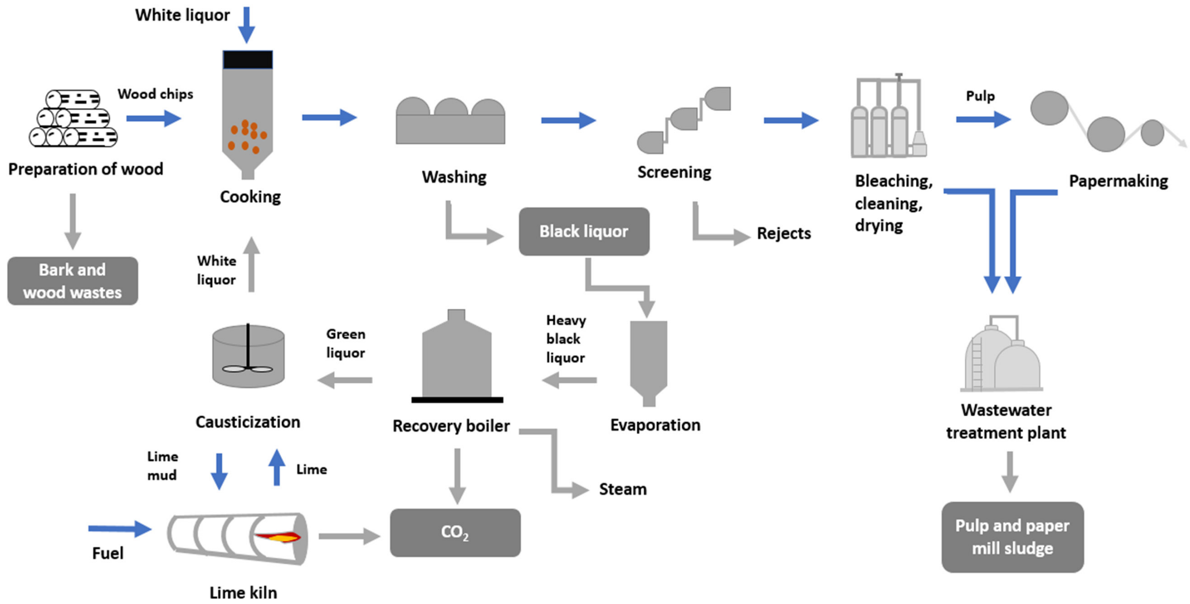

Figure 19: Simplified kraft pulp and paper production process. Source: own elaboration

The most dominant chemical pulping process is the kraft (or sulphate) process, which separates the non-cellulose wood components by adding an alkaline mixture called white liquor into the digester, leaving the cellulose fibres intact (Roth et al., 2016). The so-called cooking step results in a brown stock that is washed in 3–5 stages to remove the pulp from spent cooking chemicals, degraded lignin, and hemicellulose. In this step, a liquid stream called weak black liquor is formed from the degraded lignin and hemicellulose together with the spent pulping chemicals (Tran & Vakkilainnen, 2007).

Black liquor is the major by-product of the pulp and paper production process. In the kraft pulp production process, approximately half of the wood entering the cooking process is converted into pulp, and the black liquor formed is reused and combusted in the recovery boiler (Kuparinen & Vakkilainen, 2017). The black liquor is sent to the kraft recovery system, where the inorganic pulping chemicals are recovered for reuse, while the dissolved organics are generally used as fuel to make steam and power (Tran & Vakkilainnen, 2007). As shown in Figure 19, the black liquor is evaporated to a higher dry solid content before being burned in the recovery boiler.

The recovery boiler produces exhaust gases that are utilized for steam production and result in biogenic CO_2 emissions with a factor of 1.6-2.4 tons of CO_2 per ton of air-dry pulp (Kuparinen et al., 2019). The rest of the liquor left at the bottom of the boiler is dissolved in water to form green liquor. The green liquor is then sent to the causticizing plant, where it reacts with lime from the lime kiln to result again in white liquor and returned to the digestor for reuse in pulping (Tran & Vakkilainnen, 2007). In the lime kiln, fossil fuels are primarily used to reduce lime mud to lime in the presence of high temperatures. The lime kiln is typically fired with oil when the mill is not located near the natural gas grid. The lime kiln is the only unit operation using fossil fuels during normal operations, mostly oil or natural gas, and produces 0.1–0.25 ton of CO_2 per ton of air-dry pulp (Kuparinen et al., 2019).

After the pulping process follows the screening step, whereby the pulp is separated from large shives, knots, dirt, and other debris. The material separated from the pulp is called reject and is reprocessed partly and sent back to the pulping process. After the screening, the pulp can be bleached, cleaned and dried to be further processed to paper in an integrated mill or transported to a paper mill.

Papermaking: in the papermaking process, the pulp is mixed in water with other additives (clay, chalk, or titanium dioxide) into a slurry and further processed into paper. Because the major by-products suitable for syngas production are created before the papermaking process, we will not go into more detail.

Pulp and paper production requires large amounts of water, which produce effluents that need to be treated in a wastewater treatment plant before being released to the environment (Faubert et al., 2016). The by-product of this treatment is an organic residual named pulp and paper mill sludge (CEPI, 2003; EPE, 2018). In general, about 40 kg–50 kg of pulp and paper mill sludge is generated in the production of 1 ton of paper (Cho et al., 2017). The pulp and paper mill sludge can be used for land application, energy recovery, integration in materials, or landfilling (Faubert et al., 2016). Although it is commonly dispatched to landfill, the industry is confronted with more stringent rules and management practices (Cho et al., 2017). There are different methods to treat this organic residue, like anaerobic digestion, fermentation, or thermochemical processes. Among these, the thermochemical processes such as pyrolysis and gasification to syngas hold several beneficial features besides energy recovery.

3.4.3.2. Mass flow of the industrial pulp production with suitable by-products and residues

Pulp and paper, as one of the most energy-intensive industries in Brazil, and the growth in pulp production are encouraging the efforts to increase their efficiency and turn to a circular economy (EPE, 2018). According to the National Bank for Economic and Social Development (*Banco Nacional de Desenvolvimento Econômico e Social*, BNDES), the agenda for pulp is based on the development and application of the concept of integrated biorefineries to make use of its by-products and residues to create value-added products and maintain the competitiveness of the industry in the long run (DEPEC, 2019). The value-added products created through syngas could increase the overall economics and sustainability to reposition this industry in the market. Figure 20 presents a simplified mass and energy flow of a eucalyptus kraft pulp mill located in South America (Kuparinen & Vakkilainen, 2017).

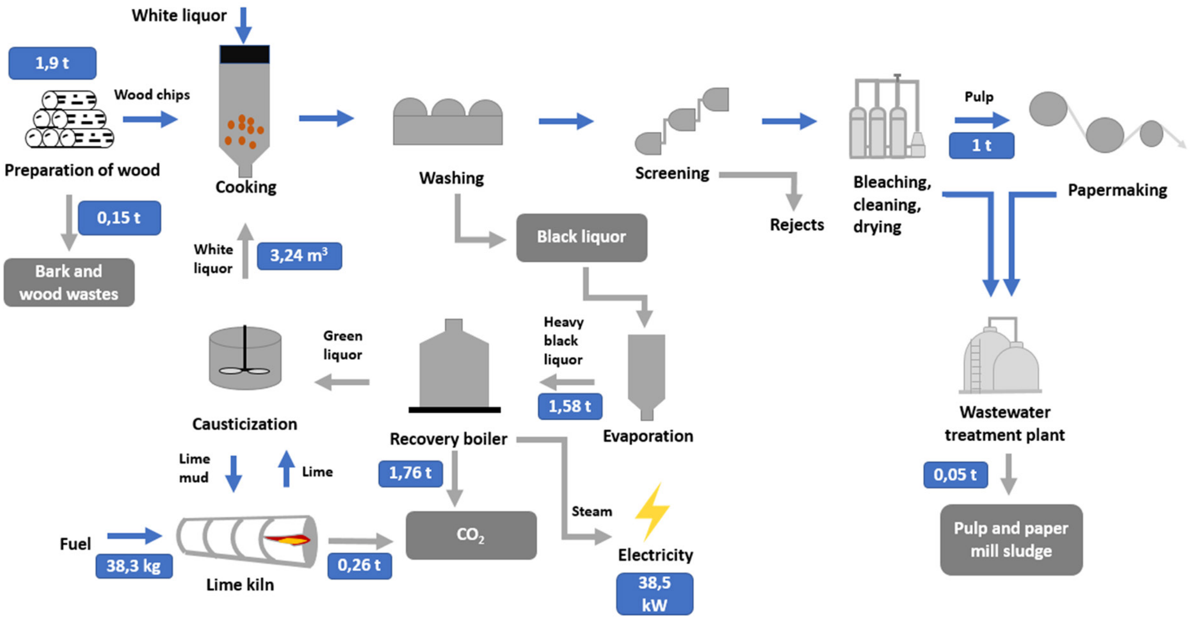

Figure 20: Mass flow of a South American eucalyptus kraft pulp mill. Source: own elaboration

3.4.4. Agro-industries

Brazil is one of the world leaders in the production and exportation of agricultural and animal commodities. The country is important for the global biomass market—it is projected that until 2030 one-third of the products traded will be from Brazil, especially due to the increasing demand in Asia (Forster-Carneiro et al., 2013). The Brazilian agro-industrial sector generates significant biomass through harvesting and processing agricultural products such as sugarcane, soybeans, corn, cotton, rice, wheat, cassava, coffee, and tobacco (Portugal et al., 2014).

According to the Food and Agriculture Organization (FAO), in 2018, Brazil ranked fifth in the world and first in South America regarding annual grain production, with a total output of about 117 million ha per year, especially due to the favourable climate of the country (FAO, 2021). Livestock production in Brazil includes poultry, bovine, and swine, and is mainly extensive, developed in large areas with low application level of technology (Forster-Carneiro et al., 2013). The agro-industrial sector produces large amounts of by-products and residues yearly. These residues can lead to environmental problems and pollution and be harmful to human and animal health if not disposed of properly (Sadh et al., 2018).

Most of the residues are untreated, underutilized, and often disposed of either by burning, dumping, or unplanned landfilling (Sadh et al., 2018). Their use as raw material is becoming more interesting from the economic and environmental point of view. Most of the residues of the Brazilian agro-industrial sector, which are renewable and practically free, and do not threat food availability, represent a potential source of feedstock to produce bioenergy or other value-added products such as syngas (Welfle, 2017). The use of these residues as raw materials could help to reduce production costs, contribute to waste recycling and decrease the environmental impacts of the agro-industrial sector (Sadh et al., 2018).

Examples of agricultural crop residues are leaves, roots, stalks, bark, bagasse, straw, and seeds (Forster-Carneiro et al., 2013). Agricultural residues are generally composed of cellulose, hemicellulose, and lignin, and can be considered as raw materials to produce syngas through thermochemical conversion. In Forster-Carneiro et al. (2013) and Portugal et al. (2014), the potential of agricultural residues and wastes for biorefinery concepts in Brazil was studied. It was concluded that the most promising crops in terms of the potential use of residues are sugarcane, soybean, corn, and rice. In the following, these industries are analysed in more detail.

3.4.4.1. Sugarcane industry

Sugarcane is the most produced crop in the world, with Brazil accounting as the major producer worldwide. Sugarcane, the main feedstock source for the Brazilian sugar and bioethanol industry, is the most harvested product in Brazil, with about 674 million tons in 2018 (IBGE, 2019). Sugarcane production goes in hand with the increasing manufacturing and exportation of sugar and ethanol. In Brazil, the ethanol supply chain is almost always integrated with sugar production (Bajay et al., 2010). In Figure 21, a simplified schematic of a typical first-generation industrial production process is shown.

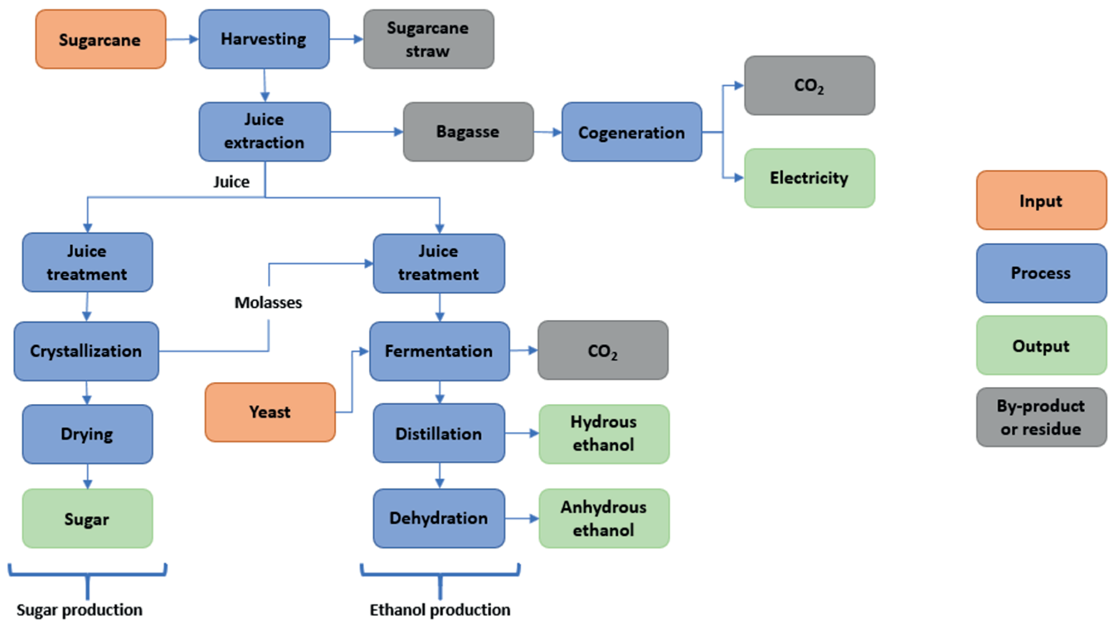

Figure 21: Simplified schematic of a typical first-generation industrial sugarcane conversion process. Source: adapted from Dias et al. (2015) and Fritsche et al. (2016)

Besides the main processes, Figure 21 shows the main inputs and outputs as well as the by-products and residues of the sugarcane industry. Sugarcane processing produces sugarcane straw (leaves and tips) during harvesting, and sugarcane bagasse and CO_2 during sugar and ethanol production, as will be described below.

3.4.4.1.1. Harvesting

Starting with sugarcane cultivation, the harvesting process includes the field operations and the transportation of the crop to the sugarcane mill, which is generally done by trucks and trailers (Lamsal et al., 2013). The main residue during the harvesting process is sugarcane straw. During the field operations, the crop can be harvested manually or mechanically (Sampaio et al., 2019). In manual harvest, the residues are burnt pre-harvest, which enables the manual pickers to collect the crop easier. This burning process has negative impacts on the environment, human health, and the potential energy value of the plant. Mechanical harvest eliminates the need for burning and increases productivity (ELLA, n.d.). A transition from manual to mechanical harvesting is taking place in Brazil, and this residue is gaining more and more importance (Sampaio et al., 2019). Sugarcane straw can be used, instead of burnt, to generate high value-added products through thermochemical conversion such as syngas.

According to Forster-Carneiro et al. (2013), every ton of sugarcane results in 220 kg of leaves and tips, assuming a moisture content of 80%–85% and a residue loss of 30%–50% that remain on the field. In Carvalho et al. (2019), it is reported that every ton of sugarcane results in 0.22 ton of straw with an availability of the residue (AR) of 65%. The EPE also gives information about the factor for estimating sugarcane straw in SI Energy, a model to calculate the energy potential from agricultural residues which assumes that every ton of sugarcane results in 0.14 ton of straw and that only 40% of the sugarcane straw is collected from the fields (EPE, 2021).

Table 13: Factors for the generation of sugarcane straw. Source: own elaboration

Factor (ton)	AR	Source
0.22	100%	Forster-Carneiro et al. (2013)
0.22	65%	Carvalho et al. (2019)
0.14	40%	EPE (2021)

In this study, we calculated the mean of these factors, considering the AR, for the conversion factor. This resulted in a factor of 0.14 ton of sugarcane straw for every ton of sugarcane harvested.

3.4.4.1.2. Sugar and bioethanol production

The main products of the Brazilian sugarcane industry are sugar and ethanol. Brazil has a long history regarding cane sugar exportation and production. Today the country is the world's largest sugar exporter and the second-largest sugar producer after India. A variety of factors in the mid-1970s led in the increasing development and production of ethanol, especially for fuel use (Lago et al., 2012). Ethanol blending in Brazil started with the National Alcohol Program (*Programa Nacional do Álcool*, Proálcool) in 1975. Since then, the ethanol mandate for gasoline has increased from a 4.5% blend in 1977 to a current blend of 27% (E27), resulting in 33.06 billion litres of ethanol produced in 2018—up 15.6% from 2017 (ANP, 2019).

Brazil is the second-largest ethanol producer, right after the United States, and the world leader in ethanol production from sugarcane. The most common sources for first-generation ethanol production are corn and sugarcane. In Table 14, the Brazilian feedstock use for fuel ethanol and their shares in the national ethanol production in 2018 are given (Barros & Flake, 2019). Sugarcane is the main source of feedstock for ethanol production, with a share of 99.5%, followed by corn and sugarcane bagasse, which are used by the few existing second-generation ethanol production plants (ANP, 2019; Barros & Flake, 2019).

Table 14: Brazilian feedstock use for ethanol production in 2018. Source: adapted from Barros & Flake (2019)

Feedstock	Feedstock use (ton)	Share in ethanol production (%)
Sugarcane	404,163,000	99.5
Corn	1,897,000	0.48
Bagasse for cellulosic ethanol	139	0.02

As shown in Figure 21, the raw material for sugar and ethanol production is sugarcane juice, which is extracted by crushing the crops in a milling process. After the juice is treated and removed from impurities, it is used for sugar and ethanol production. During the sugar production, a concentrated residual solution is obtained after sugar crystallization (molasses) which is blended with the sugarcane juice for use in ethanol production (Dias et al., 2015). Ethanol, also called ethyl alcohol (CH_3CH_2OH), is produced by fermentation of the sugarcane juice using yeast. During the fermentation process, a relatively pure stream of CO_2 (99%) is released that can be used as raw material and converted indirectly to syngas.

This CO_2 stream released requires no specific carbon capture technology in atmospheric pressure. Therefore, the capturing of CO_2 from the fermentation process represents a feasible opportunity for conversion into value-added products. According to Restrepo-Valencia and Walter (2019), the fermentation process results in 0.96 kg of CO_2 per kg of hydrous or anhydrous ethanol produced. The hydrous ethanol produced by distillation of the fermentation product can be used directly in ethanol-only engines or by flex-fuel vehicles, which can run on a variable gasoline-ethanol mixture. The anhydrous ethanol with purity over 99% needs an additional dehydration step and is blended with gasoline for use in conventional Otto motor engines (Bajay et al., 2010). Hydrous ethanol is the most consumed biofuel by the Brazilian light vehicle fleet and the main product of the Brazilian ethanol production, with a total output share of 71% in 2018 (ANP, 2019).

Another important by-product of the industrial process is sugarcane bagasse, which results from the crushing and juice extraction of the sugarcane. This by-product is used in sugar mills as fuel to supply their energy demand. The steam and electricity generated during the cogeneration process often not just maintain self-supply but also provide a substantial surplus that is sold to electricity distribution companies or large consumers especially in the offseason (Dias et al., 2015). According to Restrepo-Valencia and Walter (2019) and Forster-Carneiro et al. (2013), every ton of sugarcane results in approximately 0.27–0.28 ton of bagasse with 50% moisture content. In Carvalho et al. (2019), it is assumed that every ton of sugarcane results in 0.22 ton of bagasse with an AR of about 10% due to the cogeneration and self-supply. The cogeneration process results also in CO_2 emissions which can be captured by a carbon capture technology and further used for syngas conversion. In this study, this is categorized as "energy generation from biomass" and is not further analysed according to the evaluation matrix in this chapter.

As the largest biofuel industry in Brazil, the ethanol industry is expected to further expand over the next decade with the 27% blend for gasoline. Especially the growth of the Brazilian ethanol consumption and the RenovaBio policy, which introduces carbon pricing into the Brazilian fuel policy, could lead to even further expansion. The dominant conventional production process (first-generation) results in by-products and residues which can lead to significant environmental and economic problems if not treated properly. The increasing production of first-generation ethanol brings some disadvantages such as growing land use and dependence on the cost of the raw material and the end price of its products (Lenartsson et al., 2014). The second-generation lignocellulosic ethanol plants in Brazil aim at more sustainable ethanol industry, but its growth is rather low (Lenartsson et al., 2014). The most significant by-products and residues of the Brazilian sugarcane industry are sugarcane straw, bagasse, and CO_2.

A biorefinery concept can make use of the by-products and residues as raw materials to produce higher value-added products which could be more economically, socially, and environmentally beneficial for this industry.

3.4.4.2. Soybean industry

Soybean accounts as the second major harvested agricultural crop in Brazil right after sugarcane. In 2018, Brazil was the second-largest producer, right after the United States, and the number one exporter worldwide. Soybean is regarded as one of the most important and profitable export commodities of the country (IBGE, 2019). About 117 million tons of soybean was harvested in Brazil in 2018, an output that is increasing yearly (IBGE, 2019). Alongside the export of soybean, its use as livestock feed or traditional food is a key factor for the increase in Brazilian soybean production. Since the beginning of the 21st century, the biodiesel industry also plays an important role in the Brazilian soybean industry by making use of its by-products. In Figure 22, a simplified schematic of the soybean industry and the interconnected biodiesel industrial production process is shown.

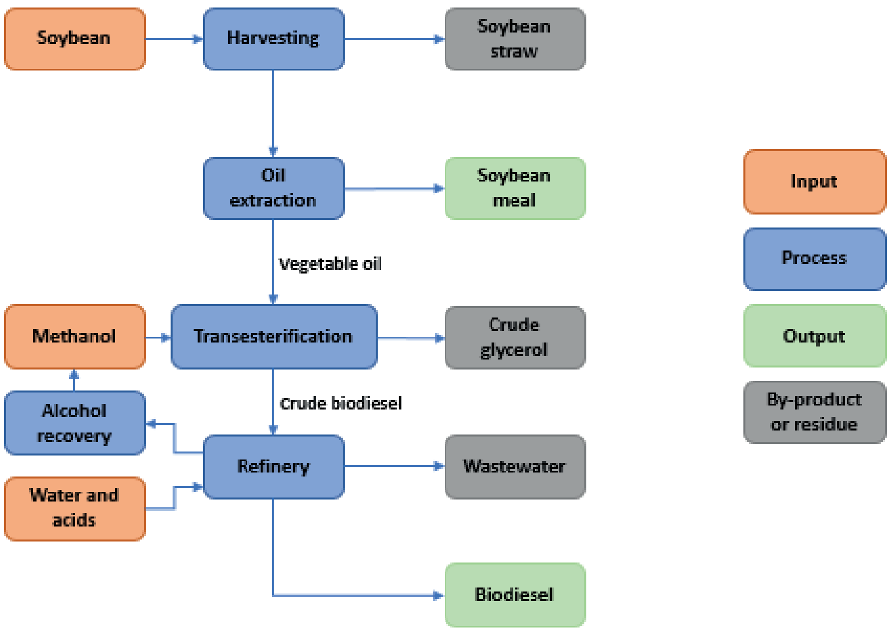

Figure 22: Simplified schematic of the soybean industry and the interconnected biodiesel industrial production process. Source: own elaboration

Besides the main processes, Figure 22 shows the inputs and outputs as well as the by-products and residues of the soybean industry. By-products and residues from the harvest of soybean are soybean straw (Portugal et al., 2014). The vegetable oil resulting from the crushing of the soybean crop harvested is utilized as the main feedstock for biodiesel production, which generates by-products and residues such as glycerol and wastewater. In this study, this industrial process is divided into two parts: harvesting, and the soybean and biodiesel production. Both are discussed in the following.

3.4.4.2.1. Harvesting

The harvesting process results in soybean straw from field operations. These residues include stalks, stems and leaves, which are usually discarded in the field (Portugal et al., 2014). However, soybean straw can be used to generate high value-added products through thermochemical conversion.

According to Forster-Carneiro et al. (2013), every ton of soybean results in 2.05 tons of leaves and tips when assuming a moisture content of 15%–20% and a residue loss of 75% that remain on the field. Carvalho et al. (2019) report that every ton of soybean results in 2.01 tons of soybean straw with an AR of 100%. The EPE also gives information about the factor for estimating the soybean straw in SI Energy, a model to calculate the energy potential from agricultural residues which assumes that 1.68 ton of straw results from every ton of soybean with an AR of 30% (EPE, 2021).

Table 15: Factors for the generation of soybean straw

Factor (ton)	AR	Source
2.05	100%	Forster-Carneiro et al. (2013)
2.01	100%	Carvalho et al. (2019)
1.68	30%	EPE (2021)

In this study, we calculated the mean of these factors, considering the AR, for the conversion factor. This resulted in a factor of 1.52 ton of soybean straw for every ton of soybean harvested.

3.4.4.2.2. Soybean and biodiesel production

As shown in Figure 22, after the harvest, the cleaned soybeans enter the oil extraction process. This is done by mechanical press extraction or solvent extraction, which results in vegetable oil and soybean meal or seed straw and cake. Pressed seed cakes are mainly composed of cellulose, hemicellulose, and lignin, and are generally used in livestock feed. According to the literature, in the extraction process, about 35% of the seeds are converted into vegetable oil and the remaining 65% will remain as seed cake and soybean meal (Santibáñez & Varnero, 2014). According to Santibáñez and Varnero (2014) and Thiagarajan et al. (2018), every ton of soybean produces 0,8 ton of seed cake depending upon the seed quality. The vegetable oil extracted varies from feedstock to feedstock and is the main raw material used in biodiesel production. Both products can be converted thermochemically into syngas, but because only low-value residues or by-products are considered in this study, this will not be an option.

Biodiesel is a mixture of fatty acid alkyl esters obtained from natural lipids such as vegetable oil and/or animal fat through industrial processes of transesterification or esterification reaction using alcohol (methanol or ethanol) in the presence of a catalyst (Mata & Martins, 2010; Nda-Umar et al., 2019; Plácido & Capareda, 2016; Vasudevan & Fu, 2010). Biodiesel is produced from a range of lipid feedstocks that are usually specific to the regional climate and geographical location (Bala-Litwiniak & Radomiak, 2018; Mata & Martins, 2010). Some of the commonly used raw materials for biodiesel production are soybean, cottonseed, palm oil, rapeseed, Jatropha, sunflower, animal fat (chicken, bovine, and swine), and waste oils (Plácido & Capareda, 2016; Vasudevan & Fu, 2010). In Brazil, vegetable oil from soybean is the main feedstock used in biodiesel production. Table 16 shows the feedstocks and their shares in the national biodiesel production.

Table 16: Brazilian feedstock share in biodiesel production in 2018. Source: adapted from ANP (2019)

Feedstock	Share in biodiesel production
Soybean oil	70%
Bovine fat	13.24%
Swine fat	2.14%
Palm oil	1.33%
Cottonseed oil	0.86%
Other*	12.43%

* Includes corn oil, canola oil, cooking oil, chicken, and other fats.

In recent years, there has been a significant increase in the worldwide production of biodiesel (Bala-Litwiniak & Radomiak, 2018; Plácido & Capareda, 2016). The world's five top producers in 2018, in descending order, were the United States, Brazil, Indonesia, Germany, and Argentina (REN21, 2019). Biodiesel production is rising in Brazil since the federal government implemented the Brazilian Biodiesel Production and Use Program (*Programa Nacional de Produção e Uso de Biodiesel*, PNPB) in 2004 (Quispe et al., 2013). Since January 1st 2008, biodiesel has been compulsorily mixed with petroleum diesel fuel and has been participating in the national energy mix (Leoneti et al., 2012). In September 2019, a resolution allowed the use of biodiesel blends of up to 15% with a minimum of 11% mandate. The biodiesel production in 2018 was 5.35 billion litres, up 25% from 2017 (ANP, 2019). Since the mix of biodiesel has been mandatory in Brazil, the average annual growth rate of biodiesel production was 16.44% from 2008 to 2018.

As explained above, the biodiesel production process in Brazil is based on the transesterification alkaline reaction between vegetable oil or animal fat and methanol in the presence of a catalyst (Leoneti et al., 2012). In Figure 23, the overall transesterification reaction of triglycerides is given. In this reaction, 1 mol of triglyceride reacts with 3 moles of methanol to produce 3 moles of methyl ester and 1 mol of glycerol. Although the theoretical stochiometric alcohol/oil molar ratio is 3:1, the suitable alcohol amount may vary for different catalysts and case to case. In Vasudevan and Fu (2010) and Mata and Martins (2010), it is shown that the transesterification reaction of soybean oil with methanol and different catalysts produces a biodiesel yield of around 0.95.

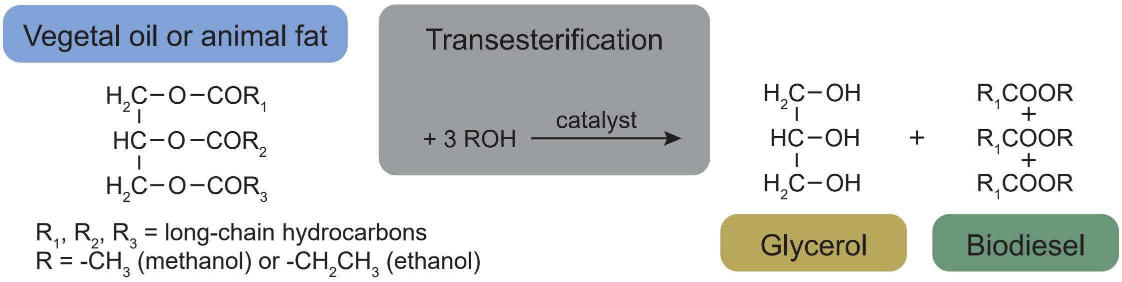

Figure 23: Transesterification reaction of triglycerides into biodiesel and glycerol. Source: adapted from Leoneti et al. (2012)

1,2,3 propanetriol, commonly named glycerol (or glycerine), is one of the main by-products of the transesterification reaction and raises great interest due to its potential to generate large revenue for this industry (Plácido & Capareda, 2016). Glycerol from biodiesel production, also called crude glycerol, is considered an unrefined raw product (Leoneti et al., 2012; Plácido & Capareda, 2016). According to several works from the literature, the production of biodiesel generates approximately 10% of crude glycerol by volume. The crude glycerol is then separated from biodiesel in a tank (Mata & Martins, 2010).

The production and quality of crude glycerol vary for different biodiesel plants. The composition of crude glycerol depends on the type of catalyst, the feedstock used, the efficiency of the process and the recovery of methanol (Nda-Umar et al., 2019). Generally, it is composed of pure glycerol ($C_3H_8O_3$), methanol (CH_3OH), moisture, fatty acid methyl esters, ash, soap, and catalyst salt leftovers. The percentage of glycerol content in crude glycerol varies according to the feedstock. In Table 17, the glycerol content of soybean oil, the main feedstock in Brazil, for different biodiesel production plants is shown.

Table 17: Glycerol content of soybean oil in different biodiesel production plants. Source: Nda-Umar et al. (2019) and Quispe et al. (2013)

Feedstock	Glycerol content
Commercial pure glycerol	99.5%
Soybean oil	67.8%
Soybean oil 1	63.0%
Soybean oil 2	22.9%
Soybean oil 3	33.3%
Waste cooking oil	83.4%

The crude glycerol produced has low quality and low commercial value, and often its purification is considered too expensive for the biodiesel industry (Leoneti et al., 2012; Nda-Umar et al., 2019; Plácido & Capareda, 2016). Due to this, great attention has been paid to the utilization of crude glycerol to create higher-value products. One of these is syngas, which can be produced directly from crude glycerol using thermochemical conversion (Nda-Umar et al., 2019; Plácido & Capareda, 2016).

After the separation of crude glycerol, impurities must be removed in a washing process for the biodiesel to meet the production standards. The remaining impurities consist of oil, methanol, residual catalyst, soap, and glycerol. Before the washing step, the methanol is normally recovered by distillation techniques up to 85% and recycled back to the transesterification process (Plácido & Capareda, 2016). The wastewater from the biodiesel washing process is considered the largest residue and must be treated efficiently before being released into the environment (Plácido & Capareda, 2016). There is no literature found on its possible conversion into syngas. The removal of the impurities generates between 20–120 litres of wastewater for every 100 litres of biodiesel produced (Plácido & Capareda, 2016).

The increasing production of biodiesel in Brazil has led to a parallel increase in by-products and residues, which raises economic and environmental concerns. In light of the concept of biorefineries, a further upgrade of these by-products and residues into higher-value products like syngas could expand the output of the biodiesel industry. With the identification and selection of the most appropriate by-products and residues of the biodiesel process, the potential syngas production can be determined.

3.4.5. Corn industry

Brazil is one of the world's leading corn producers after the United States and China. The country's long growing season allows the cultivation of corn in all regions of Brazil with two harvests per year (Brazilian Association of Rice Industry – Abiarroz, 2021). Corn is one of the most important grains in Brazil. In 2018, about 81 million tons of corn was harvested, especially for domestic livestock feeding (IBGE, 2019). Since 2015, there has been an increase in the use of corn as a feedstock for Brazilian ethanol production (Barros & Flake, 2019). The share of corn as feedstock in ethanol production was 0.5% in 2018. In Figure 24, a simplified schematic of the corn industry and the possible interconnected ethanol industrial production process is shown.

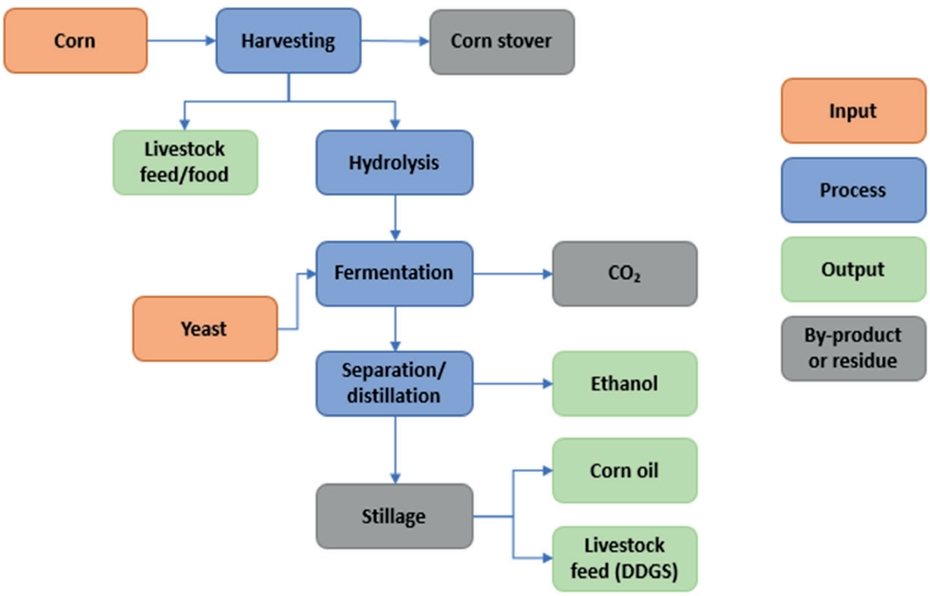

Figure 24: Simplified schematic of the corn industry with its suitable by-products and residues. Source: adapted from Fritsche et al. (2016)

Besides the main processes, Figure 24 shows the main inputs and outputs as well as the by-products and residues of the corn industry. The most significant residues of this industry are those from harvesting. These agricultural residues, or corn stover, include stem, straw, bark, and corn cobs (Forster-Carneiro et al., 2013). The use of corn in ethanol production results in filter cake and distillery wastewater, also known as stillage. After centrifugation, stillage produces corn oil and distiller's dried grains and solubles (DDGS), which are mainly used for animal feed. During the fermentation process, relatively pure CO_2 is emitted. All these by-products and residues can be used to produce high value-added products such as syngas. Due to the share of corn used in the Brazilian ethanol production, only the agricultural residues from harvesting are considered further in this study.

According to Forster-Carneiro et al. (2013), every ton of corn results in 1,46 ton of residues when assuming a moisture content of 25%-30% and a residue loss of 70% that remain on the field. Carvalho et al. (2019) report that every ton of corn results in 1.53 ton of corn stover with 100% of AR. The EPE also gives information about the factor for estimating the corn stover in SI Energy, a model to calculate the energy potential from agricultural residues which assumes that 1.98 ton of stover results from every ton of corn with an AR of 40% (EPE, 2021).

Table 18: Factors for the generation of corn stover.

Factor (ton)	AR	Source
1.46	100%	Forster-Carneiro et al. (2013)
1.53	100%	Carvalho et al. (2019)
1.98	40%	EPE (2021)

In this study, we calculated the mean of these factors, considering the AR, for the conversion factor. This resulted in a factor of 1.25 ton of corn stover for every ton of corn harvested.

3.4.6. Rice industry

After some Asian countries, Brazil is the largest rice producer and consumer. In 2018, nearly 12 million tons of unmilled rice was harvested in Brazil. Though the country exports part of its production, most of the harvested rice is used in domestic consumption (Abiarroz, 2021). The harvest of rice results in agricultural residues such as rice husk and straw, which have a high percentage of organic matter and are suitable residues for the generation of value-added products.

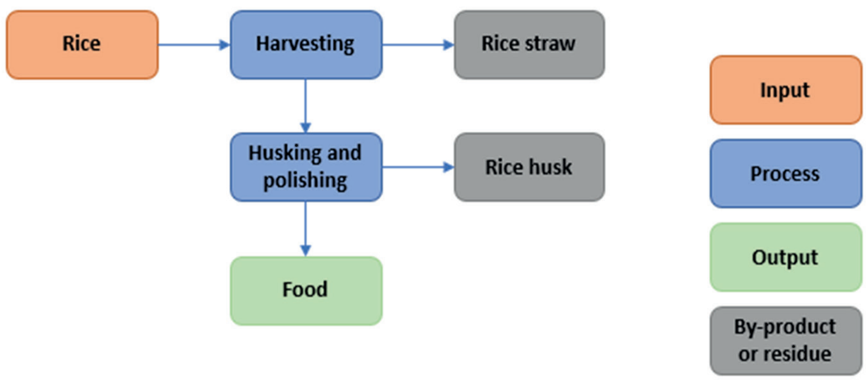

Figure 25: Simplified schematic of the rice industry with its suitable by-products and residues. Source: own elaboration

According to Forster-Carneiro et al. (2013), every ton of rice results in 1.49 ton of residues when assuming a moisture content of 18%-23% and a residue loss of 75% that remain on the field. Carvalho et al. (2019) report that every ton of rice results in 1.54 ton of rice straw with 100% of AR and 0.26 ton of rice husk with an availability of 30%. Every ton of rice harvested results in 1.24 ton of agricultural residues with an AR of 100%. The EPE also gives information about the factor for estimating the rice residues in SI Energy, a model to calculate the energy potential from agricultural residues which assumes that 1.5 ton of agricultural residues results from every ton of rice with an AR of 40% (EPE, 2021).

Table 19: Factors for the generation of rice straw and husk

Factor (ton)	AR	Source
1.49	100%	Forster-Carneiro et al. (2013)
1.24	100%	Carvalho et al. (2019)
1.50	40%	EPE (2021)

In this study, we calculated the mean of these factors, considering the AR, for the conversion factor. This resulted in a factor of 1.24 ton of agricultural residues for every ton of rice harvested.

4. Potential syngas production of the industries selected in Brazil

In this chapter, the potential syngas production of every industry is mapped by region and state according to the methodology described in Chapter 1. Firstly, the by-products and residues selected are estimated by region and state. The factors for residue generation identified in the previous chapter are summarized in Annex Table 1. It should be reminded that this study only considers the low-value residues or by-products whose industrial processes are not changed. After estimating the by-products and residues, their potential syngas production is calculated by using one of the conversion processes described in Chapter 2. Eventually, the potential syngas production mapped by region and state is further analysed.

4.1. Cement industry

In Chapter 3, we identified the by-products and residues from the Brazilian cement industry. The CO_2 emission in the flue gas resulting from the calcination process and the fuel combustion for the clinker production can be captured and converted into syngas. There was no literature found on the use of cement kiln dust to produce syngas.

In Figure 26, the distribution of the cement industry in Brazil is shown. At the moment, there are 100 production plants in 24 Brazilian states. Especially the Southeast region covers a large area in terms of cement production plants. Out of the 100 plants, 62 are integrated plants (green dots), and the rest are separate blending and grinding plants that do not include clinker production (red dots) (Visedo & Pecchio, 2019).

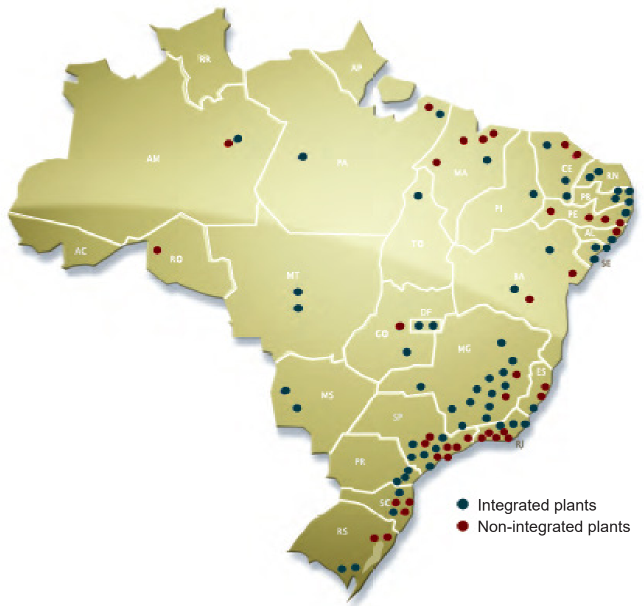

Figure 26: Distribution of the Brazilian cement industry by integrated plants and non-integrated plants. Source: Visedo & Pecchio (2019)

4.1.1. Estimation of by-products and residues

To estimate the amount of CO_2 emitted by the Brazilian cement industry, data were taken from the SNIC (2018), which updates information regarding the regional cement production yearly. The emission factor was retrieved from the *Technological roadmap of cement* (Visedo & Pecchio, 2019) and consists of 0.55 ton of CO_2 per ton of produced cement, considering only the direct emissions in integrated plants. Table 20 shows the regional distribution of the cement production and the estimated CO_2 emissions in 2018.

Table 20: Cement production and estimated CO_2 emissions by region and state. Source: SNIC (2018) and own elaboration

Brazilian region and state	Production of cement (million tons)	CO_2 emission (million tons)
North	**2.49**	**1.37**
Rondônia	(0.22)*	-
Acre	-	-
Amazonas	0.51*	0.28
Roraima	-	-
Pará	0.89	0.49
Amapá	-	-
Tocantins	0.68	0.37
Adjustments	0.41	0.23
Northeast	**10.85**	**5.967**
Maranhão	0.32	0.17
Piauí	-	-
Ceará	2.22	1.22
Rio Grande do Norte	0.81	0.45
Paraíba	2.32	1.27
Pernambuco	20 .0	0.011
Alagoas	0.047	0.026
Sergipe	1.86	1.03
Bahia	1.01	0.55
Adjustments	2.06	1.13
Southeast	**25.37**	**13.95**
Minas Gerais	12.74	7.00
Espírito Santo	0.75	0.41
Rio de Janeiro	2.34	1.28
São Paulo	5.16	2.84
Adjustments	4.38	2.41
South	**8.81**	**4.85**
Paraná	6.06	3.36
Santa Catarina	1.36	0.75
Rio Grande do Sul	1.31	0.73
Adjustments	0.060	0.033

Central-West	**6.04**	**3.32**
Mato Grosso do Sul	0.62	0.34
Mato Grosso	1.18	0.65
Goiás	1.72	0.94
Distrito Federal	2.53	1.39
Brazil	**53.55**	**29.45**

*Considering that the clinker production of the state of Rondônia takes place in the state of Amazonas.

The data published by the SNIC also include estimations of non-associated integrated plants and mixers which will only be considered at the regional level. The data do not distinguish between cement produced in integrated plants or by blend and grinding plants, which do not produce clinker by themselves. Regarding the distribution of the plants in Brazil (see Figure 26), Rondônia is the only state that has only a grinding plant and does not produce clinker. In this case, it is assumed that the clinker is transported from the nearest state of the same region, Amazonas. For all the other blend and grinding plants, it is assumed that the clinker is produced in the same state.

The Southeast region leads by far the cement production in Brazil with a share of 47% (and consequently the CO_2 emissions), followed by the Northeast with 20%. A comparison of the total CO_2 emission with the yearly updated database of Greenhouse Gas Emission and Removal Estimating System – Brazil (*Sistema de Estimativas de Emissões e Remoções de Gases de Efeito Estufa*, SEEG) shows a difference of 1.9 Mt CO_2 in the emissions estimated (SEEG, 2018).

4.1.2. Syngas production

From the estimated regional CO_2 emissions by the industrial process, the potential syngas production is determined through an indirect conversion process, the co-SOEC electrolysis. The CO_2 emissions in the cement production process from both source streams are combined in the flue gas. To be used, the CO_2 in the flue gas must first be separated and cleaned by a carbon capture technology (see Chapter 2). The application of pos-tcombustion technology has received great attention and is potentially suitable for old and newer cement plants (IEAGHG, 2017).

According to Oliveira et al. (2016), which assessed the carbon capture potential in the Brazilian cement sector, the only commercially available capture technology for the existing plants in Brazil is based on the post-combustion capture route, relying on chemical absorption. Therefore, in this study, the post-combustion technology is considered to capture the CO_2 from cement plants for syngas production.

In Chapter 2, this post-combustion carbon capture technology was described which has a capture efficiency of 90%. With the conversion factor of the co-SOEC electrolysis process considered in this study (see also in Chapter 2), the potential syngas production by region and state is determined. According to this process, every kg of CO_2 results in 0.84 kg of syngas.

Table 21: Syngas production of the cement industry by region and state. Source: own elaboration

Brazilian region and state	CO2 emission after capturing (million tons)	Potential syngas production (million tons)
North	**1.23**	**1.03**
Rondônia	-	-
Acre	-	-
Amazonas	0.25	0.21
Roraima		-
Pará	0.44	0.37
Amapá	-	-
Tocantins	0.33	0.28
Adjustments	20.0	0.17
Northeast	**5.37**	**4.51**
Maranhão	0.16	0.13
Piauí		-
Ceará	1.10	0.92
Rio Grande do Norte	0.40	0.34
Paraíba	1.15	0.96
Pernambuco	0.010	0.0084
Alagoas	0.023	0.019
Sergipe	0.93	0.78
Bahia	0.50	0.42
Adjustments	1.02	0.86
Southeast	**12.56**	**10.55**
Minas Gerais	6.31	5.29
Espírito Santo	0.37	0.31
Rio de Janeiro	1.16	0.97
São Paulo	2.55	2.14
Adjustments	2.17	1.82
South	**4.36**	**3.66**
Paraná	3.01	2.52
Santa Catarina	0.68	0.57
Rio Grande do Sul	0.65	0.55
Adjustments	0.029	0.025
Central-West	**2.99**	**2.51**
Mato Grosso do Sul	0.31	0.26
Mato Grosso	0.58	0.49
Goiás	0.85	0.71
Distrito Federal	1.25	1.05
Brazil	**26.51**	**22.27**

The results were mapped by region and state in QGIS. The potential syngas production by region and state is shown in Figure 27 and Figure 28, respectively. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to higher syngas production. The subdivision by states with localization of the plants allows a better analysis of the syngas potential. Because information about the production of each unit, its production process and location was not available, the integrated plants in Brazil were located according to the information given by Visedo and Pecchio (2019), SNIC (2013), and Google Maps.

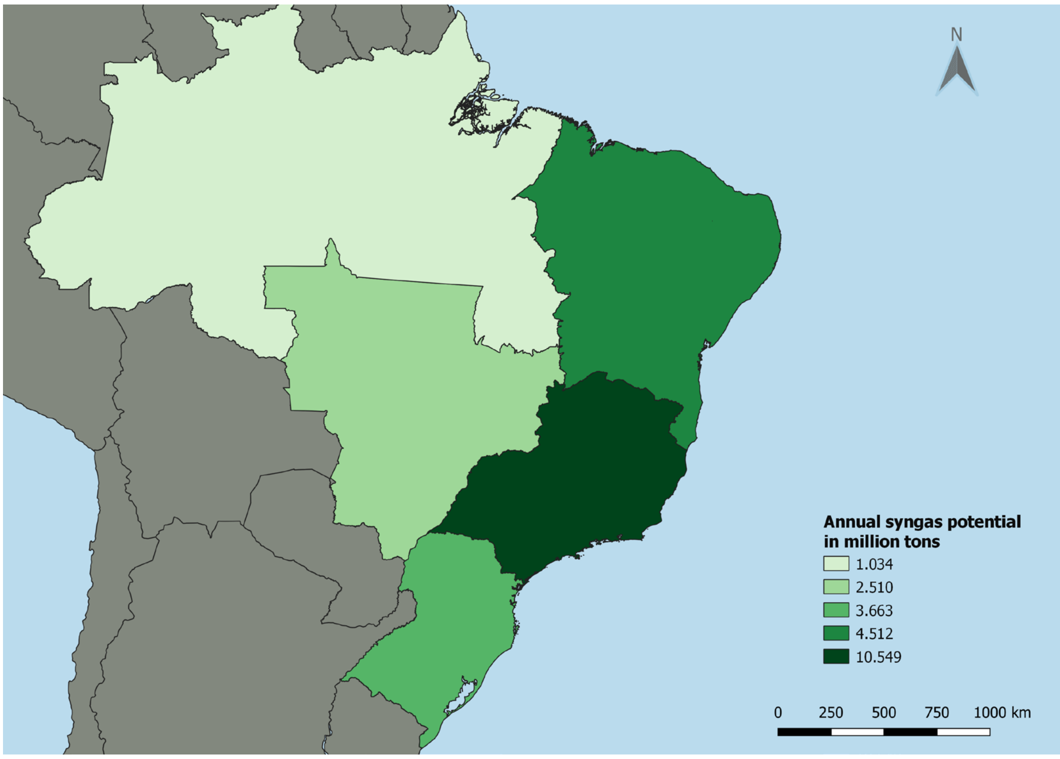

Figure 27: Potential regional syngas production of the cement industry. Source: own elaboration

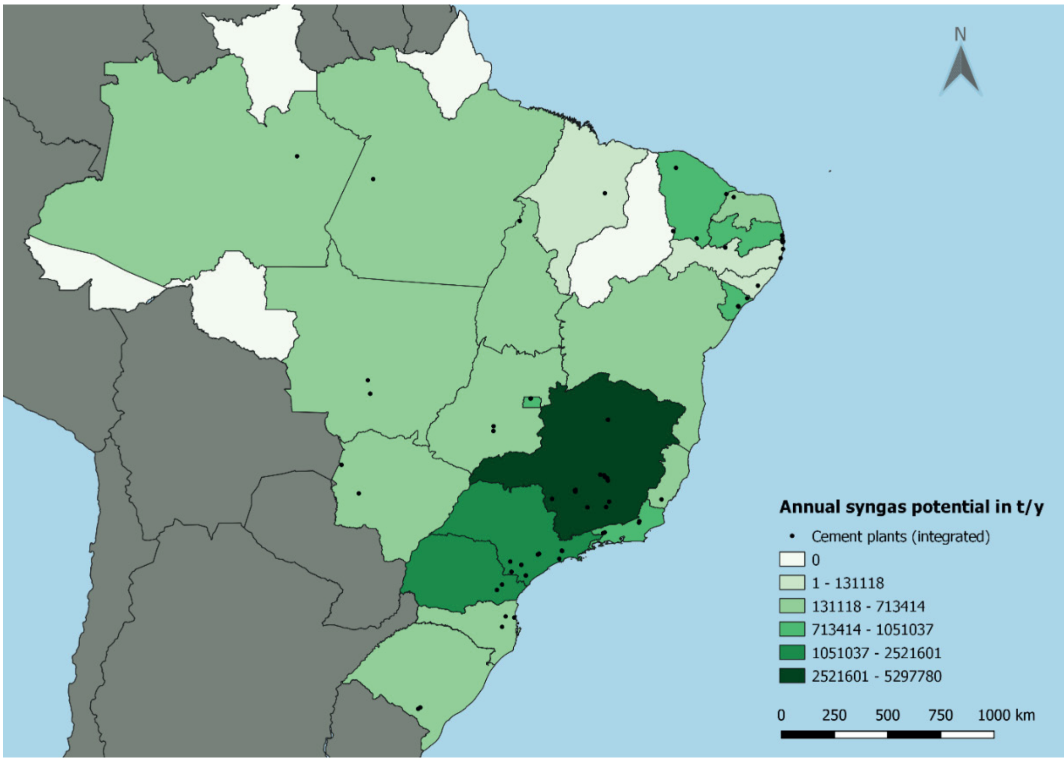

Figure 28: Potential syngas production of the cement industry by state and integrated cement plant distribution. Source: own elaboration

The Southeast region of Brazil has the highest potential to generate syngas, followed by the Northeast. The state of Minas Gerais, in this region, has the highest potential with 23% of the total syngas production, followed by the states of Paraná, in the South, and São Paulo, in the Southeast, with 11% and 9.6%, respectively.

4.2. Steel industry

In Chapter 3, we identified the by-products and residues from the Brazilian iron and steel industry. the solid wastes from this industry are mainly reused, and there is no specific literature on their use to produce syngas. Therefore, just the CO_2 emission is considered suitable for syngas production.

In Figure 29, the 32 steel production plants in Brazil are shown. Out of these, 17 are integrated and 15 are semi-integrated (IABr, 2019). The steel industry is represented in 11 states with a large concentration in the Southeast.

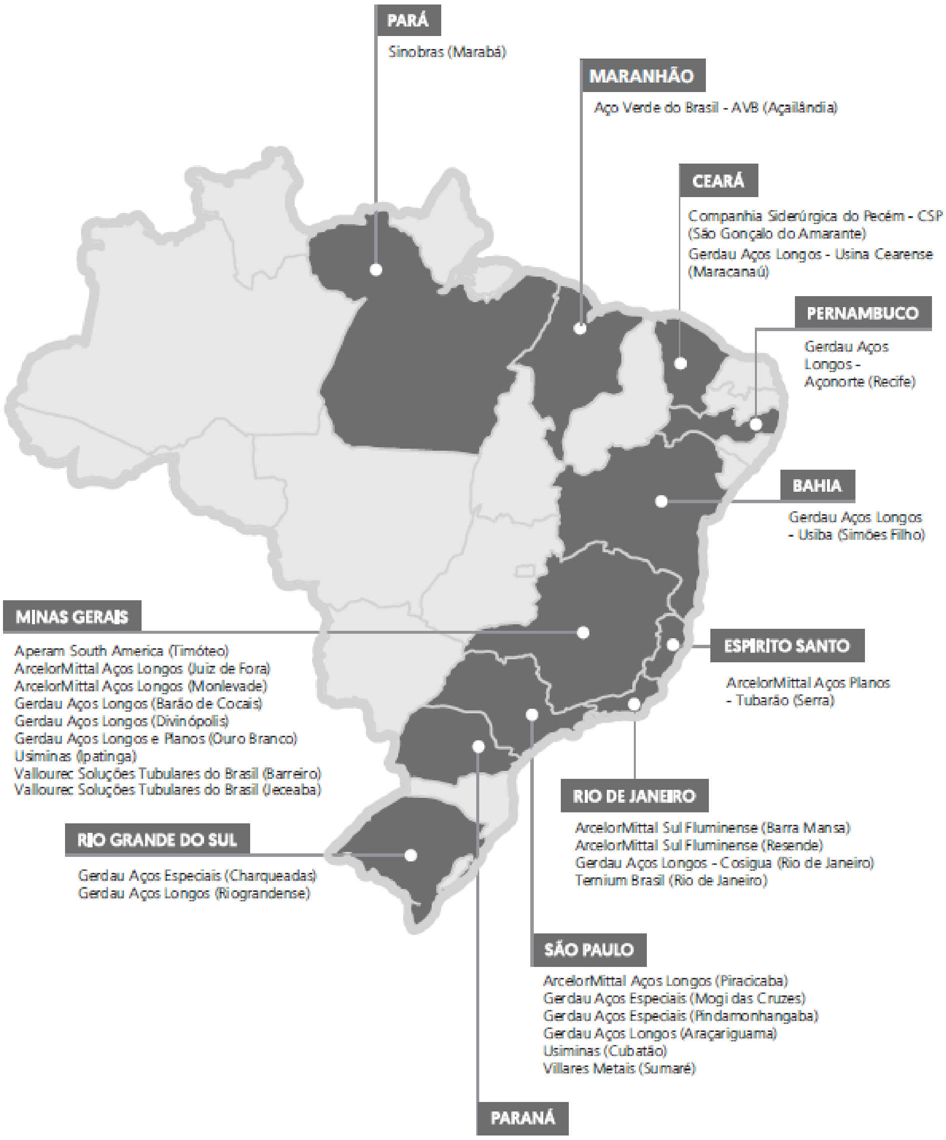

Figure 29: Distribution of the Brazilian steel industry. Source: IABr (2019)

4.2.1. Estimation of by-products and residues

To estimate the amount of CO_2 emitted by the Brazilian steel industry, data were taken from the *Brazil Steel Databook of 2019* by the IABr (2019). The emission factor, calculated by the IABr in 2016 with the IPCC methodology, is 1.9 ton of CO_2 per ton of crude steel produced through the whole process (CNI, 2017). Information about the steelmaking process used by region and state was not be found; due to that, the CO_2 calculation was done by assuming 76.5% of the regional crude steel production, which represents the share of the integrated mill route.

The CO_2 emissions were calculated once considering the emission factor of only the blast furnace, as it represents the most significant source of CO_2 (1.56 ton of CO_2 per ton of crude steel), and once considering the emissions during the whole process. In Table 22, the regional distribution of the production of crude steel and the estimated CO_2 emissions in 2018 are shown.

Table 22: Brazilian crude steel production and estimated CO_2 emissions by region and state. Source: IABr (2019) and own elaboration

Brazilian region and state	Total crude steel production (million tons)	Crude steel production by integrated mill route (million tons)	CO_2 emission by blast furnace* (million tons)	CO_2 emission by integrated mill route** (million tons)
North	**0.34**	**0.26**	**0.41**	**0.5**
Pará	0.34	0.26	0.41	0.5
Northeast	**3.60**	**2.75**	**4.29**	**5.23**
Maranhão	0.28	0.21	0.33	0.41
Ceará	3.09	2.36	3.69	4.48
Pernambuco	0.23	0.17	0.27	0.33
Southeast	**30.68**	**23.47**	**36.62**	**44.60**
Minas Gerais	10.60	8.10	12.64	15.39
Espírito Santo	7.30	5.59	8.71	10.61
Rio de Janeiro	10.41	7.96	12.42	15.12
São Paulo	2.38	1.82	2.84	3.46
South	**0.78**	**0.59**	**0.93**	**1.13**
Rio Grande do Sul	0.78	0.59	0.93	1.13
Central-West	**0**	**0**	**0**	**0**
Brazil	**35.41**	**27.09**	**42.25**	**51.46**

*1.56 ton of CO_2 per ton of crude steel. **1.9 ton of CO_2 per ton of crude steel (based on IABr in 2016 with the IPCC methodology)

The Southeast region leads by far the steel production in Brazil with a share of 86% (and the CO_2 emissions), followed by the Northeast. A comparison of the CO_2 emissions with the absolute CO_2 emissions calculated by the IABr in 2016 (CNI, 2017) shows a difference of 6.5 Mt CO_2 which can be due to the assumption of only the integrated mill route, neglecting the semi-integrated route.

4.2.2. Syngas production

From the estimated regional CO_2 emissions by the industrial process, the potential syngas production was determined through an indirect conversion process, the co-SOEC electrolysis. To be used, the CO_2 emissions must be captured by a carbon capture technology. The CO_2 emitted during the iron making process in the blast furnace accounts for 82% of the emissions of the whole production process, and its concentration in the flue gas varies between 27% and 28% according to Patricio et al. (2017), IEAGHG (2017), and IPCC (2005). The emissions from the blast furnace could be captured either precombustion or postcombustion. Neither approach captures all the CO_2 from the integrated mill, since large volumes of CO_2 are also emitted in the non-core processes such as the sinter plants, coke oven, and the BOF (IEAGHG, 2017).

Therefore, in this study, the syngas potential was calculated by considering only the CO_2 emissions during the blast furnace process. The post-combustion carbon capture technology is considered the most mature option in the steel industry (Cormos, 2016). Due to that, in this study, a post-combustion technology was considered to capture the CO_2 for syngas production. In Chapter 2, this technology was described which has a capture efficiency of 90%. With the conversion factor of the co-SOEC electrolysis considered in this study (see also in Chapter 2), the potential syngas production by region and state was determined. According to this process, every kg of CO_2 results in 0.84 kg of syngas.

Table 23: Syngas production of the steel industry by region and state. Source: own elaboration

Brazilian region and state	CO_2 emission after capturing by blast furnace (million tons)	Potential syngas production by blast furnace (million tons)
North	**0.37**	**0.31**
Pará	0.37	0.31
Northeast	**3.86**	**3.25**
Maranhão	0.3	0.25
Ceará	3.32	2.79
Pernambuco	0.25	0.21
Southeast	**32.96**	**27.69**
Minas Gerais	11.38	9.56
Espírito Santo	7.84	6.60
Rio de Janeiro	11.18	9.39
São Paulo	2.56	2.15
South	**0.84**	**0.70**
Rio Grande do Sul	0.84	0.70
Central-West	**0**	**0**
Brazil	**38.03**	**31.94**

The results were mapped by region and state in QGIS. In Figure 30 and Figure 31, the potential syngas production by region and state is shown. The subdivision by states with localization of the plants allows a better analysis of the syngas potential. Because information about the production of each unit, its production process, and location was not available, the steel production plants in Brazil were located based on the information given by the IABr (2019) and Google Maps. Though 27 of the 32 steel production units were located, they could not be distinguished between integrated and semi-integrated.

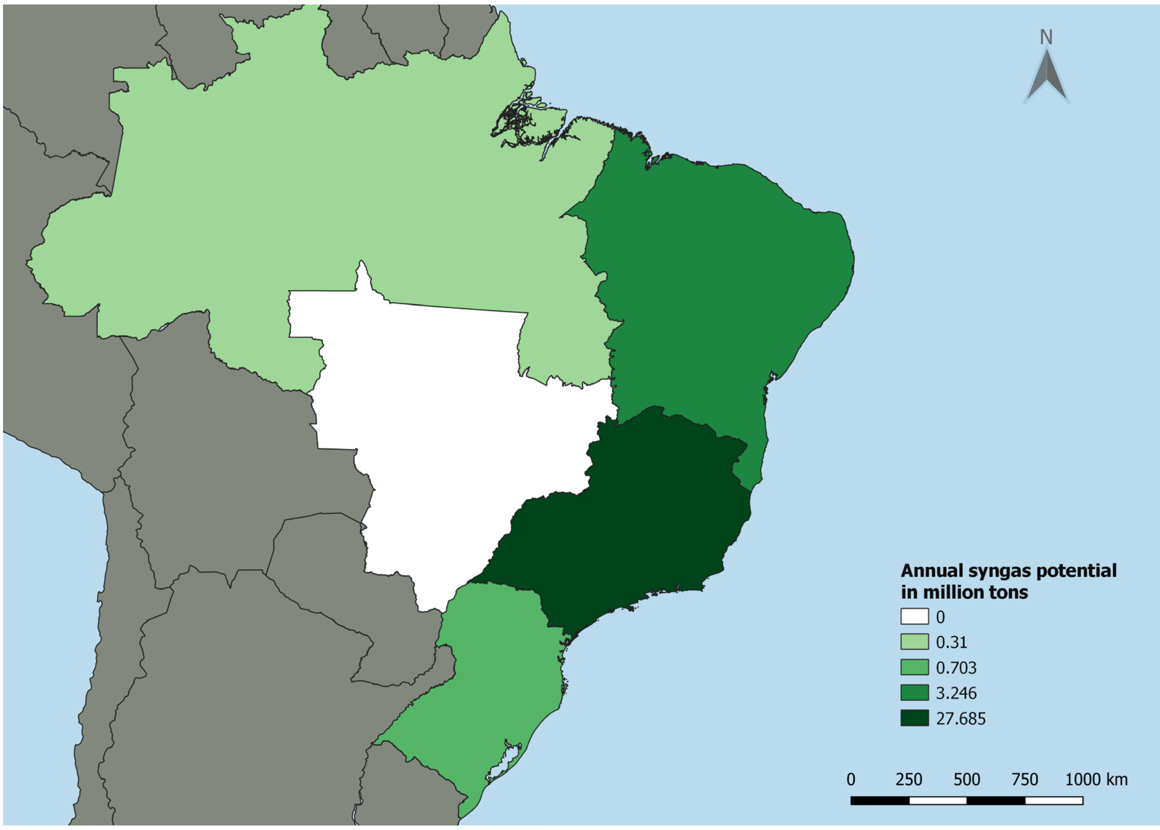

Figure 30: Potential regional syngas production of the steel industry. Source: own elaboration

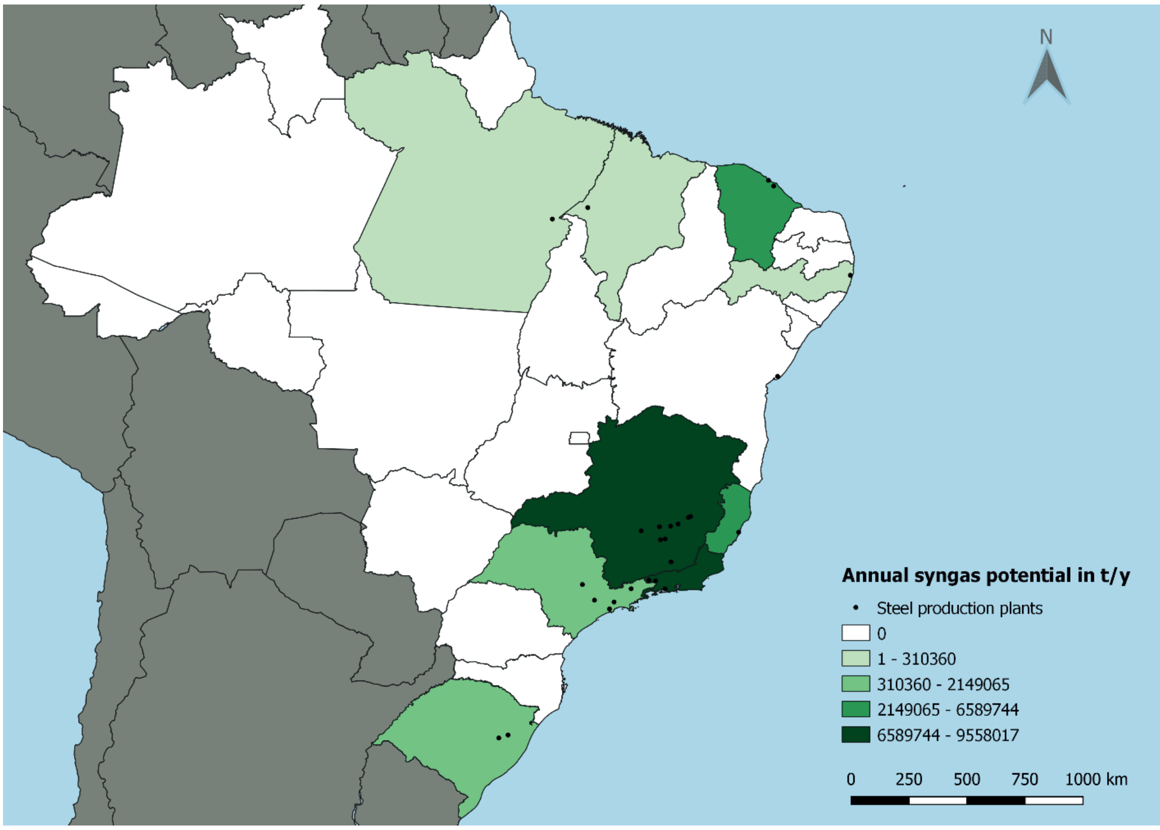

Figure 31: Potential syngas production of the steel industry by state and plant distribution. Source: own elaboration

The Southeast region of Brazil has the highest potential, with 86% of the total syngas production. The states of Minas Gerais and Rio de Janeiro, in the Southeast region, respectively account for 30% and 29% of the total syngas production, followed by the state of Espírito Santo with 20%.

4.3. Sugarcane industry

In Chapter 3, the agro-industries and their suitable by-products and residues for syngas production were identified. The sugarcane industry is one of them with the interconnected bioethanol industry. The suitable residues of the sugarcane industry are sugarcane straw from harvesting, and sugarcane bagasse and CO_2 emissions from the bioethanol industry. In the following, the suitable by-products and residues and their potential syngas production are estimated and mapped.

4.3.1. Agricultural residues

4.3.1.1. Estimation of residues

To estimate the agricultural residues from sugarcane industry in Brazil, data on the annual sugarcane production by region and state in 2018 were obtained from the Systematic Survey of Agricultural Production (*Levantamento Sistemático da Produção Agrícola*, LSPA), published by the Brazilian Institute of Geography and Statistics (*Instituto Brasileiro de Geografia e Estatística*, IBGE) (IBGE, 2019). As we assumed in Chapter 3, every ton of sugarcane results in 0.14 ton of straw. The residue estimated by region and state is shown in Table 24.

4.3.1.2. Syngas production

Based on the estimated sugarcane straw production in 2018, the potential syngas production through a direct conversion process was determined. For this purpose, the gasification of the sugarcane straw by a fluidized bed gasifier was considered, as introduced in Chapter 2. The amount of syngas produced through the gasification of 1 kg of straw was estimated by using general equation 4 (see Chapter 2).

$$\eta_{FB} = \frac{LHV_{Syngas} * X_{kgSyngas}}{LHV_{Sugarcane\ straw} * X_{kgSugarcane\ straw}} \tag{8}$$

The conversion factor for the agricultural residue was determined following this equation and information from Table 5 and Annex Table 2, which summarizes the LHVs of the by-products and residues. The fluidized bed gasification of 1 kg of sugarcane straw results in 1.55 kg of syngas. By entrained flow gasification, 1 kg of sugarcane straw results in 1.23 kg of syngas. Table 24 shows the syngas production by region and state through fluidized bed gasification.

Table 24: Estimated agricultural residues and potential syngas production of the sugarcane industry by region and state. Source: IBGE (2019) and own elaboration

Brazilian region and state	Production of sugarcane in 2018 (million tons)	Production of sugarcane residues in 2018 (million tons)	Potential syngas production from sugarcane straw (million tons)
North	**4.33**	**0.61**	**0.94**
Rondônia	0.015	0.0021	0.0032
Acre	0.011	0.0016	0.0025
Amazonas	0.26	0.37	0.57
Roraima	3.976	0.0005	0.0009
Pará	0.93	0.13	0.20
Amapá	0.004	0,0006	0.0009
Tocantins	3.10	0.43	0.67
Northeast	**49.15**	**6.88**	**10.66**
Maranhão	2.43	0.34	0.53
Piauí	0.84	0.12	0.18
Ceará	0.57	0.08	0.12
Rio Grande do Norte	3.86	0.54	0.84
Paraíba	5.54	0.78	1.20
Pernambuco	11.96	1.67	2.59
Alagoas	17.24	2.41	3.74
Sergipe	2.05	0.29	0.44
Bahia	4.68	0.65	1.02
Southeast	**434.15**	**60.78**	**94.21**
Minas Gerais	70.79	9.91	15.36
Espírito Santo	2.47	0.35	0.54
Rio de Janeiro	2.44	0.34	0.53
São Paulo	358.43	50.18	77.78
South	**43.06**	**6.03**	**9.35**
Paraná	42.07	5.89	9.13
Santa Catarina	0.31	0.044	0.067
Rio Grande do Sul	0.68	0.095	0.15
Central-West	**143.48**	**20.09**	**31.14**
Mato Grosso do Sul	49.58	6.94	10.76
Mato Grosso	20.43	2.86	4.43
Goiás	73.45	10.28	15.94
Distrito Federal	0.017	0.0024	0.0037
Brazil	**674.18**	**94.39**	**146.30**

The results were mapped by region and state in QGIS. In Figure 32 and Figure 33, the potential syngas production by region and state is shown. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to a higher syngas production. The subdivision by state allows a better analysis of the syngas potential.

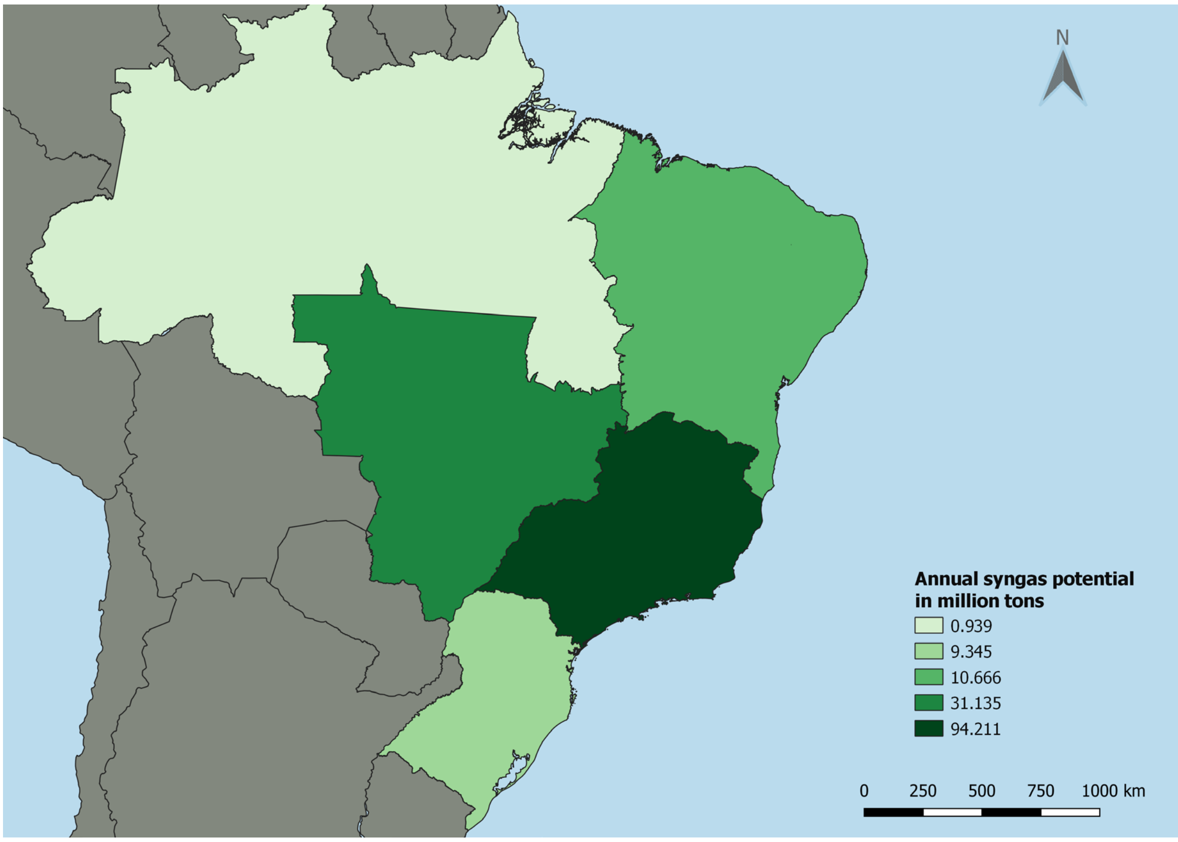

Figure 32: Potential regional syngas production from sugarcane agricultural residues. Source: own elaboration

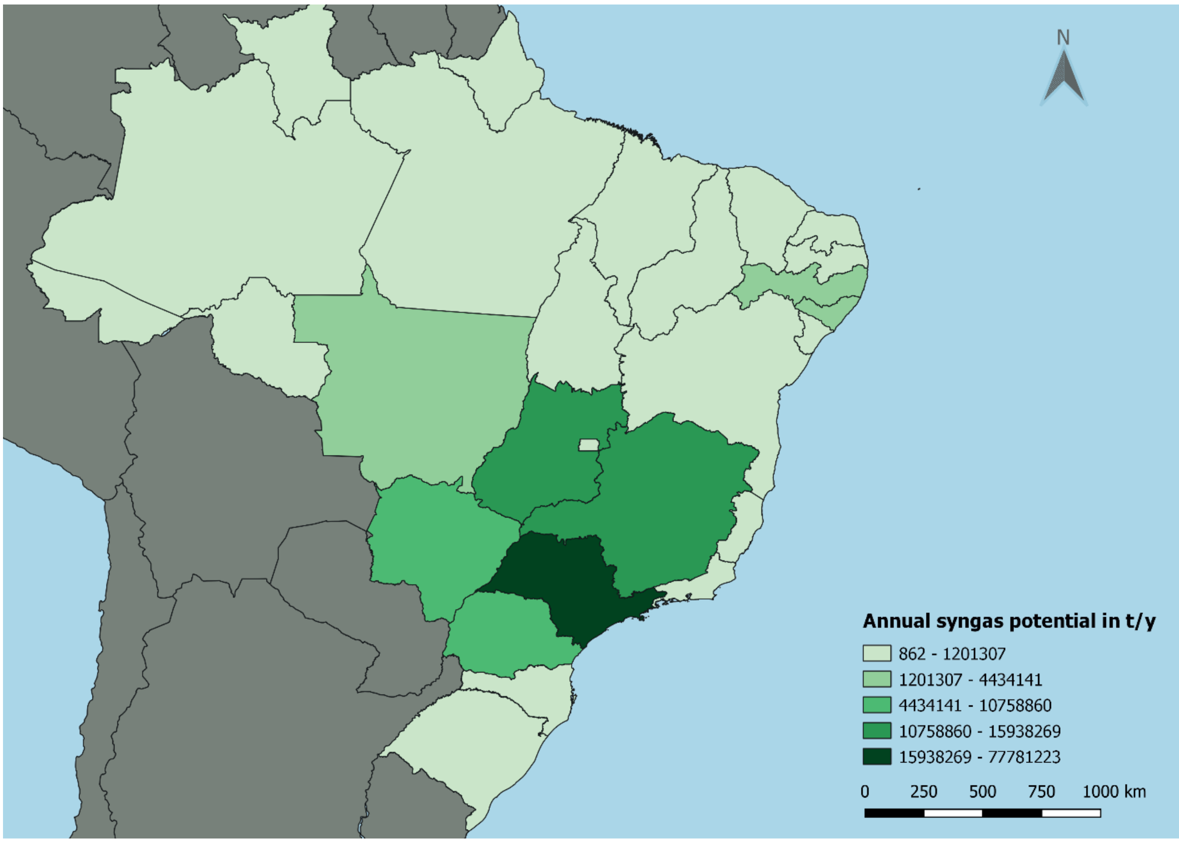

Figure 33: Potential syngas production from the conversion of sugarcane straw by state. Source: own elaboration

Sugarcane production is strongly concentrated in the Southeast region of the country with an output share of 64% of the total sugarcane harvested in 2018. As a consequence, syngas production from sugarcane straw in this region is the highest, followed by the Central-West region, with 21%. In 2018, sugarcane production was present in all 26 Brazilian states and the Federal District. São Paulo alone was responsible for 53% of the total harvest of sugarcane and is the state with the highest syngas potential. It is followed, in descending order, by the states of Goiás, Minas Gerais, Mato Grosso do Sul and Paraná, all located around São Paulo.

4.3.2. Bioethanol industry

In Chapter 3, we identified the by-products and residues from the Brazilian sugarcane ethanol industry. The sugarcane bagasse resulting from the sugar extraction process and the CO_2 emission from both its cogeneration and the fermentation process are considered suitable for syngas production. Sugarcane bagasse is used in conventional sugar and ethanol production to generate energy for self-supply, especially for the domestic energy supply in Brazil, which results in CO_2 emission from combustion. Sugarcane bagasse itself is not further considered in this study, since there is no interference with the actual industrial process. The CO_2 which results from combustion is not considered further because of the evaluation matrix in Chapter 3, which does not include the energy generation sector (neither biomass nor fossil fuels). In this study, only the relatively pure CO_2 emissions during the fermentation process of the bioethanol industry are considered for syngas production.

Currently, nearly all industrial-scale production of ethanol belongs to the first generation of biofuels (Lenartsson et al., 2014). In 2019, there were 373 ethanol plants in Brazil, of which 370 had a production share of more than 99% and belonged to the first-generation, and 3 belonged to the second-generation (lignocellulosic) ethanol production (Barros & Flake, 2019).

4.3.2.1. Estimation of by-products and residues

To estimate the CO_2 emissions from the fermentation process, data on the annual production of ethanol were obtained from the statistical yearbook of the ANP (2019). The production data of hydrous and anhydrous ethanol were merged because both include the fermentation process. The emission factor of the relatively pure CO_2 emission is 0.96 ton of CO_2 per ton of hydrous or anhydrous ethanol produced (calculated for an ethanol density of 789 kg/m^3). In Table 25, the regional distribution of the production of ethanol and the estimated CO_2 emissions in 2018 are shown.

4.3.2.2. Syngas production

Based on the estimated regional CO_2 emissions of the industrial process, the potential syngas production through an indirect conversion process, the co-SOEC electrolysis, was determined. The CO_2 stream released is pure and no specific carbon capture technology is needed to obtain the released CO_2 in atmospheric pressure. Therefore, the CO_2 emissions can be captured easily and converted to syngas. The conversion factor of the co-SOEC electrolysis process considered in this study (see also in Chapter 2) is that every kg of CO_2 results in 0.84 kg of syngas.

Table 25: Potential syngas production of the bioethanol industry from estimated CO_2 emissions by region and state. Source: ANP (2019) and own elaboration

Brazilian region and state	Production of ethanol in 2018 (m^3)	CO_2 by fermentation process (million tons)	Syngas production (million tons)
North	**205,540**	**0.16**	**0.13**
Rondônia	1,390	0.001	0.0008
Amazonas	5,470	0.004	0.0035
Pará	43,460	0.033	0.028
Tocantins	176,270	0.13	0.11
Northeast	**2,006,090**	**1.52**	**1.28**
Maranhão	147,620	0.12	0.11
Piauí	37,480	0.028	0.024
Rio Grande do Norte	114,900	0.087	0.073
Paraíba	430,810	0.33	0.27
Pernambuco	465,510	0.35	0.29
Alagoas	459,870	0.35	0.29
Sergipe	104,200	0.079	0.066
Bahia	245,700	0.19	0.15
Southeast	**19,700,000**	**14.92**	**12.53**
Minas Gerais	3.257,510	2.47	2.07
Espírito Santo	127,570	0.097	0.081
Rio de Janeiro	97,260	0.074	0.062
São Paulo	16,217,660	12.28	10.32
South	**1,626,200**	**1.23**	**1.03**
Paraná	1.624,010	1.23	1.03
Rio Grande do Sul	2,190	0.0016	0.0013
Central-West	**9,518,600**	**7.21**	**6.06**
Mato Grosso do Sul	3,264,480	2.47	2.08
Mato Grosso	1,757,560	1.33	1.12
Goiás	4,496,560	3.41	2.86
Brazil	**33,056,440**	**25.04**	**21.03**

The results were mapped by region and state in QGIS. In Figure 34 and Figure 35, the potential syngas production by region and state is shown. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to a higher syngas production. The subdivision by state and the distribution of the plants shown in Figure 35 allow a better analysis of the syngas potential. The distribution of the plants was obtained from the EPE.

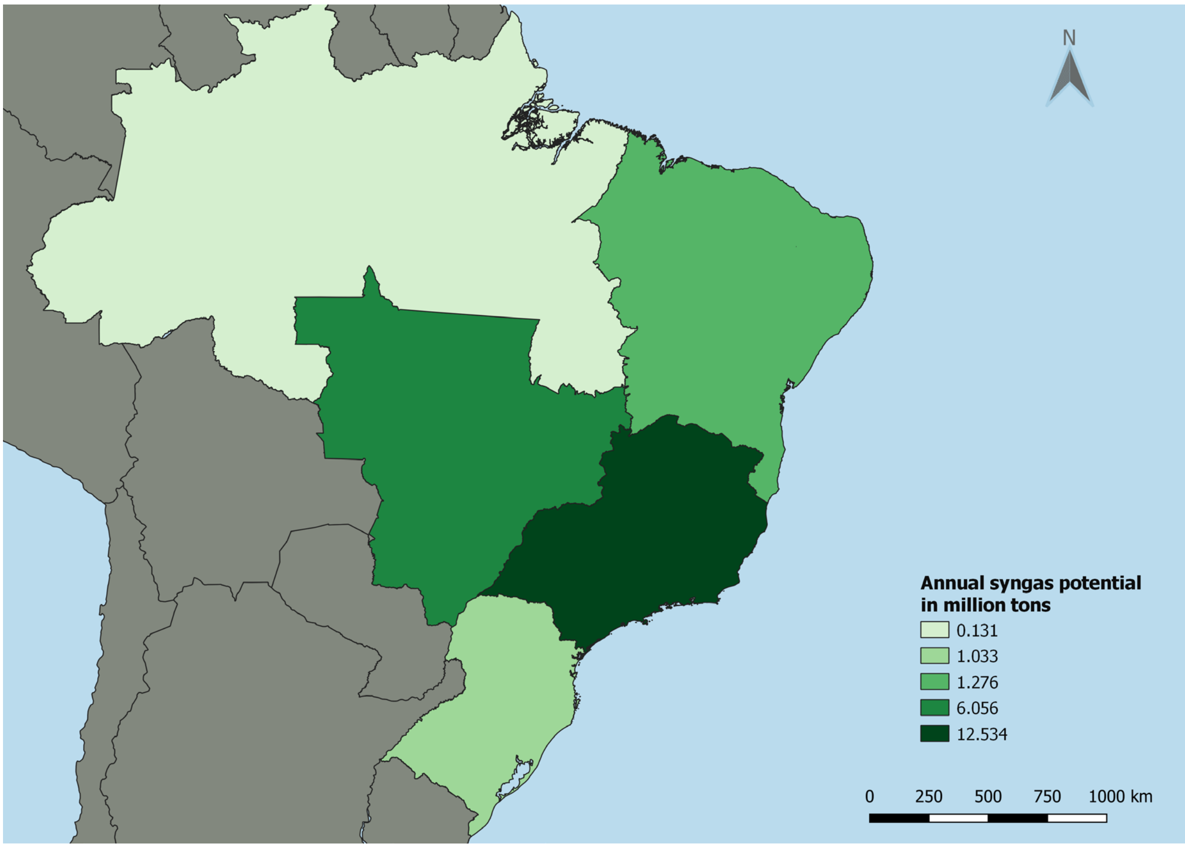

Figure 34: Potential regional syngas production of the bioethanol industry. Source: own elaboration

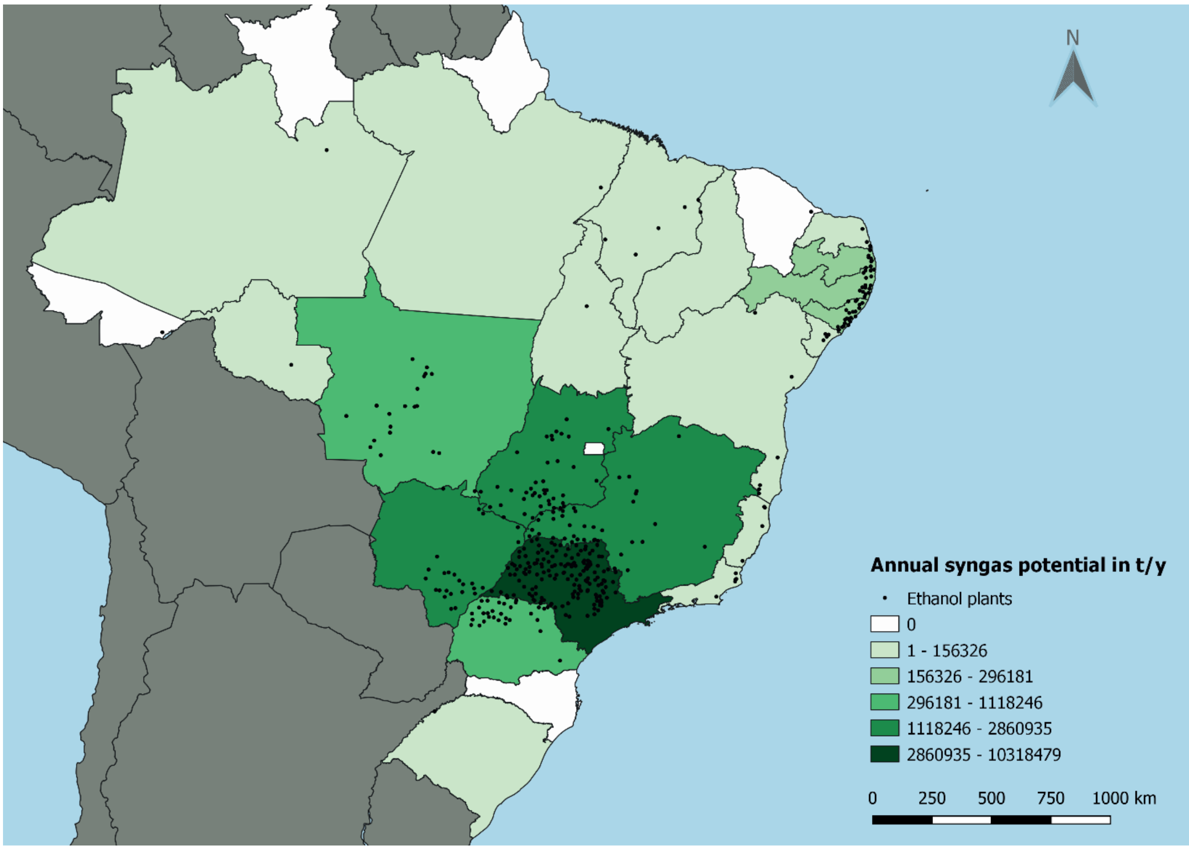

Figure 35: Potential syngas production of the bioethanol industry by state and plant distribution. Source: own elaboration

The Southeast, the region with the largest number of production plants, had a share of 59.6% of the total ethanol production in Brazil in 2018. Therefore, the potential syngas production in this region is the highest, followed by the Central-West with a share of 28%. The state of São Paulo, where most of the ethanol plants are located, has the highest potential syngas production with 49% of the total production. It is followed by the states of Goiás and Mato Grosso do Sul, in the Central-West, and Minas Gerais, in the Southeast, with shares of 13.6%, 9.9%, and 9.8%, respectively.

4.4. Soybean industry

The residues of the soybean industry are soybean straw from the harvesting and glycerol and wastewater from the biodiesel industry. In the following, the suitable by-products and residues and their potential syngas production are estimated and mapped.

4.4.1. Agricultural residues

4.4.1.1. Estimation of residues

To estimate the agricultural residues from soybean production in Brazil, data on the annual soybean production by region and state in 2018 were obtained from the LSPA (IBGE, 2019). Considering the factor assumed in Chapter 3, every ton of soybean results in 1.52 ton of soybean straw. The residues estimated by region and state are shown in Table 26.

4.4.1.2. Syngas production

Based on the estimated soybean straw generated in 2018, the potential syngas production through a direct conversion process was determined. For this purpose, the fluidized bed gasification of the soybean straw was considered, as introduced in Chapter 2. The amount of syngas produced through the gasification of 1 kg of straw was estimated by using general equation 4 (see Chapter 2).

$$\eta_{FB} = \frac{LHV_{Syngas} * X_{kgSyngas}}{LHV_{Soybean\ straw} * X_{kgSoybean\ straw}} \tag{9}$$

The conversion factor was determined following this equation and information from Table 5 and Annex Table 2, which provides the LHV for soybean straw. The fluidized bed gasification of 1 kg of soybean straw results in 1.67 kg of syngas. By entrained flow gasification, 1 kg of soybean straw results in 1.33 kg of syngas. Table 26 shows the syngas production by region and state through fluidized bed gasification.

Table 26: Estimated agricultural residues and potential syngas production of the soybean industry by region and state. Source: IBGE (2019) and own elaboration

Brazilian region and state	Production of soybean in 2018 (million tons)	Production of soybean residues in 2018 (million tons)	Syngas production from soybean straw (million tons)
North	**5.32**	**8.08**	**13.51**
Rondônia	0.99	1.50	2.51
Acre	0.0014	0.0021	0.0036
Roraima	0.053	0.081	0.13
Pará	1.64	2.49	4.16
Amapá	0.054	0.082	0.14
Tocantins	2.58	3.93	6.55
Northeast	**11.47**	**17.44**	**29.12**
Maranhão	2.75	4.18	6.98
Piauí	2.47	3.75	6.27
Bahia	6.24	9.49	15.85
Southeast	**8.85**	**13.45**	**22.45**
Minas Gerais	5.44	8.26	13.79
São Paulo	3.41	5.18	8.65
South	**39.15**	**59.51**	**99.39**
Paraná	19.27	29.28	48.91
Santa Catarina	2.34	3.57	5.96
Rio Grande do Sul	17.54	26.65	44.52
Central-West	**53.04**	**80.62**	**134.64**
Mato Grosso do Sul	9.87	14.99	25.05
Mato Grosso	31.61	48.04	80.23
Goiás	11.31	17.19	28.72
Distrito Federal	0.25	0.38	0.64
Brazil	**117.83**	**179.11**	**299.11**

The results were mapped by region and state in QGIS. In Figure 36 and Figure 37, the potential syngas production by region and state is shown. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to a higher syngas production. The subdivision by state allows a better analysis of the syngas potential.

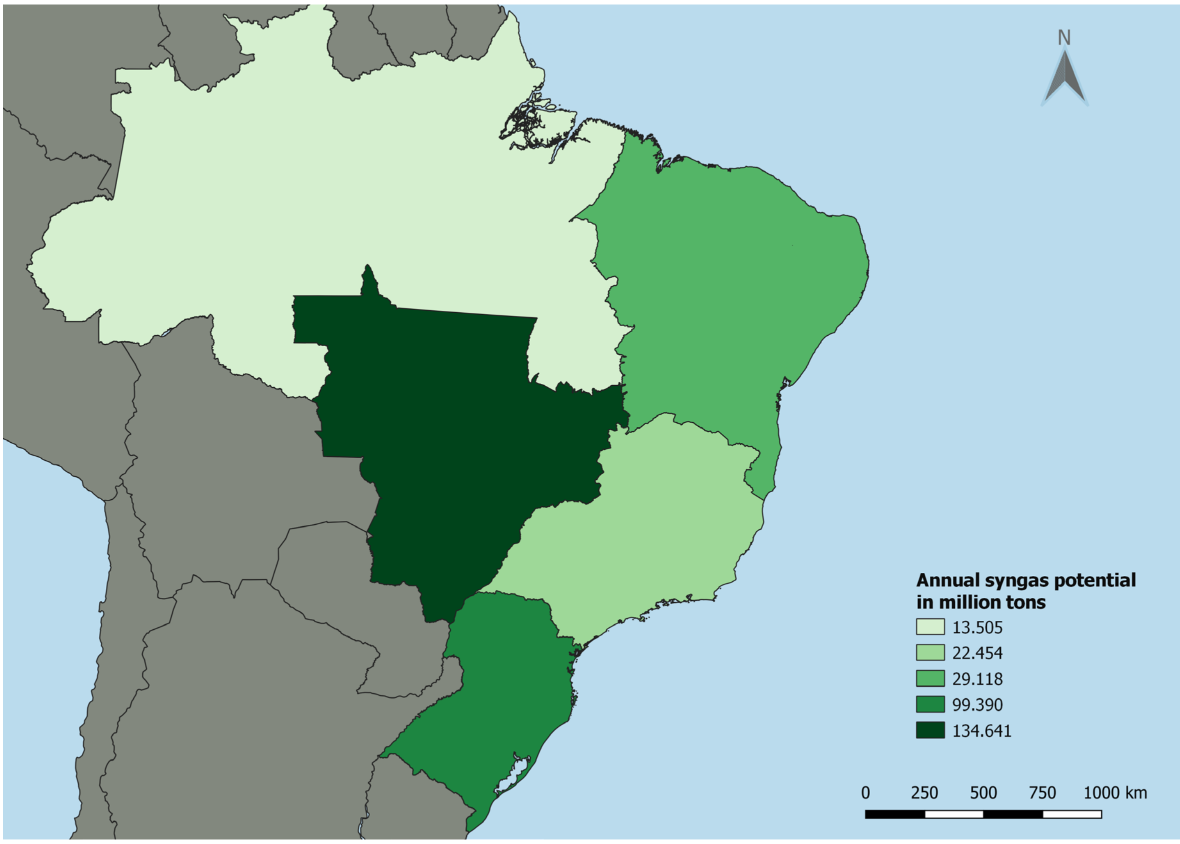

Figure 36: Potential regional syngas production from soybean agricultural residues. Source: own elaboration

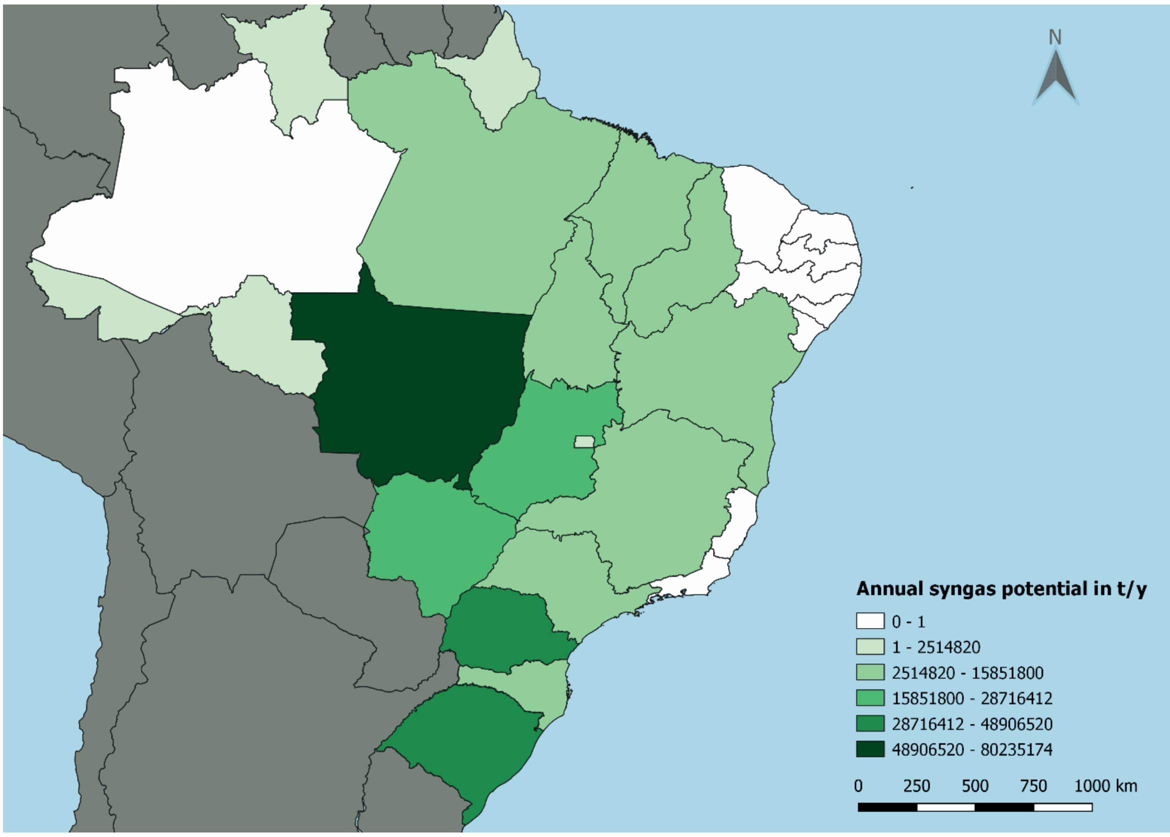

Figure 37: Potential syngas production from the conversion of soybean straw by state. Source: own elaboration

The soybean production is strongly concentrated in the Central-West and South of Brazil. The Central-West region has the highest potential to produce syngas, and the North has the lowest potential. The state of Mato Grosso, in the Central-West, has the highest potential syngas production with a share of 26.8% of the total potential. It is followed by the states of Paraná and Rio Grande do Sul, in the South, and Goiás, in the Central-West, with respective syngas production shares of 16.3%, 14.9%, and 9.6%.

4.4.2. Biodiesel industry

In Chapter 3, we identified the by-products and residues from the Brazilian biodiesel industry. Crude glycerol from the transesterification process is the most suitable by-product for syngas production. As for the wastewaters that result from the washing process, there is no literature found for their conversion into syngas; therefore, they will not be considered any further.

In 2018, there were 51 biodiesel production plants installed in Brazil with a nominal production capacity of 8.5 billion litres (ANP, 2019). They are shown in Figure 38. As the Central-West has the highest soybean production, it is also the largest region in terms of biodiesel production plants, followed by the South.

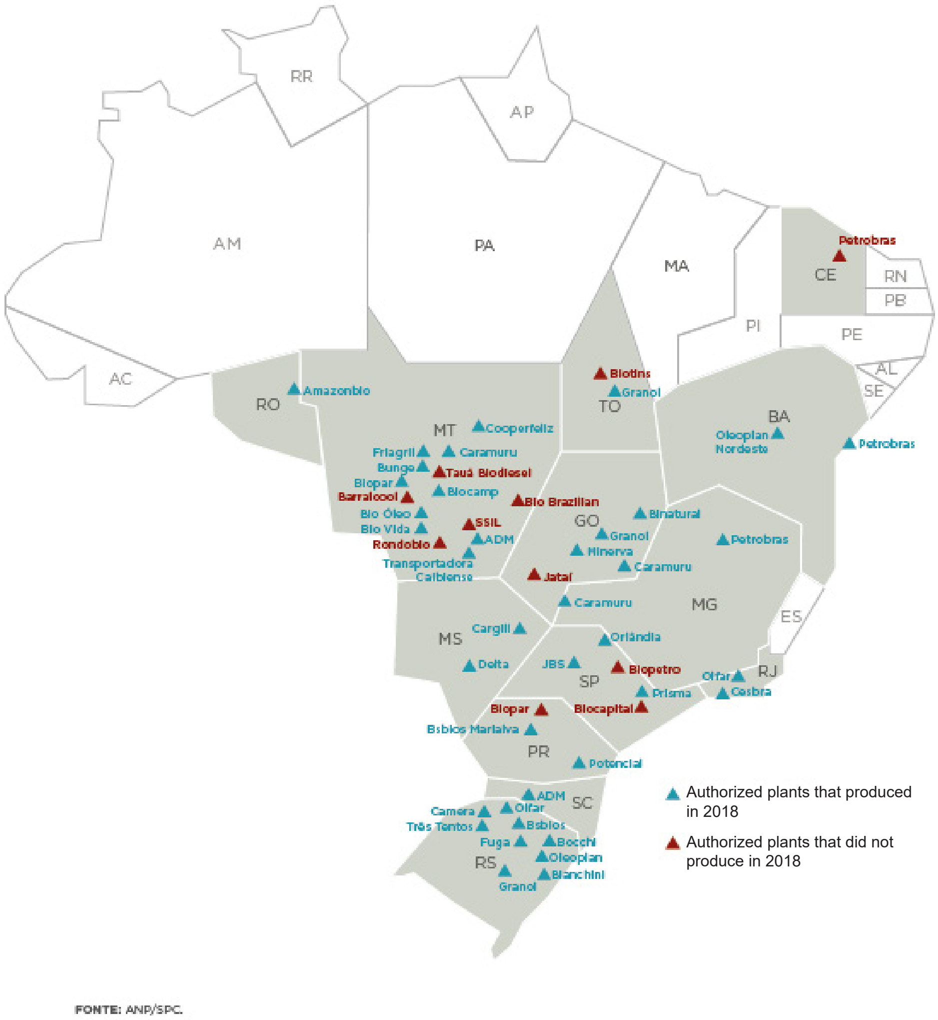

Figure 38: Distribution of the Brazilian biodiesel industry in 2018. Source: ANP (2019)

4.4.2.1. Estimation of by-products and residues

The yearly amount of glycerol produced by the Brazilian biodiesel industry is given and updated by the ANP. The data for the glycerol production in 2018 were obtained from the statistical yearbook of the ANP (2019) and converted into tons considering a density of 1,261.3 kg/m^3. In Table 27, the glycerol production by region and state in 2018 is shown. In 2018, the glycerol production in Brazil was about 440.6 million tons, up 17.6% from 2017. The South leads this production with a share of 40.7%, followed closely by the Central-West, with 39.7%.

4.4.2.2. Syngas production

Based on the glycerol production in 2018, the potential syngas production was determined through a direct conversion process. In Chapter 2, different conversion processes of glycerol to syngas were introduced. A reforming process of glycerol was considered due to its advantages. This reforming process converts 1 kg of glycerol with a content of 30% to 0.43 kg of syngas. By using this conversion factor, the potential syngas production by region and state was estimated and is shown in Table 27.

Table 27: Potential syngas production of the biodiesel industry by region and state. Source: yearly production data from ANP (2019) and own elaboration

Brazilian region and state	Production of glycerol in 2018 (thousand tons)	Syngas production from glycerol (thousand tons)
North	**16.235**	**6.981**
Rondônia	9.458	4.067
Pará	0	0
Tocantins	6.777	2.914
Northeast	**42.858**	**18.429**
Ceará	0	0
Rio Grande do Norte	0	0
Bahia	42.858	18.429
Southeast	**49.898**	**21.456**
Minas Gerais	15.305	6.581
Rio de Janeiro	8.581	3.690
São Paulo	26.013	11.186
South	**225.968**	**97.166**
Paraná	64.449	27.713
Santa Catarina	13.868	5.963
Rio Grande do Sul	147.652	63.490
Central-West	**220.804**	**94.946**
Mato Grosso do Sul	30.159	12.968
Mato Grosso	125.151	53.815
Goiás	65.494	28.163
Brazil	**555.764**	**238.979**

The results were mapped by region and state in QGIS. In Figure 39 and Figure 40, the potential syngas production by region and state is shown. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to a higher syngas production. The subdivision by state and the distribution of the plants allow a better analysis of the syngas potential. The distribution of the plants was obtained from the EPE.

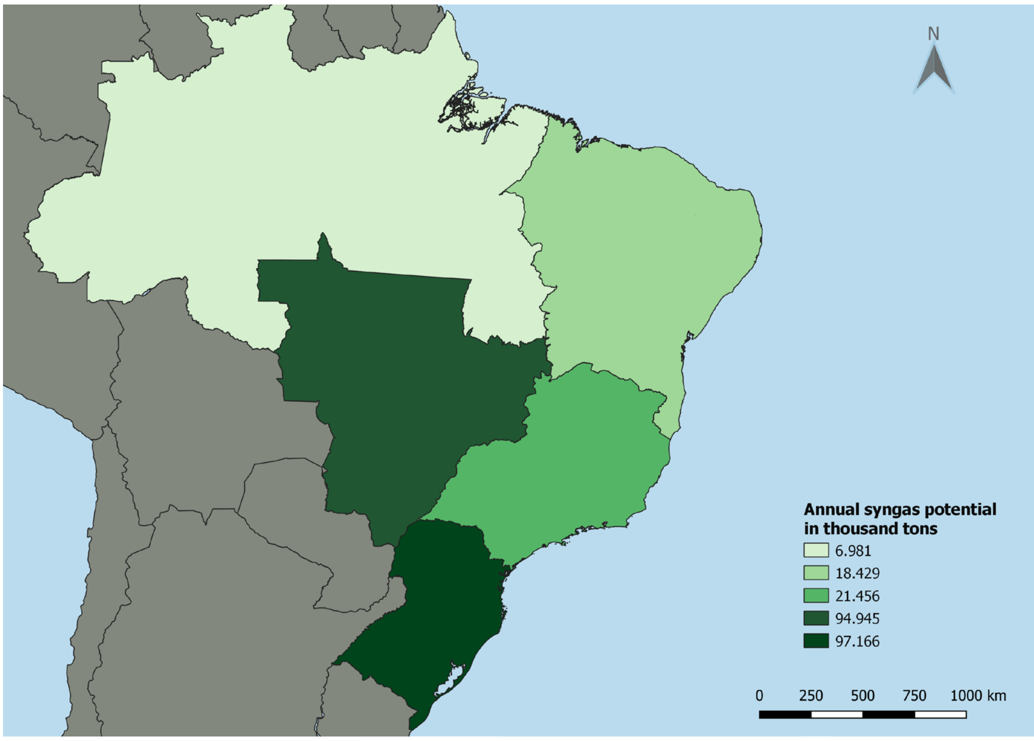

Figure 39: Potential regional syngas production of the biodiesel industry. Source: own elaboration

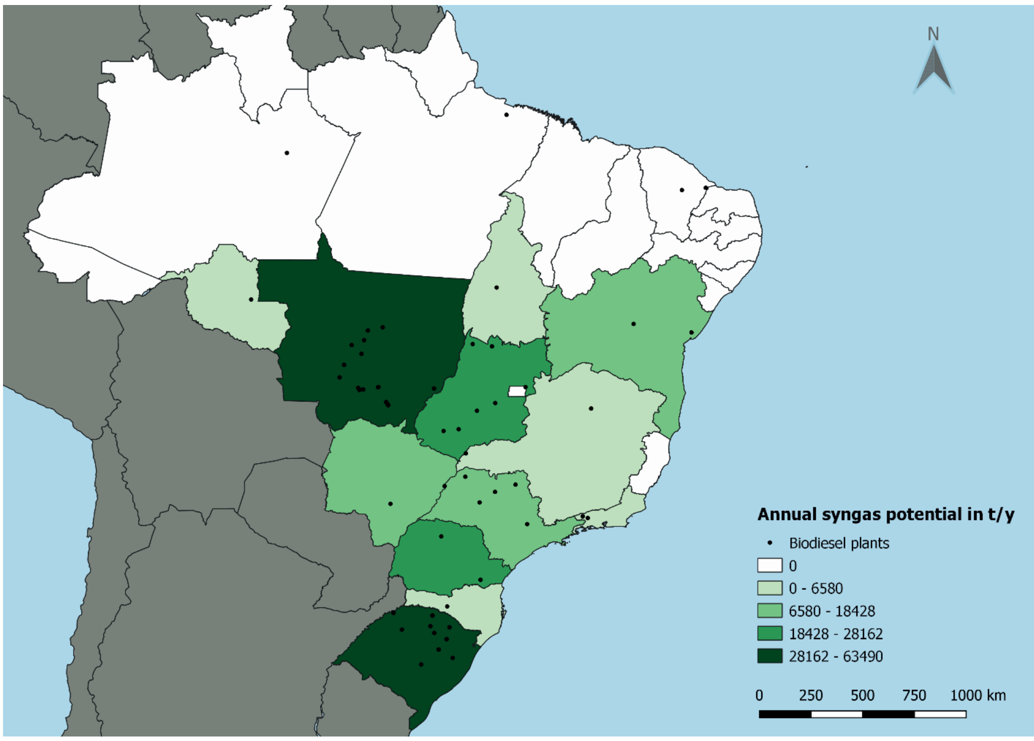

Figure 40: Potential syngas production of the biodiesel industry by state and plant distribution. Source: own elaboration

The South and the Central-West are the most favourable regions for syngas production. The state of Rio Grande do Sul has the highest syngas potential, due to its share of 26.5% of the total production and to the close localisation of different biodiesel plants in this state. Rio Grande do Sul is followed by the state of Mato Grosso, in the Central-West, which accounts for 22.5% of the total syngas potential. Especially the south of this state is favoured by the close localisation of several biodiesel plants. Rio Grande do Sul and Mato Grosso are followed by the states of Goiás, Paraná, and Bahia. The North, with a share of 2.9%, is the region with the lowest potential to produce syngas. The state of Bahia is the only in the Northeast with high potential, with a share of 7.7% of the total syngas production.

4.5. Corn industry

In Chapter 3, we identified the by-products and residues from the corn industry, among which corn stover is considered suitable for syngas production. In the following, this agricultural residue and its potential syngas production are estimated and mapped.

4.5.1. Estimation of residues

To estimate the agricultural residues from the Brazilian corn industry, data on the annual corn production by region and state in 2018 were obtained from the LSPA (IBGE, 2019).

Although these data are divided into first and second harvest, they are considered as one harvest in this study. As discussed in Chapter 3, every ton of corn results in 1.25 ton of corn stover. Based on the regional corn production in 2018, the residue by region and state was estimated and is shown in Table 28.

4.5.2. Syngas production

Based on the estimated corn stover generated in 2018, the potential syngas production through a direct conversion process was determined. For this purpose, the fluidized bed gasification of corn stover was considered, as introduced in Chapter 2. The amount of syngas obtained through the gasification of 1 kg of corn stover was estimated by using general equation 4 (see Chapter 2).

$$\eta_{FB} = \frac{LHV_{Syngas} * X_{kgSyngas}}{LHV_{Corn\ stover} * X_{kgCorn\ stover}} \tag{10}$$

The conversion factor was determined following this equation and information from Table 5 and Annex Table 2, which provides the LHV for corn stover. The fluidized bed gasification of 1 kg of corn stover results in 1.56 kg of syngas. By entrained flow gasification, 1 kg of corn stover results in 1.23 kg of syngas. Table 28 shows the syngas production by region and state through fluidized bed gasification.

Table 28: Estimated agricultural residue and potential syngas production of the corn industry by region and state. Source: yearly production data from IBGE (2019) and own elaboration

Brazilian region and state	Production of corn in 2018 – 1st and 2nd harvest (million tons)	Production of corn residues in 2018 (million tons)	Syngas production from corn residues (million tons)
North	**2.52**	**3.15**	**4,92**
Rondônia	0.76	0.96	0.15
Acre	0.081	0.10	0.16
Amazonas	0.013	0.016	0.025
Roraima	0.056	0.070	0.11
Pará	0.79	0.99	1.54
Amapá	0.0011	0.0014	0.0023
Tocantins	0.81	1.02	1.58
Northeast	**5.64**	**7.05**	**10.99**
Maranhão	1.32	1.65	2.58
Piauí	1.52	1.90	2.96
Ceará	0.47	0.59	0.93
Rio Grande do Norte	0.023	0.029	0.046
Paraíba	0.054	0.067	0.10
Pernambuco	0.055	0.068	0.11
Sergipe	0.16	0.20	0.31
Bahia	2.01	2.51	3.92
Southeast	**11.17**	**13.97**	**21.79**
Minas Gerais	6.66	8.33	12.99
Espírito Santo	0.042	0.053	0.083
São Paulo	4.46	5.57	8.70
South	**18.98**	**23.73**	**37.02**
Paraná	11.86	14.83	23.13
Santa Catarina	2.56	3.19	4.98
Rio Grande do Sul	4.56	5.71	8.90
Central-West	**40.74**	**50.92**	**83.94**
Mato Grosso do Sul	7.42	9.28	14.48
Mato Grosso	26.17	32.72	51.04
Goiás	9.05	11.32	17.66
Distrito Federal	0.39	0.49	0.77
Brazil	**81.36**	**101.71**	**158.66**

The results were mapped by region and state in QGIS. In Figure 41 and Figure 42, the potential syngas production by region and state is shown. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to a higher syngas production. The subdivision by state allows a better analysis of the syngas potential.

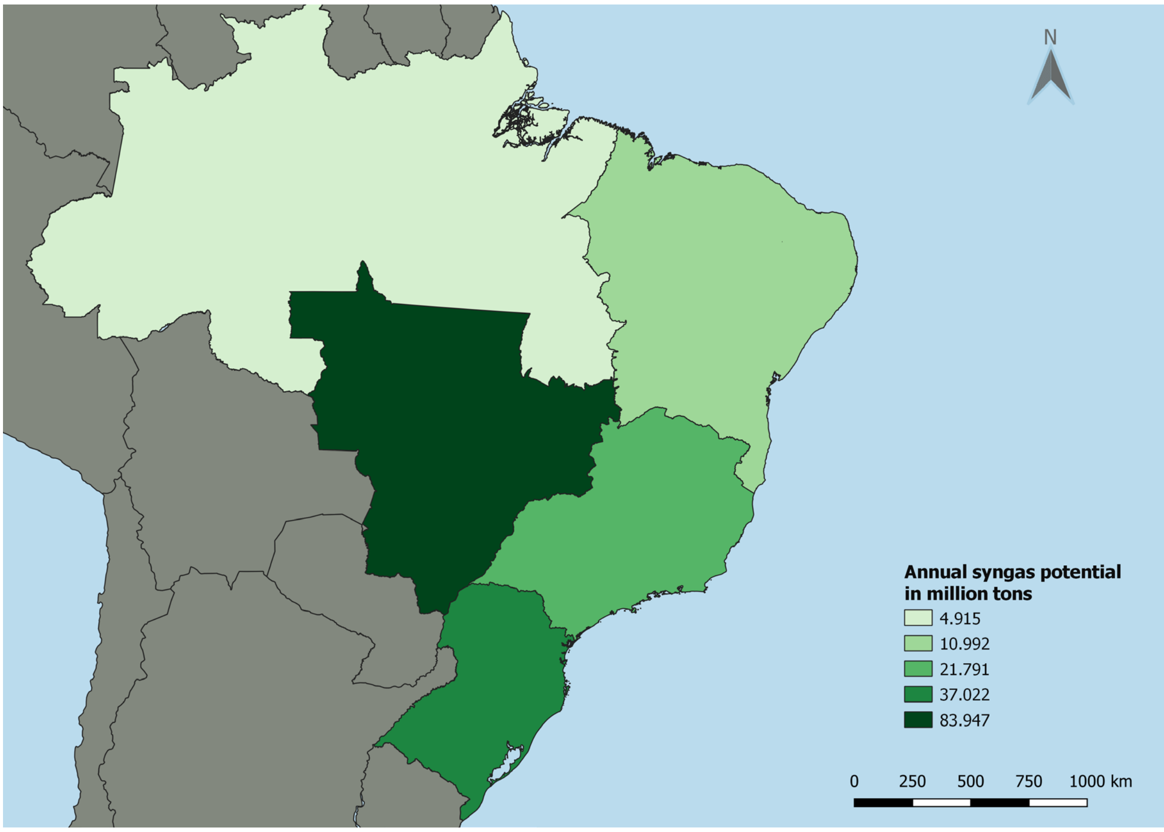

Figure 41: Potential regional syngas production of the corn industry. Source: own elaboration

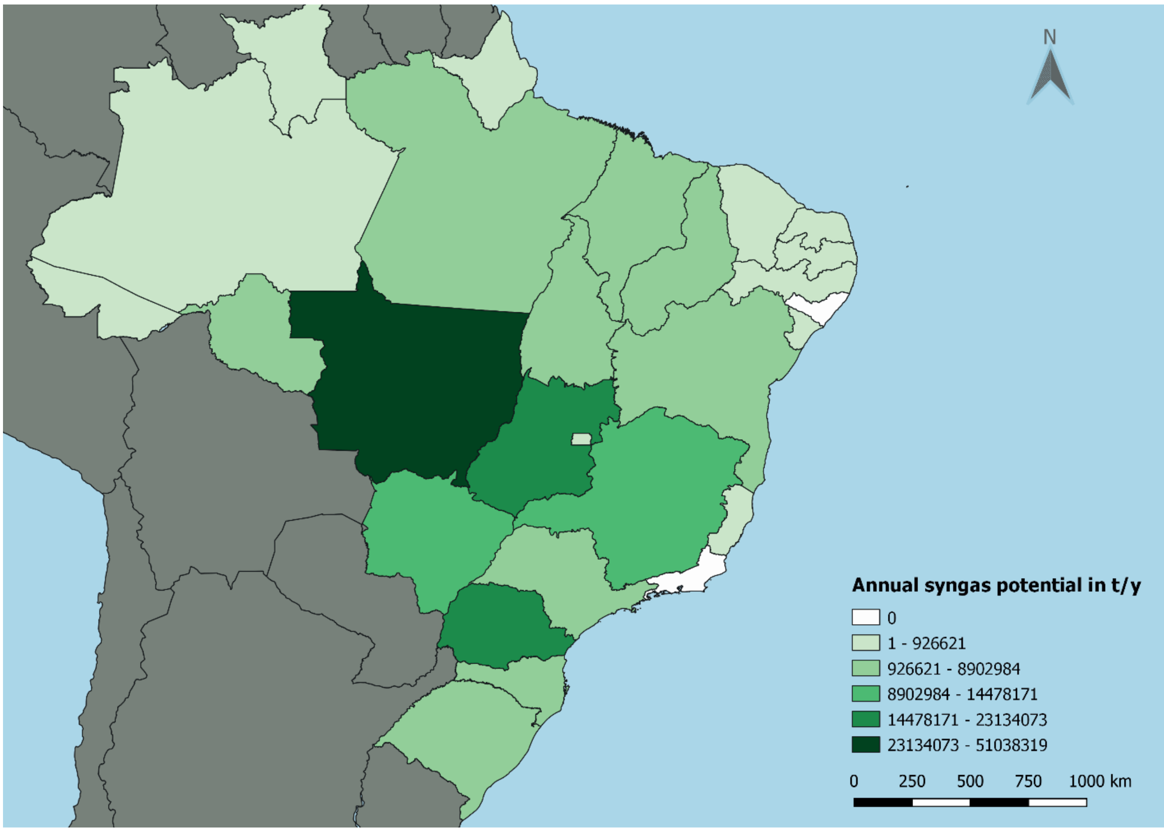

Figure 42: Potential syngas production from the conversion of corn stover by state. Source: own elaboration

The Central-West region accounts for the highest potential syngas production with a share of 50% of the total production, followed by the South and Southeast regions with 23% and 13% respectively. The North is the region with the lowest syngas potential. The most central driver of corn cultivation, the Central-West region, includes the state with the highest syngas potential in 2018—Mato Grosso, as the major producer of corn in 2018, accounted for 32% of the total syngas production in the same year. It is followed by the state of Paraná, in the South, and the states of Goiás and Mato Grosso do Sul, in the Central-West. It must be mentioned that the periods of the two harvests differ from region to region and even from state to state; therefore, the generation of residues is not constant throughout the year in Brazil.

4.6. Rice industry

In Chapter 3, we identified the agricultural residues from the rice industry, which are rice husk and straw. These residues are suitable for conversion into value-added products. In the following, these residues are estimated and their potential syngas production is determined.

4.6.1. Estimation of residues

To estimate the agricultural residues from the Brazilian rice industry, data on the annual rice production by region and state in 2018 were obtained from LSPA (IBGE, 2019). Considering the factor discussed in Chapter 3, every ton of rice results in 1.24 ton of rice husk and straw. Based on the regional rice production in 2018, the residue by region and state was estimated and is shown in Table 29.

4.6.2. Syngas production

Based on the estimated rice residues generated in 2018, the potential syngas production through a direct conversion process was determined. For this purpose, the fluidized bed gasification of the residues was considered, as introduced in Chapter 2. The amount of syngas obtained through the gasification of 1 kg of rice residues was estimated by using general equation 4 (see Chapter 2).

$$\eta_{FB} = \frac{LHV_{Syngas} * X_{kgSyngas}}{LHV_{Rice\ residues} * X_{kgRice\ residues}} \tag{11}$$

The conversion factor was determined following this equation and information from Table 5 and Annex Table 2, which provides the LHV for rice. The fluidized bed gasification of 1 kg of rice residues results in 1.43 kg of syngas. By entrained flow gasification, 1 kg of rice residues results in 1.13 kg of syngas. Table 29 shows the syngas production by region and state through fluidized bed gasification.

Table 29: Estimated agricultural residue and potential syngas production of the rice industry by region and state. Source: yearly production data from IBGE (2019) and own elaboration

Brazilian region and state	Production of rice in 2018 (million tons)	Production of rice residues in 2018 (million tons)	Syngas production from rice residues (million tons)
North	**0.96**	**1.19**	**1.70**
Rondônia	0.11	0.14	0.19
Acre	0.0068	0.0084	0.012
Amazonas	0.012	0.015	0.021
Roraima	0.055	0.068	0.097
Pará	0.11	0.14	0.20
Amapá	0.0008	0.0010	0.0014
Tocantins	0.66	0.82	1.17
Northeast	**0.39**	**0.49**	**0.69**
Maranhão	0.21	0.26	0.37
Piauí	0.11	0.14	0.19
Ceará	0.018	0.022	0.032
Sergipe	0.023	0.028	0.0040
Southeast	**0.058**	**0.072**	**0.10**
São Paulo	0.058	0.072	0.10
South	**9.63**	**11.94**	**17.07**
Paraná	0.13	0.16	0.23
Santa Catarina	1.09	1.35	1.94
Rio Grande do Sul	8.40	10.42	14.90
Central-West	**0.70**	**0.87**	**1.24**
Mato Grosso	0.50	0.62	0.89
Mato Grosso do Sul	0.087	0.11	0.15
Goiás	0.11	0.14	0.20
Brazil	**11.74**	**14.55**	**20.82**

The results were mapped by region and state in QGIS. In Figure 43 and Figure 44, the potential syngas production by region and state is shown. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to a higher syngas production. The subdivision by state allows a better analysis of the syngas potential.

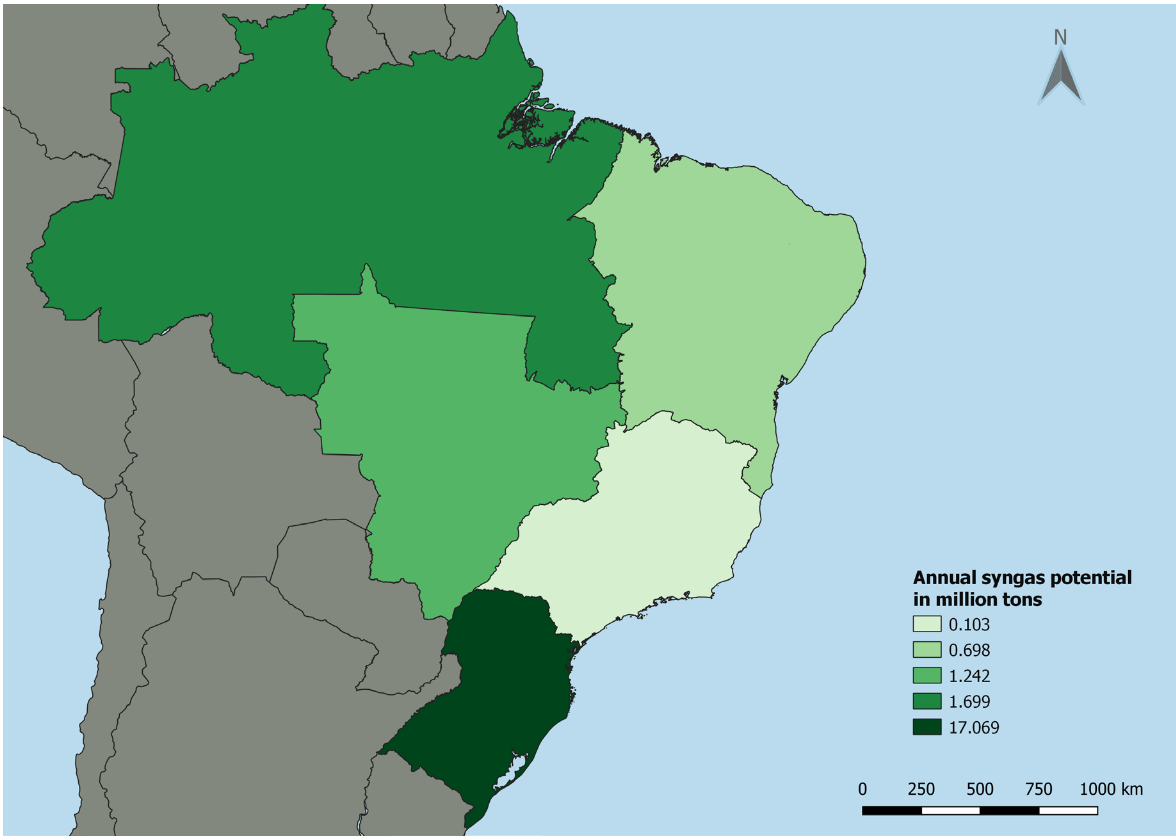

Figure 43: Potential regional syngas production of the rice industry. Source: own elaboration

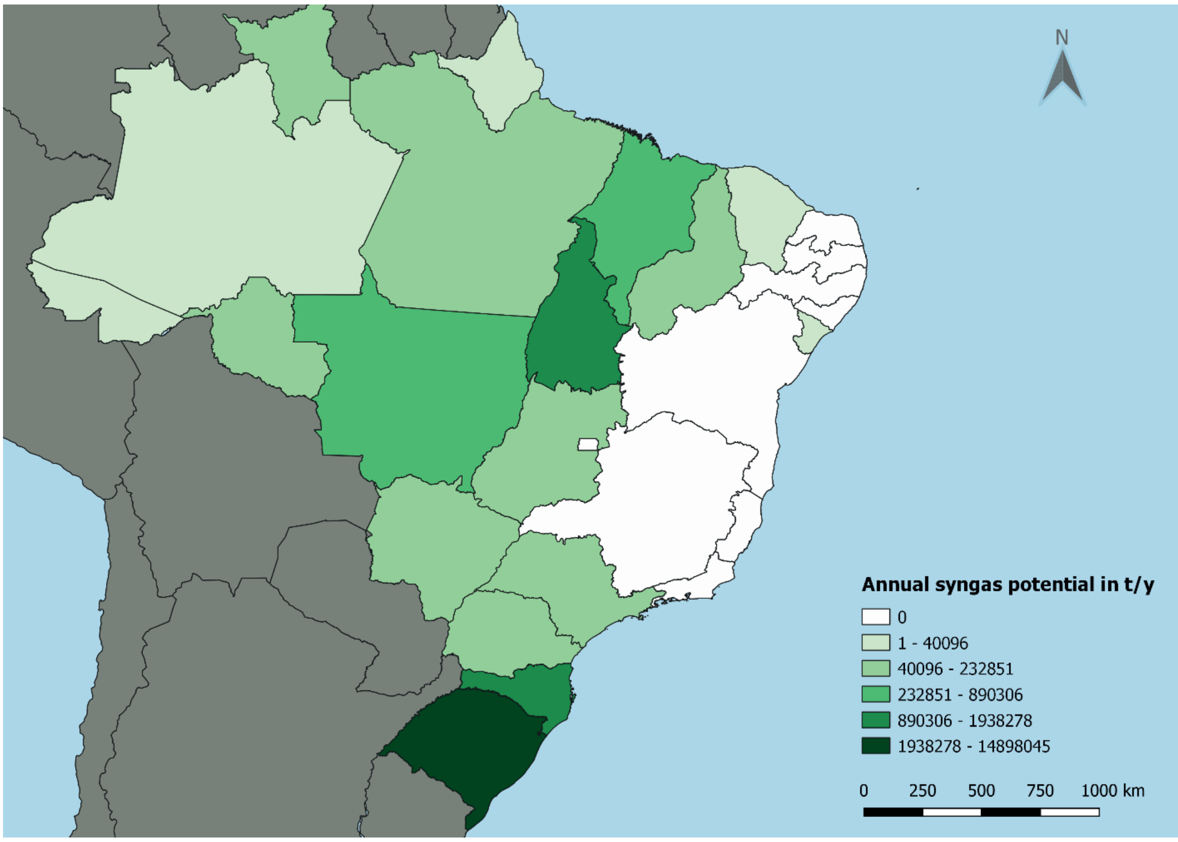

Figure 44: Potential syngas production from agricultural rice residues by state. Source: own elaboration

The South is the region with the highest rice production in Brazil. In 2018, 82% of the Brazilian rice was harvested in this region. As a consequence, this region has also the highest potential to produce syngas. The South is followed by the North and Central-West with 8.2% and 6.0% of the total production respectively. The state of Rio Grande do Sul accounts for nearly all of the rice produced in the South and has the highest syngas potential with a share of 72% of the total production in 2018. Therefore, this state is the most promising for syngas production.

4.7. Pulp industry

In Chapter 3, we identified the by-products and residues from the Brazilian pulp and paper industry through its dominant production process. The pulp industry itself accounts for nearly all the by-products and residues identified. The bark and wood wastes in the wood preparation process, the black liquor and the CO_2 emissions in the pulping process, and the pulp and paper mill sludge of the wastewater treatment plant are considered suitable for syngas production. Black liquor is used in conventional pulp production to recover white liquor and to guarantee the self-supply of the energy demand. Due to the assumption that the industrial process should not be changed, only the resulting CO_2 from black liquor combustion is further considered. The ash from the combustion of by-products and residues for energy production is generally used to produce construction materials, and there is no literature found on its conversion into syngas.

There are 61 active companies in the Brazilian pulp and paper industry. Figure 45 shows the wide geographic distribution of the pulp and paper producers in Brazil. Because this sector has a direct relationship with the consumer market, the companies are concentrated in the South and Southeast regions of the country (IBÁ, 2019). There are 71 pulp mills in 14 states, with 20 in Paraná and 17 in São Paulo (DEPEC, 2019).

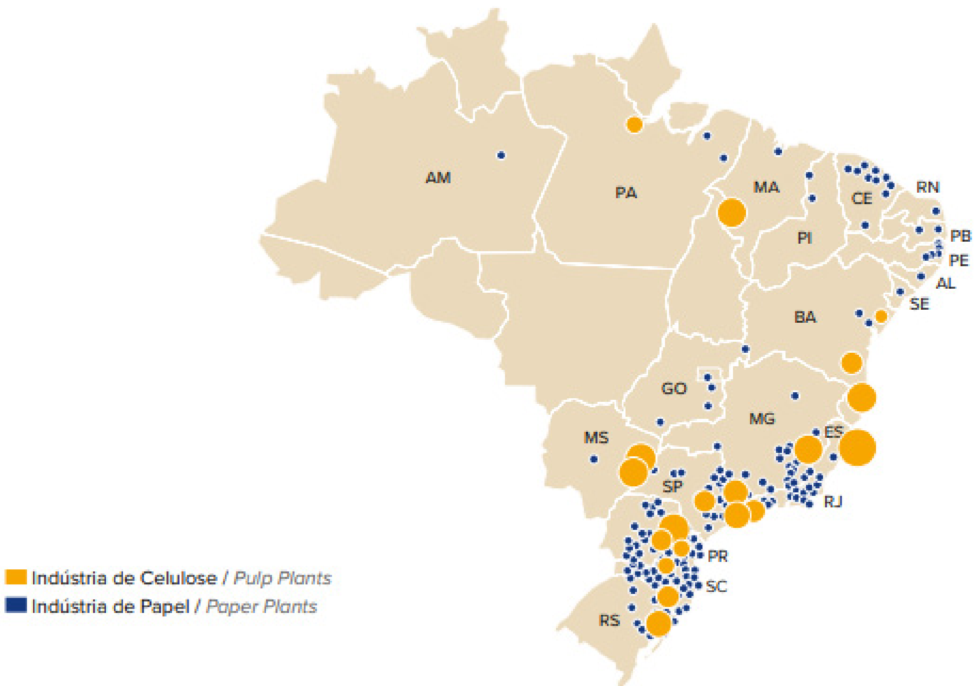

Figure 45: Distribution of the Brazilian pulp and paper industry. Source: IBÁ (2019)

4.7.1. Estimation of by-products and residues

No public data were found regarding the regional production of the Brazilian pulp industry, neither by IBÁ nor by other institutions. To estimate the by-products and residues from the Brazilian pulp industry, data were obtained from the EPE. These data were put together by the EPE in the National Energy Balance (*Balanço Energético Nacional*, BEN 2019), which is updated every year. It must be noted that these data are not complete and show a total pulp production that is lower than that reported by IBÁ (2019). In Table 30, the pulp production by region and state is given.

Table 30: Brazilian pulp production by region and state in 2018. Source: yearly production data from the EPE

Brazilian region and state	Production of pulp in 2018 (million tons)
North	-
Northeast	**4.81**
Maranhão	1.48
Bahia	3.33
Southeast	**3.13**
Espírito Santo	2.11
São Paulo	1.03
South	**4.92**
Paraná	2.47
Santa Catarina	0.58
Rio Grande do Sul	1.87
Central-West	**1.33**
Mato Grosso do Sul	1.33*
Brazil (EPE) **Brazil-total (IBÁ, 2019)**	**14.20** **21.08**

*Data from 2015 with a growth rate of 7.1%.

The data from the EPE and IBÁ show a difference of about 6.8 million tons. This difference can be due to not recorded pulp mills—for example, the states of Pará and Minas Gerais do produce pulp according to Figure 45 but are not recorded in the BEN. The pulp production data of Mato Grosso do Sul was only available for 2015, so the production in 2018 was estimated based on the annual growth of 7.1% from 2012 until now. Based on the data on the regional pulp production in 2018, the industrial by-products and residues were estimated and are shown in Table 31.

For the estimation of the *bark and wood wastes* generated in the wood preparation and handling process, a eucalyptus-based South American kraft pulp mill was considered as a reference (Kuparinen & Vakkilainen, 2017). The pulp mill results in 0.15 ton of wood residue for every ton of pulp generated.

The amount of *pulp and paper mill sludge* can be estimated with the assumption that 50 kg (0.05 ton) of pulp and paper mill sludge is generated in the production of 1 ton of paper (Cho et al., 2017), and that 1 ton of pulp results in approximately 1 ton of paper (Kuparinen et al., 2019).

In kraft pulp mills, CO_2 is primarily formed during the combustion reaction of fuels. The main CO_2 sources are the recovery boiler, the lime kiln, and the biomass boiler (when present). To be used, the CO_2 must be captured by a carbon capture technology. Most likely, it is not feasible to capture the CO_2 from all possible CO_2 streams; therefore, only the recovery boiler, which is the largest source of CO_2, was considered. To estimate the biogenic CO_2 emissions by the recovery boiler, the emission factor of 1.8 ton of CO_2 per ton of air-dry pulp was assumed (Kuparinen et al., 2019).

Table 31: Estimated by-products and residues of the Brazilian pulp production in 2018. Source: yearly production data from the EPE and own elaboration

Brazilian region and state	Production of pulp in 2018 (million tons)	Bark and wood waste in pulp production (million tons)	Pulp and paper mill sludge (million tons)	CO2 from pulp production (million tons)
North	-	-	-	-
Northeast	**4.81**	**0.72**	**0.24**	**8.66**
Maranhão	1.48	0.22	0.074	2.66
Bahia	3.33	0.50	0.17	5.99
Southeast	**3.13**	**0.47**	**0.16**	**5.64**
Espírito Santo	2.11	0.32	0.11	3.79
São Paulo	1.03	0.15	0.05	1.85
South	**4.92**	**0.74**	**0.246**	**8.85**
Paraná	2.47	0.37	0.12	4.45
Santa Catarina	0.58	0.086	0.029	1.04
Rio Grande do Sul	1.87	0.28	0.094	3.37
Central-West	**1.33**	**0.20**	**0.067**	**2.40**
Mato Grosso do Sul	1.33*	0.20	0.067	2.40
Brazil	**14.20**	**2.13**	**0.71**	**25.56**

*Data from 2015 with a growth rate of 7.1%.

4.7.2. Syngas production

4.7.2.1. Bark and wood wastes

Based on the bark and wood wastes estimated, the potential syngas production through a direct conversion process was determined. The conversion of bark and wood wastes through gasification is already in use by some pulp and paper mills, primarily for the substitution of fossil fuels in the lime kiln, but still has not been demonstrated on a commercial scale. In Isaksson (2015), a detailed literature review of studies and plants are given. Before gasification, the biomass must be pretreated and dried to remove particles and improve the efficiency of the process (see Chapter 2). In this study, for a better comparison of biomass gasification, a fluidized bed gasifier was considered, as introduced in Chapter 2. The amount of syngas obtained through the gasification of 1 kg of bark and wood waste was estimated by using general equation 4 (see Chapter 2).

$$\eta_{FB} = \frac{LHV_{Syngas} * X_{kgSyngas}}{LHV_{Bark\ and\ wood\ waste} * X_{kgBark\ and\ wood\ waste}} \tag{12}$$

The conversion factor was determined following this equation and information from Table 5 and Annex Table 2, which provides the LHV for eucalyptus wood chips. The LHV for eucalyptus wood was considered because eucalyptus with a share of 83% is the most used raw material in the pulp and paper industry. The gasification of 1 kg of bark and wood waste by the fluidized bed gasifier results in 1.69 kg of syngas. By entrained flow gasification, 1 kg of bark and wood waste results in 1.34 kg of syngas.

4.7.2.2. Paper mill sludge

The thermochemical conversion of pulp and paper mill sludge into syngas has been raising the interest of the industry, and some studies have been investigating thermochemical processes. In Cho et al. (2017), the pyrolysis of paper mill sludge with CO_2 as a reaction medium was investigated to produce syngas and magnetic biochar. The pyrolysis of the mill sludge in CO_2 generates 9.6 mol% of syngas at 720°C. In Chiang et al. (2016), a co-gasification of paper mill sludge in a commercial plant was conducted in which 2 tons of wet sludge produced 2.2 tons of syngas. The syngas production was determined by assuming this conversion factor with a fluidized bed gasifier.

4.7.2.3. Carbon dioxide

Based on the regional CO_2 emissions estimated, the potential syngas production through an indirect conversion process, the co-SOEC electrolysis, was determined. To be used, the CO_2 must be captured by a carbon capture technology. According to Kuparinen et al. (2019), there are not many detailed techno-economic analyses of carbon capture systems for pulp mills. The amine-based post-combustion is a proven and commercially available technology and will be considered in this study as the technology to capture the CO_2 from the recovery boiler for syngas production. It has a capture efficiency of 90%. Finally, with the conversion factor of the co-SOEC electrolysis process considered in this study (see also in Chapter 2), every kg of CO_2 results in 0.84 kg of syngas. In Table 32, the syngas production by region and state through fluidized bed gasification of different by-products and residues is shown.

Table 32: Potential and total syngas production of the pulp industry. Source: own elaboration

Brazilian region and state	Syngas from bark and wastes (million tons)	Syngas from pulp and paper mill sludge (million tons)	Syngas from CO2 (million tons)	Total syngas production (million tons)
North	-	-	-	-
Northeast	**1.22**	**0.53**	**6.55**	**8.30**
Maranhão	0.37	0.16	2.01	2.55
Bahia	0.84	0.37	4.53	5.75
Southeast	**0.79**	**0.34**	**4.26**	**5.40**
Espírito Santo	0.53	0.23	2.86	2.63
São Paulo	0.26	0.11	1.40	1.77
South	**1.25**	**0.54**	**6.69**	**8.48**
Paraná	0.63	0.27	3.36	4.26
Santa Catarina	0.15	0.063	0.78	0.99

Rio Grande do Sul	0.47	0.21	2.55	3.23
Central-West	**0.34**	**0.15**	**1.82**	**2.30**
Mato Grosso do Sul	0.34	0.15	1.82	2.30
Brazil	**3.60**	**2.32**	**19.32**	**25.24**

The total syngas production was mapped by region and state in QGIS. In Figure 46 and Figure 47, the potential syngas production by region and state is shown. The regions and states are divided by colours depending on their potential to produce syngas. Darker colours correspond to higher syngas production. The subdivision by state allows a better analysis of the syngas potential. The locations of the pulp production plants are not shown because no literature or data were found regarding them.

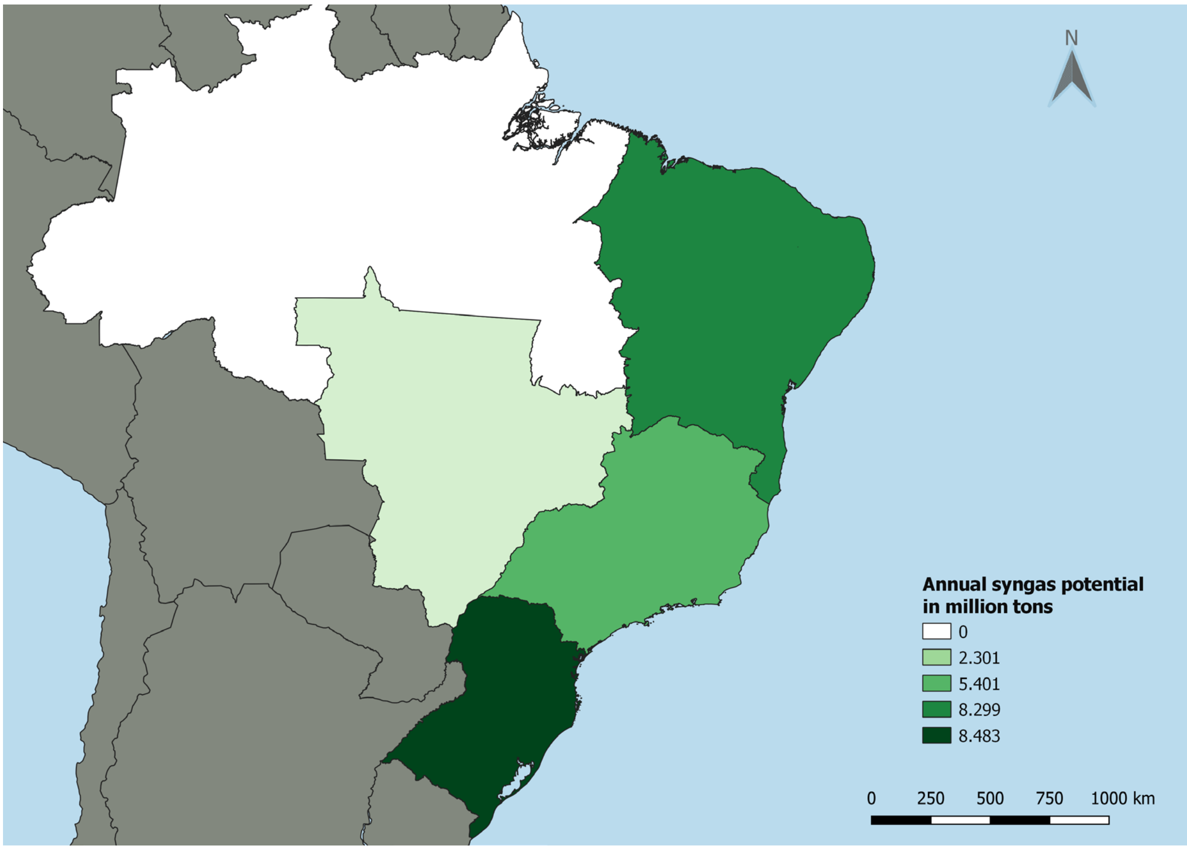

Figure 46: Potential regional syngas production of the pulp industry. Source: own elaboration

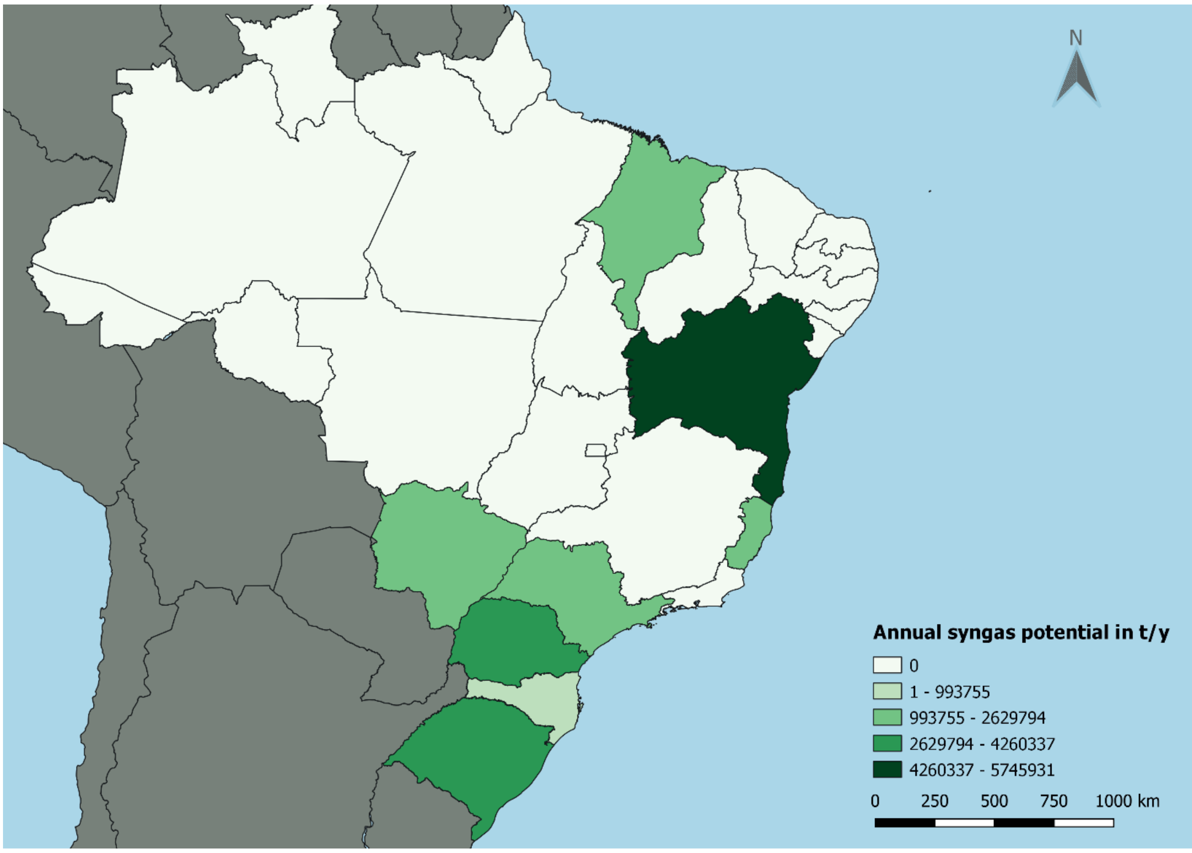

Figure 47: Potential syngas production of the pulp industry by state. Source: own elaboration

The South and Northeast of Brazil are the regions with the highest potential to produce syngas. Bahia, in the Northeast, is the state with the highest potential, with 16% of the total syngas production, followed by Paraná and Espírito Santo, with 12% and 7% respectively.

4.8. Analysis of the industries regarding their syngas potential and potential sites for PtL aviation fuel production

4.8.1. Potential syngas production

For most of the industries, the Southeast is the region with the highest potential syngas production, followed by the Central-West and the South. The Northeast and especially the North have lower potential mostly due to the lack of those industries. In Table 33, the industries analysed in this study can be compared regarding their potential syngas production.

The gasification of the agricultural residues from the soybean, corn and sugarcane industries have by far the highest potentials with yearly productions of 299, 158, and 146 million tons of syngas, respectively. The other industries, such as cement, steel, pulp, rice, and ethanol, have a yearly potential of between 20 million and 31 million tons of syngas. Though biodiesel production has the lowest potential to generate syngas, it has decisive advantages in comparison to the others.

Table 33: Potential syngas production from the by-produts of the analysed industries and the maximum potential by state. Source: own elaboration

Industry	By-product and residue	Total annual syngas potential (tons)	Max. potential by state (tons of syngas/year)
Cement industry	Carbon dioxide	22,267,418	5,297,780 (MG)
Steel industry	Carbon dioxide	31,944,563	9,558,017 (MG)
Sugarcane industry			
• Sugarcane	Sugarcane straw	146,296,782	77,781,228 (SP)
• Ethanol	Carbon dioxide	21,032,147	10,318,479 (SP)
Soybean industry			
• Soybean	Soybean straw	299,108,536	80,235,174 (MT)
• Biodiesel	Glycerol	238,979	63,490 (RS)
Corn industry	Corn straw	158,660,843	51,038,319 (MT)
Rice industry	Rice straw/husk	20,810,901	14,898,045 (RS)
Pulp industry	Wood wastes/mill sludge/ CO_2	25,236,865	5,745,931 (BA)

Besides having the highest potential to generate syngas, the gasification of the agricultural residues accounts for the lowest energy demand in comparison to the other industries analysed. However, it requires more complex treatment and gas cleaning steps. Also, the agricultural residues pose major challenges regarding logistics due to their scattered production, low bulk density, and biodegradable nature, which lead to high collection, transport, and storage costs (Carvalho et al., 2019). The cement, steel and pulp industries also have high syngas potential, but currently are the most energy-intensive conversions due to the carbon capture and SOEC co-electrolysis.

Compared to the other stationary sources, the CO_2 from ethanol production does not need an additional cleaning process, due to the purity of the feedstock. Glycerol from biodiesel production is a low-value by-product that raises high interest in the further conversion into the value-added product syngas. The possibility to reform glycerol brings the advantage of a cleaner syngas production with fewer steps than the gasification and a lower energy demand than the co-SOEC electrolysis. Therefore, despite the low potential syngas production, it is a suitable industry regarding the production of SAF in a biorefinery concept.

4.8.2. Potential sites for the production of sustainable aviation fuels

With such high potential to produce syngas, Brazil is easily able to overcome its increasing demand for aviation fuel with sustainable aviation fuels. Especially the agricultural residues of the soybean, sugarcane, and corn industries can meet the current aviation fuel demand in Brazil only by considering the states with the highest potential syngas production (Table 33). Considering that every kg of syngas results in 0.336 litres of SAF through the FT route (Löchle, 2019), by assuming a kerosene density of 0.8 kg, the soybean industry in Mato Grosso can produce 21.56 million tons of SAF from residues, which satisfies easily the projected Brazilian aviation fuel demand of 14.2 million tons in 2050. Summing up the total potential syngas production of the industries considered in this study, their potential fuel production is estimated at 193 million tons of SAF. In comparison to that, the aviation fuel consumption of Europe was 51 million tons in 2017 (Eurostat, 2019).

Not all feedstock sources and industries are available for the production of SAF; therefore, after the theoretical potential syngas production of the industries is determined and mapped for Brazil by region and state, it is of interest to identify potential sites for the implementation of PtL plants to produce SAF. For this purpose, information like the states with the highest potentials, the locations of the industrial production plants, possible hotspots for the agricultural residues, the nearest large distribution base of kerosene to blend the SAF, and the nearest international or large airports are considered. Carvalho et al. (2019), who investigated the potential bio-kerosene production by different crops, identified possible hotspots for the crops considered in this study with kernel density maps. The largest Brazilian refineries for kerosene production in 2018 were taken from Araujo (2019). Due to the lack of information about the exact production of every plant, the yearly SAF production by the whole states was considered. For further information regarding the locations of hotspots and large airports, see Carvalho et al. (2019).

Figure 48 shows the soybean industry with the biodiesel production plants and the hotspot for soybean straw located in the municipality of Sorriso, in Mato Grosso (Central-West region). Given the lack of a big distribution base in that region, a small distribution base in the neighbour municipality Sinop is considered (Carvalho et al., 2019). The nearest airport is the International Airport Marechal Rondon, 324 km away from the municipality. According to the calculations, Rio Grande do Sul has the highest potential syngas production of the biodiesel industry; however, as it is directly followed by Mato Grosso, which also has a hotspot for soybean straw, plants for the production of SAF can be more favourable in Mato Grosso. This state can produce 21.56 million tons of SAF from soybean residues and 14.5 thousand tons of SAF from the production of biodiesel.

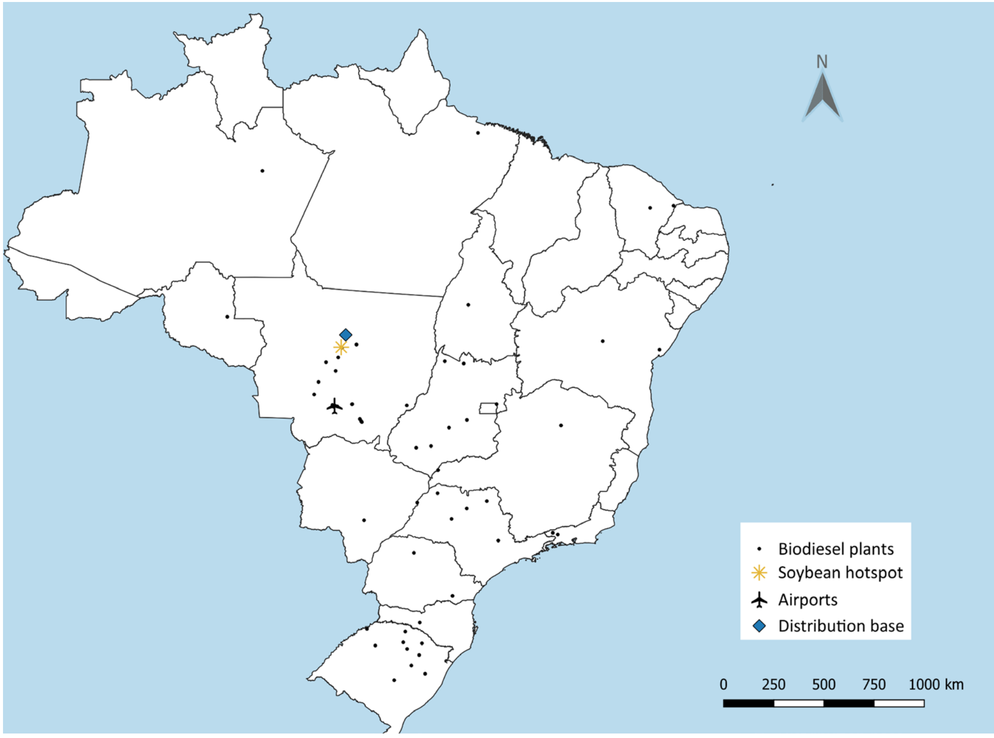

Figure 48: Soybean industry with the potential hotspot for residues and important sites for the production of SAF. Source: own elaboration

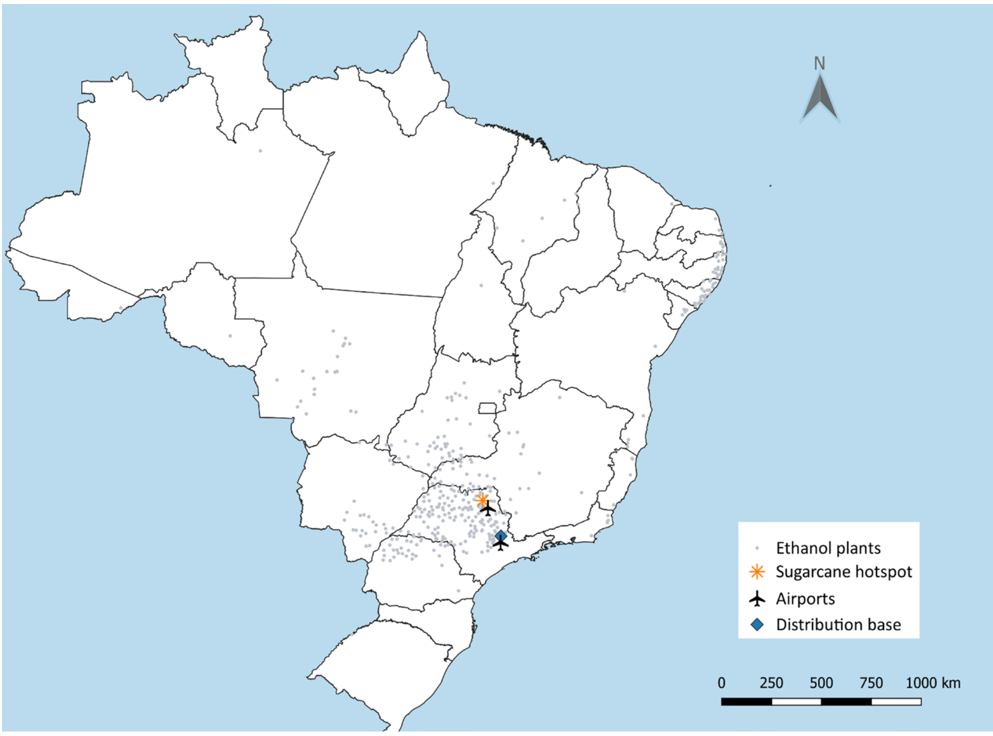

Figure 49: Sugarcane industry with the potential hotspot for residues and important sites for the production of SAF. Source: own elaboration

Figure 49 shows the ethanol production plants and the hotspot for sugarcane straw located in the municipality of Morro Agudo in the state of São Paulo (South-East region). The nearest large kerosene distribution base is REPLAN refinery near Campinas and the nearest airports to the hotspot are the Airport of Ribeirão Preto, 56 km away from the municipality, and the Viracopos International Airport, in Campinas municipality, which is closer to REPLAN refinery. The implementation of plants to produce SAF around the hotspot can be favourable. The state of São Paulo can produce 20.9 million tons of SAF from sugarcane residues and 2.77 million tons of SAF from ethanol.

In Figure 50, the case for the cement and steel industries in Brazil is presented. Minas Gerais is the state with the highest potential to produce syngas for both industries. Figure 51 shows the state of Minas Gerais and a concentration of these industries around Belo Horizonte municipality. The nearest large kerosene distribution base is the REGAP refinery, and the nearest airport is Carlos Prates Airport. The implementation of plants to produce SAF in this region can be favourable. The state can produce 1.42 million tons of SAF from the cement industry and 2.57 million tons of SAF from the steel industry.

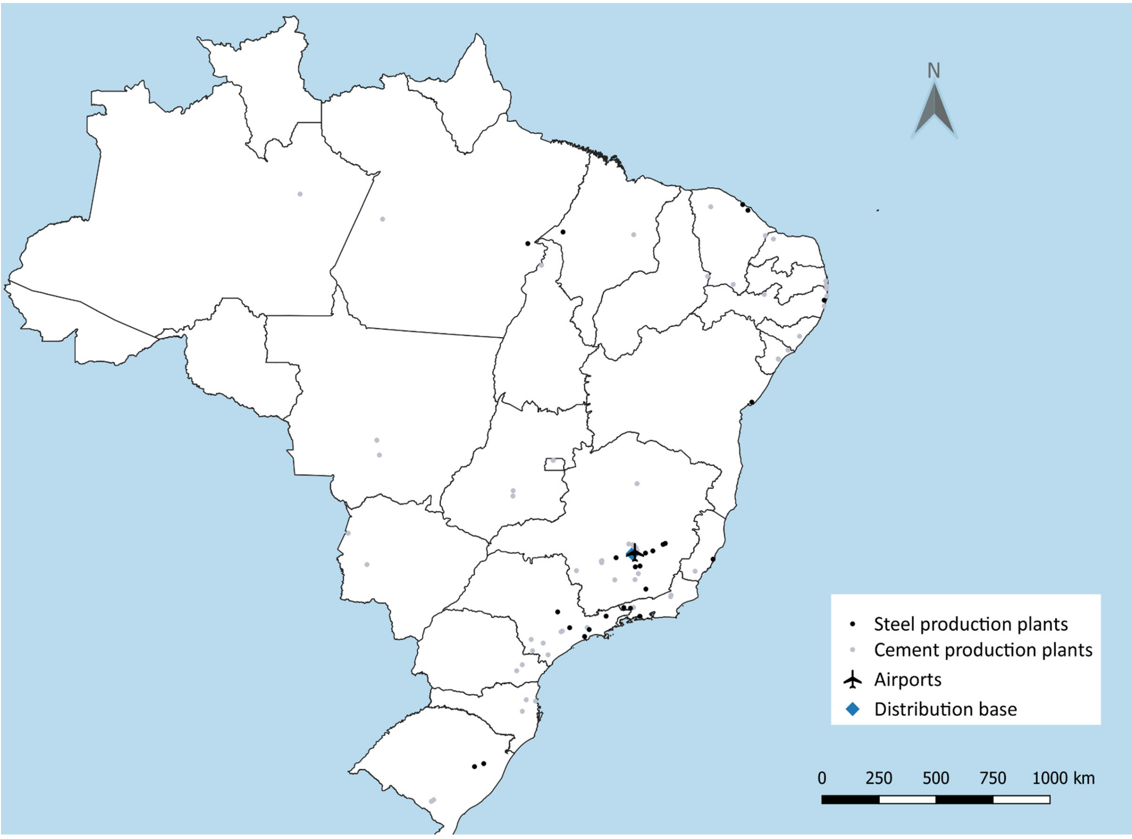

Figure 50: Cement and steel industry with important sites for SAF production. Source: own elaboration

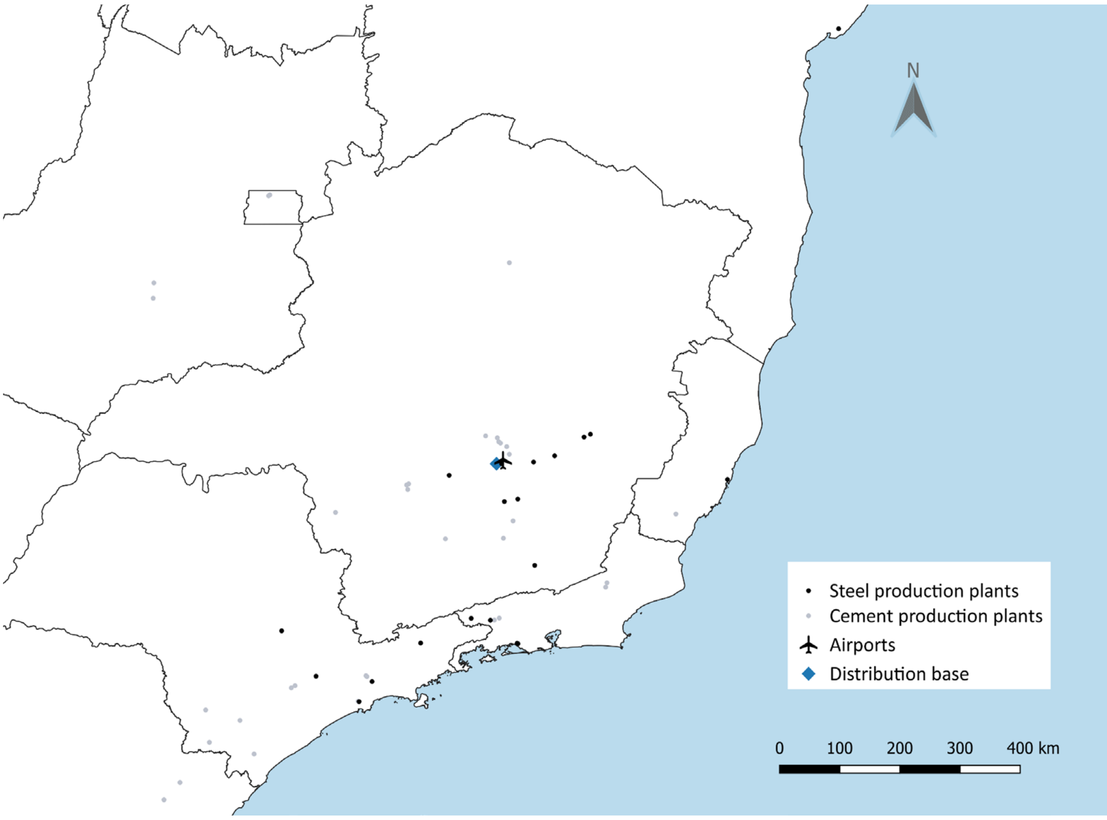

Figure 51: Detailed capture of potential sites for SAF production plants in Minas Gerais. Source: own elaboration

Figure 52 shows the corn and rice industry with their respective hotspots for agricultural residues. For corn, there are two hotspots: one in Mato Grosso (Central-West region), in the municipality of Sorriso, and the other in Paraná (South region), in the municipality of Tupassi. Because the municipality in Mato Grosso is the same for the soybean industry, this region can be of more interest. As for the rice industry, which is concentrated mostly in the South, the hotspot is in the municipality of Alegrete, in Rio Grande do Sul. The nearest large distribution bases are REPAR, in the state of Paraná, and REFAP, in the state of Rio Grande do Sul.

The suitable airports are International Airport Marechal Rondon, 316 km away from the corn hotspot, in Mato Grosso; the International Airport of Cataratas, 151 km away from the corn hotspot, in Paraná; and Salgado Filho Airport, in Rio Grande do Sul, 467 km away from the rice hotspot. The corn industry can produce 13.72 million tons of SAF in the state of Mato Grosso and 6.22 million tons in the state of Paraná. The rice industry in the state of Rio Grande do Sul can produce 4 million tons of SAF.

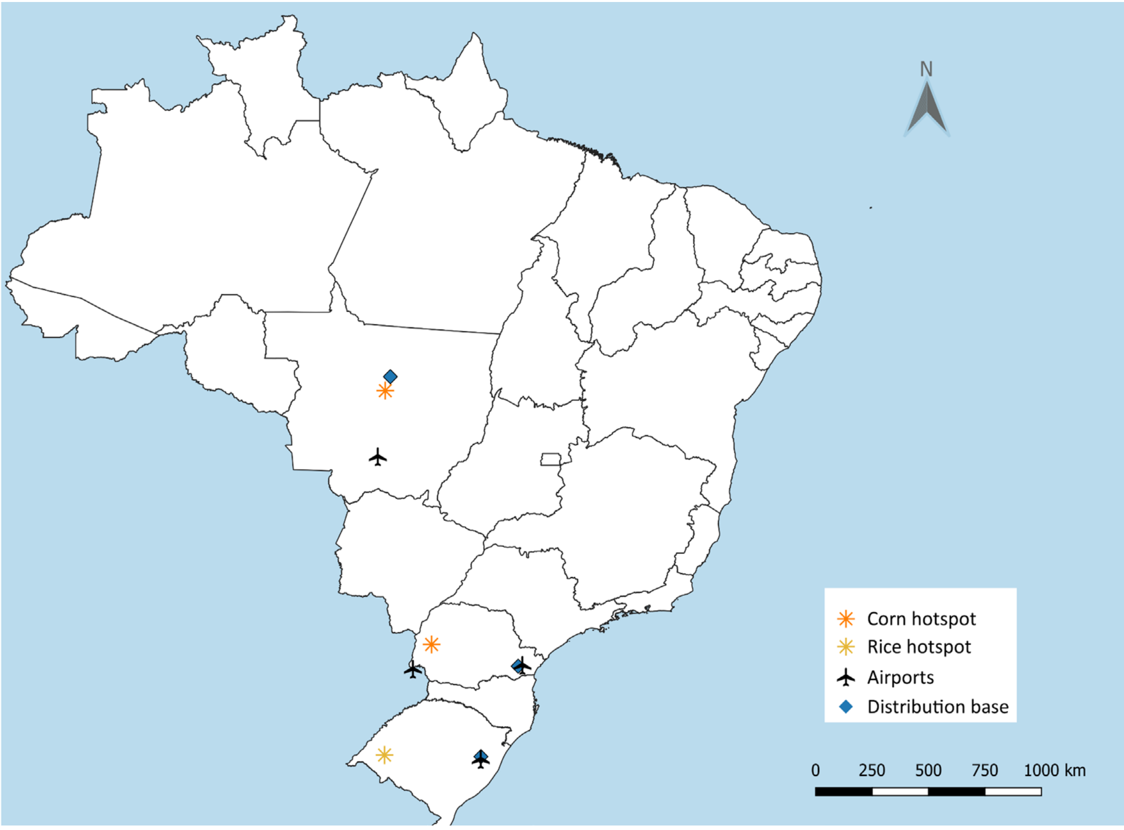

Figure 52: Corn and rice industry with potential residue hotspots and important sites for the production of SAF. Source: own elaboration

5. Conclusion and future research

5.1 Conclusion

In this study, the potential of the Brazilian industry sector to generate syngas was investigated to identify Brazil as a potential player in the production of Power-to-Liquid fuels (PtL). Syngas, as a versatile intermediate of the Fischer-Tropsch synthesis, can be derived from the conversion of a variety of feedstocks, such as industrial by-products and residues. The by-products and residues from the Brazilian industries were identified and listed in this study.

Among the suitable industries, the soybean, biodiesel, sugarcane, ethanol, corn, rice, steel, cement, and pulp and paper were selected through an evaluation matrix and had their processes analysed with respect to the Brazilian case. These industries provide suitable residues and low-value by-products that can be used to generate syngas and be converted into high value-added products, such as sustainable aviation fuel (SAF) or any other synthetic fuel, which could be more economically, socially, and environmentally beneficial.

After estimating the sum of by-products and residues that each of these industries can produce assuming 2018 as the base year, the potential syngas production through suitable conversion processes was determined. The syngas potential of every industry was mapped by region and state using a geographic information system, QGIS. This analysis revealed that the Central-West region has the highest potential to produce syngas (35% of the total), followed by the Southeast and the South, with respectively 26% and 23%. Due to the absence of the industries analysed in the Northeast and North, these regions have a lower share in the total syngas potential. The Northeast accounts for 9.3% and the North, only for 3% of the syngas potential.

The gasification of agricultural residues from the soybean, corn and sugarcane industry has by far the highest potential to produce syngas, with respective yearly productions of 299 million, 158 million, and 146 million tons. The order of the remaining industries respective to their total syngas potential is steel, pulp and paper, cement, ethanol, rice, and biodiesel.

Despite the lower syngas potential of the biodiesel industry, a possible conversion through reforming, the purity of substrate, and the consequential simplicity of gas cleaning give it advantages over the gasification of agricultural residues, which impose challenges such as collection, transport, and storage of the feedstock. In addition, a lower energy demand compared to the conversion through co-SOEC electrolysis used in the cement, steel, pulp, and ethanol industry makes biodiesel production with glycerol a potential playmaker for the production of syngas in a biorefinery concept.

Considering the potential syngas production of all industries, an impressive potential aviation fuel production of about 193 million tons of SAF would result. These high potentials, as well as the overall favourable geographical situation regarding renewable energy sources and the extensive experience in bioenergy and biofuels, make Brazil an important player for PtL fuels. Brazil is not only able to easily overcome its rising demand for aviation fuel but also can provide the European, or any other aviation sector worldwide, with climate neutral synthetic aviation fuel.

Apart from mapping the syngas production by region and state, potential sites for PtL production plants were identified for most of the industries on a state level. These sites were located considering possible industrial hotspots with high syngas potential, distribution bases to blend the SAF with Jet-A1, and airports nearby to make use of the fuel. A potential site for the soybean industry, including biodiesel production, is in Mato Grosso (Central-West). For the corn industry, Paraná (South) and Mato Grosso (Central-West) were found suitable.

As for the rice industry, Rio Grande do Sul (South) was found suitable, and for the sugarcane industry, including ethanol production, the state of São Paulo (Southeast) was considered a possible site. The state of Minas Gerais (Southeast), especially the locations near the municipality of Belo Horizonte, was found to be the most favourable for cement and steel. These are sites where the establishment of biorefineries can be more favourable.

The soybean industry, including biodiesel production, is the industry with the highest overall potential syngas production in Brazil. It can generate 21.58 million tons of SAF in the state of Mato Grosso, most of it from agricultural residues.

The location of the different industries and the potential sites for SAF production confirm that the North of Brazil remains a problematic region regarding fuel distribution. The decentralized approach with kerosene synthesized from ambient air will have to meet the demand in this region.

5.2 Limitations and future studies

This study has limitations that can be addressed in future works. Some industries and their residues are suitable but were not covered in this study, such as forestry residues, animal wastes, CO_2 from biogas and ferroalloy production, and municipal wastes like biogas from wastewater treatment. They may have high syngas potentials and lead to more interesting regional distributions.

A more accurate database may provide more reliable results for the industries, especially for the pulp industry, whose production data are more imprecise and whose production facilities could not be precisely located in Brazil. Also, a technical and economic potential analysis using data with a high spatial resolution should give more accurate estimations of the potential syngas production in Brazil.

A further techno-economic assessment of the regions identified for potential sites of SAF plants in Brazil is highly recommended to determine the most suitable plants and sites for the different industries. As for by-products used in the conventional industry process itself (therefore not analysed in this study, such as bagasse and black liquor), a conversion to syngas and SAF may be a more economical and efficient solution and can be analysed in future studies.

As for the conversion of agricultural residues, the feasibility of torrefaction as a pretreatment step could be investigated especially regarding the syngas requirements of the Fischer-Tropsch synthesis. Also, the entrained flow gasifier of the bioliq project at Karlsruhe Institute of Technology, which focuses on large scale biomass residue gasification, may be a more feasible solution to the gasification of agricultural residues than a commercial fluidized bed gasifier.

6. References

Aberg, K. (2014) *Syngas production by integrating thermal conversion processes in an existing biorefinery*. Licentiate thesis. Department of Applied Physics and Electronics. ISBN: 978-91-7601-101-0

Adhikari, S. (2013) *Biomass characterization and gasification*. Biosystems Engineering Department, UA.

Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP). (2019) *Anuário estatístico brasileiro do petróleo, gás natural e biocombustíveis*. Rio de Janeiro, 2019. Available from: http://www.anp.gov.br/publicacoes/anuario-estatistico/5237-anuario-estatistico-2019. [Accessed 22 Apr. 2021].

Agora Energiewende. (2019) *Klimaneutrale Industrie: Schlüsseltechnologien und Politikoptionen für Stahl, Chemie und Zement*. Berlin.

Allegue, L. B. & Hinge, J. (2012) *Biogas and bio-syngas upgrading*. Aarhus, Danish Technological Institute.

Almansa, G. A. & Kroon, P. (2016) *Towards green iron and steel industry: Opportunities for MILENA biomass gasification technology in Direct Reduction of Iron*. ECN.

American Coke and Coal Chemicals Institute. *The coke oven by-product plan*. [n.d.]. Available from: http://www.accci.org/Byproduct.pdf [Accessed 3 May 2021].

Amin, M., Patel, J., Selvakannan, P. R., Sage, V. (2015) *Tri-reforming of methane for the production of syngas: Review on the process, catalysts and kinetic mechanism*. Centre for Advanced Materials and Industrial Chemistry, RMIT University Melbourne Australia.

Araujo, R. B. (2019) Perspectivas e planejamento setorial para cadeia do biodiesel e novos biocombustíveis no Brasil. In: *VII Congresso da Rede Brasileira de Tecnologia e Inovação de Biodiesel*, 4-7 nov. 2019, Florianópolis.

Bajay, S. V., Nogueira, L., Sousa, F. R. de. (2010) Ethanol in the Brazilian Energy Matrix. In: Sousa, E. L. L. & Macedo, I. C. (coords.) *Ethanol and bioelectricity: Sugarcane in the future of the energy matrix*. São Paulo, Única, pp. 261-308.

Bala-Litwiniak, A. & Radomiak, H. (2018) Possibility of the utilization of waste glycerol as an addition to wood pellets. *Waste and Biomass Valorization*. 10(8), 2193-2199.

Barros, S. & Flake, O. (2019) *Brazils Biofuels Annual 2019*. USDA Foreign Agricultural Service; Global Agricultural Information Network.

Brazilian Association of Rice Industry (Abiarroz). (2021) *Brazilian rice*. Available from: http://brazilianrice.com.br/en/sobre-o-brasil/ [Accessed 1 March 2020].

Briesemeister, L., Wittmann, T., Gaderer, M. & Spielhoff, H. (2014) *Study of a decentralized entrained flow gasification plant in combination with biomass from hydrothermal carbonization for CHP*. Technical University of Munich.

Carvalho, F., da Silva, F. T. F., Szklo, A., Portugal-Pereira, J. (2019) Potential for biojet production from different biomass feedstocks and consolidated technological routes: a georeferencing and spatial analysis in Brazil. *Biofuels, Bioproducts and Biorefining*. 13(6), 1454-1475.

Confederation of European Paper Industries (CEPI). (2003) *Discovering the high potential of Pulp and Paper Production Residues*. Belgium, CEPI.

Chen, L., Gangadharan, P., Lou, H.H. (2018). Sustainability assessment of combined steam and dry reforming versus tri-reforming of methane for syngas production. *Asia-Pacific Journal of Chemical Engineering*. 13(2), e2168.

Chhiti, Y. & Kemiha, M. (2013) Thermal conversion of biomass, pyrolysis and gasification: A review. *The International Journal of Engineering and Science (IJES)*. 2(3), 75-85.

Chiang, K.-Y., Lu, C.-H., Liao, C.-K. & Ger, R. H-R. (2016) Characteristics of hydrogen energy yield by co-gasified of sewage sludge and paper-mill sludge in a commercial scale plant. *International Journal of Hydrogen Energy*. 41(46), 21641-21648.

Chiche, D., Diverchy, C., Lucquin, A.-C., Porcheron, F., Defoort, F. (2013) Synthesis gas purification. *Oil and GAS Science and Technology – Institute in France*. 68(4), 707-723.

Cho, S.-W., Kwon, G., Yoon, K. & Kwon, E. E. (2017) Simultaneous production of syngas and magnetic biochar via pyrolysis of paper mill sludge using CO2 as reaction medium. *Energy Conversion and Management*. 145, 1-9.

Climeworks AG. (n.d.). Capturing CO2 from air; Climework direct air capture plants. Available from: https://www.climeworks.com/our-technology/ [Accessed 25 March 2020].

Confederação Nacional da Indústria (CNI). (2017) *A indústria do aço no Brasil*. Brasília, CNI.

Confederação Nacional da Indústria (CNI). (2018) *Mudança do clima e indústria brasileira: iniciativas e recomendações estratégicas para implementação e financiamento da NDC do Brasil*. Brasília, CNI.

Cormos, C.-C. (2016) Evaluation of reactive absorption and adsorption systems for post-combustion CO2 capture applied to iron and steel industry. *Applied Thermal Engineering*. 105, 56-64.

Costa, M., Massarotti, N., Capuccio, G., Chang, C.T., Shiue, A., Lin, C., Wang, Y. (2014) Modeling of syngas production from biomass energy resources available in Taiwan. *Journal of the Italian Association of Chemical Engineering* (AIDIC). 37, 343-348.

Departamento de Pesquisas e Estudos Econômicos (DEPEC). (2019) *Papel e celulose*. Bradesco.

Deutsche Energie Agentur (DENA). (2019a). *Powerfuels in aviation: factsheet*. Available from: https://www.powerfuels.org/fileadmin/gap/Publikationen/Factsheets/190612_dena_FS_Aviation_eng_web.pdf [Accessed 21 April 2021].

Deutsche Energie Agentur (DENA). (2019b). *Powerfuels: missing link to a successful global energy transition*. Available from: https://www.powerfuels.org/fileadmin/gap/Publikationen/Green_Paper/Global_Alliance_Powerfuels_Powerfuels-A_missing_link_to_a_successful_global_energy_transition.PDF [Accessed 21 April 2021].

Deutscher Verein des Gas- und Wasserfaches e.V. (DVWG). (2018) *Power-to-X-Kraftstoffe: Vergleichende Bewertung von PtX-Prozessen zur Bereitstellung von Kraftstoffen aus erneuerbaren Quellen*. Available from: https://www.dvgw.de/themen/forschung-und-innovation/forschungsprojekte/dvgw-forschungsbericht-g-201603 [Accessed 21 April 2021].

Dias, M. O. S., Maciel Filho, R., Mantelatto, P. E., Cavalett, O., Rossell, C. E. V., Bonomi, A. & Leal, M. V. (2015) Sugarcane processing for ethanol and sugar in Brazil. *Environmental Development*. 15, 35-51.

Ebner, J. A. (2018) *Options for the production of sustainable synthetic aviation fuel*. Brasília: Gesellschaft für internationale Zusammenarbeit (GIZ) GmbH.

Empresa de Pesquisa Energética (EPE). (2018) *Análise da eficiência energética em segmentos industriais selecionados: segmento celulose e papel*. EPE.

Empresa de Pesquisa Energética (EPE). (2021) *SIEnergia: Sistema de Informação para Energia Integrado e Interativo*. Available from: http://www.epe.gov.br/pt/publicacoes-dados-abertos/publicacoes/sienergia. [Accessed 18 February 2020].

Eurostat. (2019) *Energy, transport and environmental statistics*. Luxembourg, Publications Office of the European Union.

Evidence and Lessons from Latin America (ELLA) (n.d.) *From manual to mechanical harvesting: Reducing environmental impacts and increasing cogeneration potential.* ELLA Policy Brief: Brazil's Ethanol Programme.

Faubert, P., Barnabe, S., Bouchard, S., Côté, R. & Villeneuve, C. (2016) Pulp and paper mill sludge management practices: What are the challenges to assess the impacts on greenhouse gas emissions? *Resources, Conservation and Recycling*. 108, 107-133.

Food and Agriculture Organization of the United Nations (FAO). (2021) *Yearly statistics*. Available from: http://www.fao.org/faostat/en/#data/QC [Accessed 2 January 2020].

Forster-Carneiro, T., Berni, M. D., Dorielo, I. L., Rostagno, M. A. (2013) Biorefinery study of availability of agricultural residues and wastes for integrated biorefineries in Brazil. *Resources, Conservation and Recycling*. 77, 78-88.

Fritsche, U. R., Iriarte, L. & Ugarte, S. (2016) *Towards advanced biofuels – Options for integrating conventional and advanced biofuel production sites (RES -T-Bioplant)*. Munich, IEA-RETD.

Fu, Q., Mabilat, C., Zahid, M., Brisse, A., Gautier, L. (2010) Syngas production via high-temperature steam/CO2 co-electrolysis: an economic assessment. *Energy and Environmental Science*, 10.

Garcia, B. B., Lourinho, G., Brito, P., & Romano, P. (2019) Review of biofuel technologies in WtL and WtE. In: Biernat, K. (ed.) *Elements of bioeconomy*. Available from: https://www.intechopen.com/books/elements-of-bioeconomy/review-of-biofuel-technologies-in-wtl-and-wte [Accessed 21 April 2021].

Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH India. (2018) *Improving energy efficiency in iron and steel sector (achievements and way forward)*. GIZ.

Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH and Ministry of Science, Technology, Innovation and Communication (MCTIC). (2019) Auf den Flügeln der Nachhaltigkeit. *Full Energy Journal*.

Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH. (2020) *Climate neutral alternative fuels*; *Project ProQR*. Available from: https://www.giz.de/en/worldwide/63299.html [Accessed 5th April 2020].

Gonçalves, R. V., Vono, L. L. R., Wojcieszak, R., Dias, C. S. B., Wender, H., Teixeira-Neto, E. & Rossi, L. M. (2017) Selective hydrogenation of CO2 into CO on a highly dispersed nickel catalyst obtained by magnetron sputtering deposition: A step towards liquid fuels. *Applied Catalysis B: Environmental*. 209, 240-246.

He, Q., McNutt, J. & Yang, J. (2017) Utilization of the residual glycerol from biodiesel production for renewable energy generation. *Renewable and Sustainable Energy Reviews*. 71, 63-76.

Hora, A. B. da. (2017) *Panoramas setoriais 2030: papel e celulose*. Rio de Janeiro, BNDES.

Hora, A., Nader, L., Mendes, R. (2017). *Visão 2035: Brasil, país desenvolvido. Agendas setoriais para o desenvolvimento Papel e Celulose*. Rio de Janeiro: BNDES.

IEAGHG. (2017) *CCS Deployment in the context of regional developments in meeting long-term climate change objectives*. Available from: https://ieaghg.org/publications/technical-reports/reports-list/9-technical-reports/812-2017-07-ccs-deployment-in-the-context-of-regional-developments-in-meeting-long-term-climate-change-objectives [Accessed 22 April 2021].

Indústria Brasileira de Árvores (IBÁ). (2019) *Relatório 2019*. São Paulo, Ibá.

Instituto Aço Brasil (IABr). (2019) *Anuário estatístico 2019*. Rio de Janeiro, IAB.

Instituto Brasileiro de Geografia e Estatística (IBGE). (2019) *Levantamento Sistemático da Produção Agrícola – LSPA*. Available from: https://www.ibge.gov.br/estatisticas/economicas/agricultura-e-pecuaria/9201-levantamento-sistematico-da-producao-agricola.html?=&t=o-que-e [Accessed 21 December. 2019].

International Energy Agency (IEA). (2018) *Technology roadmap – Low-carbon transition in the cement Industry*. Available from: https://www.iea.org/reports/technology-roadmap-low-carbon-transition-in-the-cement-industry [Accessed 22 April 2021].

Intergovernmental Panel on Climate Change (IPCC). (2005) *IPCC special report on Carbon Dioxide Capture and Storage*. Available from: https://www.ipcc.ch/report/carbon-dioxide-capture-and-storage/technical-summary/ts-03/ [Accessed 24 March 2020].

Intergovernmental Panel on Climate Change (IPCC). (2019) *Annex global warming of 1.5°C: An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty* [Masson-Delmotte, V. et al. (eds.)]. Available from: https://www.ipcc.ch/site/assets/uploads/sites/2/2019/06/SR15_Full_Report_Low_Res.pdf [Accessed 21 April 2021].

International Air Transport Association (IATA). (2021) *Climate protection plan: Three targets and four pillars*. Available from: https://www.iata.org/en/policy/environment/climate-change/ [Accessed 21 April 2021].

International Association of Oil and Gas Producers (IOGP). (2019) *The potential for CCS and CCU in Europe: Report to the thirty second meeting of the European Gas Regulatory Forum*. Available from: https://ec.europa.eu/info/sites/info/files/iogp_-_report_-_ccs_ccu.pdf [Accessed 21 April 2020].

Isaksson, J. (2015) *Biomass gasification-based biorefineries in pulp and paper mills – Greenhouse Gas Emission implications and economic performance*. PhD Thesis. Chalmers University of Technology.

Ispatguru. (2015). *Understanding sinter and sinter plant operations*. Available from: https://www.ispatguru.com/understanding-sinter-and-sinter-plant-operations/#:~:text=Understanding%20Sinter%20and%20Sinter%20Plant%20Operations%20Sintering%20is,combustion%20of%20solid%20fuel%20within%20the%20mass%20itself [Accessed 03 May 2021].

Karlsruhe Institute of Technology (KIT). (2020) *Bioliq-Concept*. Available from: https://www.bioliq.de/index.php [Accessed 3 April 2020].

Ketzer, J. M. M.; Machado, C. X.; Rockett, G. C.; Iglesias, R. S. (orgs.). (2014) *Brazilian atlas of CO2 capture and geological storage*. Porto Alegre: EDIPUCRS.

Kosov, V. F., Lavrenov, V. A., Zaichenko, V. M. (2015) Simulation of a process for the two-stage thermal conversion of biomass into synthesis gas. *Journal of Physics: Conference Series*. 653(1).

Kuparinen, K. & Vakkilainen, E. (2017) Green pulp mill: Renewable alternatives to fossil fuels in lime kiln operations. *BioResources*. 12(2), 4031-4048

Kuparinen, K., Vakkilainen, E., & Tynjälä, T. (2019) Biomass-based carbon capture and utilization in kraft pulp mills. *Mitigation and Adaption Strategies for Global Change*. 24, 1213-1230.

Lago, A. C., Bonomi, A., Cavalett, O., Cunha, M. P. da & Lima, M. A. (2012) Sugarcane as a carbon source: The Brazilian case. *Biomass and Bioenergy*. 46, 5-12.

Lamsal, K., Jones, P. C. & Thomas, Barrett W. (2013) *Sugarcane harvest logistics in Brazil*. The University of Iowa's Institutional Repository.

Larson, E. (2004) Biomass gasification systems for electric power, cogeneration, liquid fuels, and hydrogen. In: *GCEP Biomass Energy Workshop, Stanford University, 27 April 2004*.

Lenartsson, P. R., Erlandsson, P. & Taherzadeh, M. (2014) Integration of the first and second generation bioethanol processes and the importance of by-products. *Bioresource Technology*. 165, 3-8.

Leoneti, A. B., Aragão-Leoneti, V. & Borges de Oliveira, S. V. W. (2012) Glycerol as a by-product of biodiesel production in Brazil: alternatives for the use of unrefined glycerol. *Renewable Energy*. 45, 138-145.

Löchle, D. (2019) *Untersuchung zum Schließen des Kohlenstoffkreislaufs der brasilianischen Luftfahrt*. Gesellschaft für internationale Zusammenarbeit (GIZ) GmbH.

Mata, T. M. & Martins, A. A. (2010) Biodiesel production processes. In: Delgado, J. M. P. Q. *Current trends in chemical engineering*. Porto, Studium, pp. 314-343.

McCabe, W. L., Smith, J. C. & Harriott, P. (1993) *Unit operations of chemical engineering*. 5 ed. Boston, McGraw-Hill.

Mladenov, M. & Pelovski, Y. (2010). *Utilization of wastes from pulp and paper industry*. Bulgaria, University of Chemical Technology and Methalogy.

Mohammad, A. M. & Hilal, N. N. (2010) Re-using the by-product of cement industry (cement klein dist) to produce the concrete. *Anbar Journal for Engineering Sciences*. 3(2).

Nda-Umar, U. I., Ramli, I., Taufiq-Yap, Y. H. & Muhamad, E. N. (2019) An overview of recent research in the conversion of glycerol into biofuels, fuel additives and other bio-based chemicals. *Catalysts*. 9(1), 15.

Oliveira, C. C. N., Szklo, A. & Rochedo, P. (2016) Evaluation of carbon capture potential in the Brazilian cement sector. *Applied Mechanics and Materials*, 830, 46-53.

Onarheim, K., Santos, S., Kangas, P. & Hankalin, V. (2018) Potential for Bio-CCS in the pulp and paper industry. In: VTT Technical Research Centre of Finland LTD. *Workshop Brussels, 16 January 2018*.

Patricio, J., Angelis-Dimakis, A., Castillo-Castillo, A., Kalmykova, Y., Rosado, L. (2017) Method to identify opportunities for CCU at regional level – Matching sources and receivers. *Journal of CO2 Utilization*. 22, 330-345.

Penna, P. C. (2019) *A indústria do cimento*. Federação das Indústrias do Estado de São Paulo (FIESP), Associação Brasileira de Cimento Portland (ABCP), Sindicato Nacional da Indústria do Cimento (SNIC).

Plácido J. & Capareda S. (2016) Conversion of residues and by-products from the biodiesel industry into value-added products. *Bioresources and Bioprocessing*. 3(23)

Portugal, J., Rathmann, R., Soria, R., Schaeffer, R., Szklo, A. S. (2014) Techno-economic and environmental assessment of agricultural and agro-industrial waste to energy potential in Brazil. In: *5th International Conference on Engineering for Waste and Biomass Valorization*.

Psarras, P., Comello, S., Bains, P., Charoensawadpong, P., Reichelstein, S. & Wilcox, J. (2017). Carbon capture and utilization in the industrial sector. *Environmental Science & Technology*. 51(19), 11440-11449.

Quispe, C. A. G., Coronado, C. J. R. & Carvalho Jr., J. A. (2013) Glycerol: production, consumption, prices, characterization and new trends in combustion. *Renewable and Sustainable Energy Reviews*. 27, 475-493.

REN21 Renewables Now. (2019) *Renewables 2019: Global Status Report*. Available from: https://www.ren21.net/gsr-2019/ [Accessed 22 April 2021].

Resolution 778 of the Agência do Petróleo, Gás Natural e Biocombustíveis (ANP). Available from: http://legislacao.anp.gov.br/?path=legislacao-anp/resol-anp/2019/abril&item=ranp-778-2019 [Accessed 8 April 2020].

Restrepo-Valencia, S. & Walter, A. (2019) *Techno-Economic Assessment of Bio-Energy with Carbon Capture and Storage systems in a Typical Sugarcane Mill in Brazil*. Universidade de Campinas (Unicamp).

Rostrup-Nielsen, J. R. (2000) New aspects of syngas production and use. *Catalysis Today*. 63(2-4), 159-164.

Roth, S., Zetterberg, L., AcWorth, W., Kangas, H.-L., Neuhoff, K. & Zipperer, V. (2016) *The pulp and paper overview paper: Sector analysis for the Climate Strategies Project on Inclusion of Consumption in Carbon Pricing*. London, Climate Strategies.

Sadh, P. K., Duhan, S. & Duhan, J. S. (2018) Agro-industrial waste and their utilization using solid state fermentation: a review. *Bioresources and Bioprocessing*. 5(1).

Sampaio, I., Cardoso, T. F., Souza, N., Watanabe, M., Carvalho, D., Bonomi, A. & Junqueira, T. L. (2019) Electricity production form sugarcane straw recovered through bale system: Assessment of retrofit projects. *Bioenergy Research*. 12, 865-877.

Santibáñez, C. & Varnero, M. T. (2014) Evaluation of chañar seed cake from biodiesel production as a soil amendment. *Journal of Soil Science and Plant Nutrition*. 14(1).

Sarkar, S. & Mazumder, D. (2015) Solid wastes generation in steel industry and their recycling potential. In: Millenium Institute of Energy & Environment Management (org.) *Management & utilisation of wastes from metal processing industries and thermal power stations*. pp. 1-14.

SEEG Brasil. (2018) *Greenhouse Gas Emissions Estimation System – 2018*. Available from: http://seeg.eco.br/en/ [Accessed 12 February 2020].

Sindicato Nacional da Indústria do Cimento (SNIC). (2013) *Relatório anual 2013*. Rio de Janeiro.

Sindicato Nacional da Indústria do Cimento (SNIC). (2018) *Números da indústria*. Available from: http://snic.org.br/numeros-industria.php [Accessed 10 February 2020].

Skoulou, V. K. & Zabaniotou, A. A. (2013) Co-gasification of crude glycerol with lignocellulosic biomass for enhanced syngas production. *Journal of Analytical and Applied Pyrolysis*. 99, 110-116.

Soares, R. R., Simonetti, D. A. & Dumesic, J. A. (2006) Glycerol as a source for fuels and chemicals by low-temperature catalytic processing. *Angewandte Chemie*. 45(24), 3982-3985.

Sricharoenchaikul, V. & Atong, D. (2012) Fuel gas generation from thermochemical conversion of crude glycerol mixed with biomass wastes. *Energy Procedia*. 14, 1286-1291.

Thiagarajan, J., Srividya, P. K. & Balasurbramanian, P. (2018) Thermal kinetics and syngas production and co-gasification of deoiled Jatropha seed cake residues with wood chips. *International Journal of Renewable Energy Research*. 8(2).

Tomosiunas, A., Gimzauskaite, D., Uscila, R. & Aikas, M. (2019) Thermal arc plasma gasification of waste glycerol to syngas. *Applied Energy*. 251, 113306.

Tran, H. & Vakkilainnen, E. (2007) *Advances in the kraft chemical recovery process*. Toronto, University of Toronto.

Vasudevan, P. T. & Fu, B. (2010) Environmentally sustainable biofuels: advances in biodiesel research. *Waste and Biomass Valorization*. 1, 47-63.

Visedo, G. & Pecchio, M. (coords.) (2019) *Roadmap tecnológico do cimento: Potencial de redução das emissões de carbono da indústria do cimento brasileira até 2050*. Rio de Janeiro: SNIC.

von der Assen, N., Müller, L., Steingrupe, A., Voll, P. & Bardow, A. (2016) Selecting CO2 sources for CO2 utilization by environmental-merit-order curves. *Environmental Science & Technology*. 50(3), 1093-1101.

Wang, Y., Liu, T., Lei, L., & Chen, F. (2016) High temperature solid oxide H2O/CO2 co-electrolysis for syngas production. *Fuel Processing Technology Journal*. 161, 248-258.

Wang, Y., Winans, K., Shao, Y, Whalen, J. & Matovic, D. (2014) *Life cycle assessment of biomass integrated gasification combined cycle in cement industry*. Montreal: McGill University.

Wei, L., Pordesimo, L. O., Haryanto, A. & Wooten, J. (2011) Co-gasification of hardwood chips and crude glycerol in a pilot scale downdraft gasifier. *Bioresource Technology*. 102(10), 6266-6272.

Welfle, A. (2017) Balancing growing global bioenergy resource demands – Brazil's biomass potential and the availability of resource for trade. *Biomass and Bioenergy*. 105, 83-95.

Worldsteel Association. (2016). *Fact sheet: Steel and raw materials*. Available from: https://www.worldsteel.org/en/dam/jcr:16ad9bcd-dbf5-449f-b42c-b220952767bf/fact_raw%2520materials_2019.pdf [Accessed 22 April 2021].

Yoon, S. J., Choi, Y.-C., Son, Y.-I., Lee, S.-H. & Lee, J.-G. (2010) Gasification of biodiesel by-product with air or oxygen to make syngas. *Bioresour Technology*. 101(4), 1227-1232.

Yoon, S. J., Yun, Y. M., Seo, M. W. (2013) Hydrogen and syngas production from glycerol through microwave plasma gasification. *International Journal of Hydrogen Energy*. 38(34), 14559-14567.

7. Annex

Table 1. Conversion factors for different industrial residues

Industry	Residue	Conversion factor	Source
Biodiesel	Glycerol	0.0984	ANP (2019)
	Seed cake	2.5–3	Santibáñez & Varnero (2014)
	Wastewater	0.2–1.2	Plácido & Capareda (2016)
Cement	CO_2	0.55	Visedo e Pecchio (2019)
Iron and steel	CO_2	1.9/1.56 (BF)	CNI (2017)
Pulp and paper	Bark and wood wastes	0.15	Kuparinen & Vakkilainen (2017)
	Black liquor	1.7–1.8	IEAGHG (2017)
	Pulp and paper mill sludge	0.05	Cho et al. (2017)
	CO_2	1.6–2.4	Kuparinen et al. (2019)
Ethanol	Sugarcane bagasse	0.28 0.22 AR: 10%	Restrepo-Valencia e Walter (2019) Carvalho et al. (2019) Portugal et al. (2014)
	Filter cake	0.02 AR: 10%	Carvalho et al. (2019)
	CO_2	0.76 0.78	IPCC (2005) Restrepo-Valencia e Walter (2019)
Agricultural residues-crop	Sugarcane straw	0.22 0.14 AR: 40% 0.22 AR: 65%	Forster-Carneiro et al. (2013) EPE (2021) Carvalho et al. (2019)
	Soybean straw	2.05 1.68 DR: 30% 2.01	Forster-Carneiro et al. (2013) EPE (2021) Carvalho et al. (2019)
	Corn stover	1.42 1.98 AR: 40% 1.53 AR: 100%	Forster-Carneiro et al. (2013) EPE (2021) Carvalho et al. (2019)
	Rice straw and husk	1.49 1.50 AR: 40% 1.54 AR: 100% Straw 0.26 AR: 30% Husk	Forster-Carneiro et al. (2013) EPE (2021) Carvalho et al. (2019)
Agricultural residues-animal	Poultry	1.58 0.04	Forster-Carneiro et al. (2013) EPE (2021) (esterco de pássaro)
	Bovine	0.07 5.47	Forster-Carneiro et al. (2013) EPE (2021) (esterco de gado)
	Swine	0.06 0.91	Forster-Carneiro et al. (2013) EPE (2021) (esterco suíno)

Table 2. LHVs for different residues

Crop	Residue	LHV (MJ/kg)
Sugarcane	Straw	18.62
	Bagasse	19.81
Soybean	Straw	20.09
Corn	Stover	18.67
Wood	Wood chips (Eucalyptus) Wood chips (Pinus)	20.26 21.81
Rice	Straw	17.22
	Husk	17.08

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