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Assessment of the Brazilian Market for Products by Carbon Dioxide Conversion

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Several international agreements, focused on regulating greenhouse gases emissions in the atmosphere, were created due to the growing concern about the climate change due to human action. The carbon dioxide (CO_2) emissions account for more than 70% of the total greenhouse gases emissions; among the CO_2 emitting sectors, electricity generation accounts for 25% of the global emissions. CO_2 emissions from Brazilian power plants motivated their mapping, a method was proposed to performance a local market analysis for potential products from CO_2 chemical conversion. The forecast behavior of this market for 2030 was also calculated. Among the studied products, methanol, polycarbonates, formic acid and acetaldehyde are the most promising for local manufacture. The States of São Paulo, Paraná, Amazonas, Bahia, Rio Grande do Sul and Santa Catarina are the most promising regions in terms of potential of CO_2 utilization.

Keywords: power plant mapping, CO_2 chemical conversion, Brazilian market, forecasting, CO_2 utilization

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1. INTRODUCTION

The increasing concern about the environmental impact generated by global warming has stimulated a series of international agreements aimed at regulating greenhouse gases (GHG) emissions in the atmosphere. The UNCHE (United Nations Conference on the Human Environment) in Stockholm (1972) is considered the first discussion about the global human influence on the environment. More recently, in 2005, the Kyoto Protocol entered into force, committing its Parties by setting internationally binding GHG emission reduction targets at least 18% below 1990 levels until 2020 (United Nations, 1998; UNFCCC, 2015). The Paris Agreement (the last one signed) goal is to enhance the global response to the threat of climate change by ensuring the average global temperature increase, in this century, below 2°C above pre-industrial levels and to continue efforts to limit temperature rise to up to 1.5°C above pre-industrial levels (UNFCCC, 2015).

In 2016, total global GHG emissions continued to increase steadly by about 0.5% (±1%), to about 53.4 Gt $CO_{2\text{-eq}}$ (including land use, land-use change and forestry emissions, estimated at about 4.1 Gt), the slowest since the early 1990s, except for global recession years, according to Olivier et al. (2017). This result is justified by the partial replacement of coal consumption from fuel to natural gas and the increasing renewable power generation (wind and solar power, mostly).

GHG are basically composed of carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and fluorinated gases (F-gases). Although CO_2 is not the worse gas, its emissions account for more than 70% of the total GHG emissions, according with **Figure 1A**. Emphasizing CO_2, **Figure 1B** shows the CO_2 emitting sectors. Among them, electricity generation stands out, accounting for 25% of the global emissions (IPCC, 2014).

Since thermoelectric plants represent large, capital-intensive facilities with a 40-year technical (and economic) lifetime, there must be a link between profit maximization and concern for the environment and GHG emissions (Bogmans et al., 2017).

According to Azevedo and Angelo (2018), in 2016, Brazil emitted about 1.7 billion tons of carbon dioxide equivalent ($GtCO_2$). This represents nearly 3% of global emissions (around 56 $GtCO_2$), placing Brazil as the sixth largest emitter of the globe. Natural gas has increased its share in electricity generation since 2000, with the third source in the matrix accounting for 8% of total capacity. In 2014, 81 TWh of electricity from natural gas were produced, representing a growth of twenty times compared to the year 2000 (Empresa de Pesquisa Energética, 2017). According to the Energy Research Company (Empresa de Pesquisa Energética, 2017), installed capacity in the 2016-2026 expansion program forecasts an increase of more than 38%, from 12,532 MW in 2016 to 17,339 MW in 2026 for natural gas. Due in part to the increase in the supply of natural gas being estimated with pre-salt production and unconventional gas sources expanding from 55 million m^3 in 2014 to 180 million m^3 in 2050 (Campos et al., 2017). These data show the importance and necessity of the country adopting low carbon policies.

In 2015, at COP-21, the Paris Agreement was drafted, involving commitments to reduce GHG emissions. Brazil proposed to reduce its emissions by 37% in 2025, based on the 2005 emissions (Empresa de Pesquisa Energética, 2017).

To this end, several treatment systems to reduce CO_2 have been proposed by researchers and industries. Among them are: (i) more efficient energy production, (ii) changing the fuel matrix, (iii) Carbon Capture, Use and Storage (CCUS) (do Espirito Santo and Gallo, 2017).

The term Carbon Dioxide Utilization (CDU), a subcategory of CCUS, describes a number of technologies that consume CO_2 to provide services or to manufacture products aiming at an economic benefit. In some cases, the capture of CO_2 is included in the definition, and the term is also referred to as Carbon Capture and Utilization (CCU) in an analogy to the term often used, CCS. The difference between the two concepts is that in CCS, carbon dioxide is stored (underground/marine reservoirs), while in the CDU/CCU, it is used in the economy (Zimmermann and Kant, 2015). According to Aresta et al. (2013), CDU technologies, due to their inherent potential, can be complementary to the CCS techniques.

Research and development is, therefore, crucial to move toward a competitive CCUS technology, from the most fundamental level of research (e.g., Haunschild, 2015, focusing on catalyst research) to integrated studies at the conceptual design level as a complete plant in the work by Milani et al. (2015). Thus, there is a need for a detailed analysis regarding the impact that different CDU options/processes have on the energy of the system and under which conditions the products obtained can have a sustainable market (Pérez-Fortes et al., 2016a).

The CDU represents a new economy for CO_2, since captured CO_2 could be used as a feedstock for other processes, including the synthesis of chemicals and materials (such as methanol, formic acid, polyols for polyurethanes, carbonates), fuels (such as methane or kerosene) and direct use in applications based on the physicochemical properties of CO_2 (as the supercritical state) (Peters et al., 2011).

Since CO_2 is emitted from a source and, therefore, supplied at a rate faster than its current consumption, CO_2 for utilization can be considered a renewable alternative source of carbon, ideally leading to carbon neutral cycles in processes with sources of large amounts of CO_2 (such as power plants) (Gale et al., 2005).

The use of CO_2 can reduce emissions through two main effects: first, -directly, – through CO_2 consumption, thus preventing its release into the atmosphere and second, – indirectly, – by replacing inputs in intensive emission of GHG. According to von der Assen et al. (2013), the indirect effect may have a greater impact than the direct effect, but its quantification requires substantial simulation efforts and is the object of future research studies.

Worldwide, about 37 billion tons of CO_2 were issued in 2010 (Mikkelsen et al., 2010; Parsons Brinckerhoff, 2011). According to Inagendo (2015) and Pérez-Fortes et al. (2016b), 0.4–0.5% of the emitted carbon is used, it represents 144–185 Mton of CO_2 used in the industry. According to Aresta et al. (2013) the estimate is that 172 million tons of CO_2 are directly consumed in industrial processes per year (2013 base year): urea accounts for 114 Mton/year, methanol 8 Mton/year, inorganic carbonates ca 50 Mton/year and the group of organic carbonates and salicylic acid together represent less than 1 Mton/year. The growth potential, however, can reach 10% of the carbon emitted today, totalling 3.7 billion tons per year (Mikkelsen et al., 2010; Parsons Brinckerhoff, 2011).

CDU technologies can be divided into two main categories: technological use (physical processes) and chemical/catalytic conversion (chemical processes or biological/biochemical processes). **Figure 2A** displays CO_2 utilization alternatives.

The technological use is related to the physical nature, including compression, recycle, phase transition, etc. Among practical uses are the preservation of cereals (bactericidal), beverage additives, food packaging, dry cleaning, extraction, mechanical industries, fire extinguishers, air conditioning, as well as water treatment (Aresta et al., 2014).

Concerning CO_2 conversion, three main groups may be considered: chemical, mineralization, and bio-based routes (Chauvy et al., 2019). The first category is focused on organic synthesis [including photocatalysis and chemical photocatalysis (Li et al., 2016), thermochemical processes (Pakhare and Spivey, 2014), and electrochemistry (Albo et al., 2015)]. The second category is inorganic mineralization (building materials Pekdemir, 2014) and the last category uses microorganism to consume CO_2 and produce high added-value products (Aresta et al., 2014).

So, based on important factors, such as distribution cost of energy, resources and implementation time, conversion of CO_2 into fuels or chemicals is an attractive solution, which, in addition to reducing greenhouse gases, provides alternative sources of profit from the sale of manufactured products. In the manuscript, the focus was on organic synthesis of chemicals from CO_2, a more embracing study is important, however is out of the scope of this study.

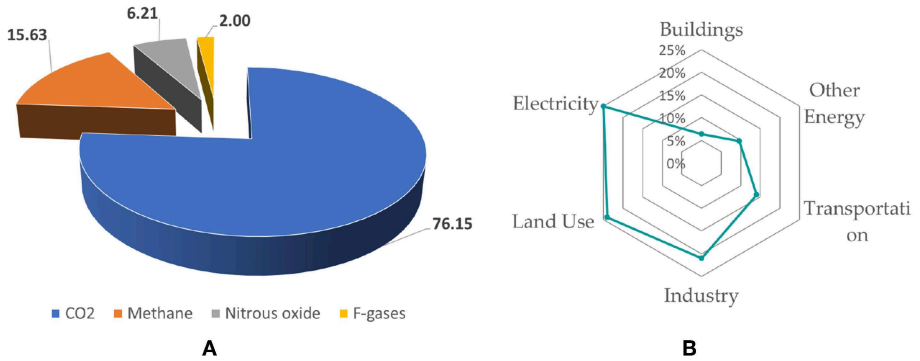

FIGURE 1 | GHG and CO_2 emissions: **(A)** GHG emission composition (Olivier et al., 2017) and **(B)** CO_2 emissions (%) per sector (IPCC, 2014).

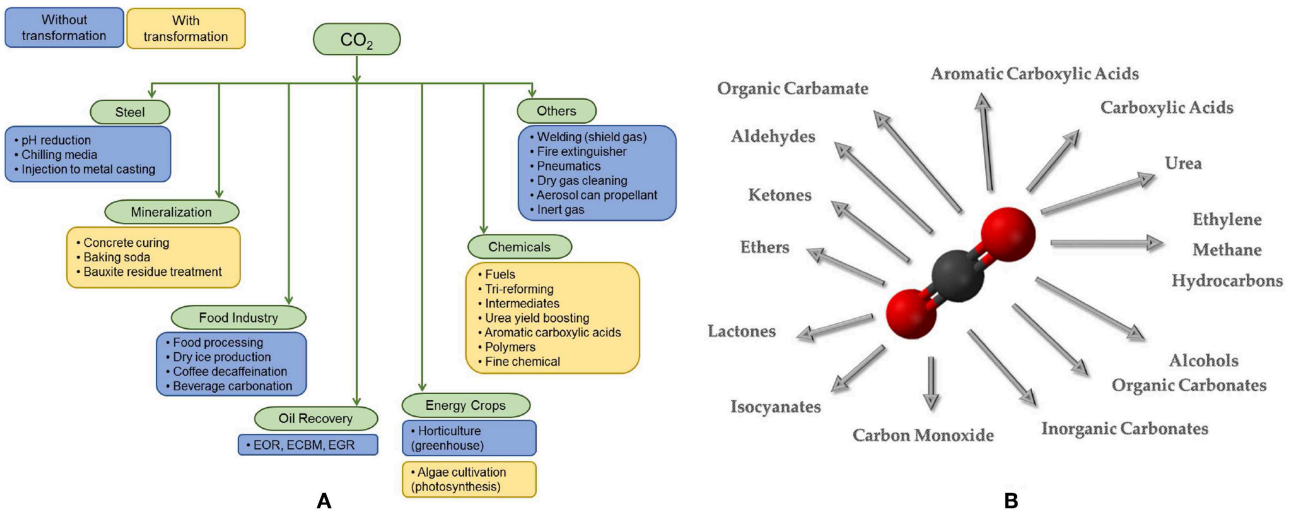

FIGURE 2 | (A) CO_2 utilization alternatives. **(B)** Synthetic processes for some products obtained from CO_2, divided into categories.

Many products and processes can use CO_2 as raw material to synthesize different chemicals (**Figure 2B**). Each product or production process brings some advantages and some penalties, making important to define some criteria to evaluate and to choose the most attractive products and processes.

Markewitz et al. (2012) show two environmental criteria and one commercial criterion. The amount of CO_2 is computed by energy and carbon balances and represents how much carbon is fixed and the weight of the contribution to minimize global warming. The duration of fixation is evaluated by life-cycle assessment and represents how long this carbon will be out of the atmosphere. Value generation represents the commercial attractiveness and how the product or process is self-sustainable.

Dairanieh (2016) shows two environmental and three commercial criteria. CO_2 potential and permanence of capture are similar to the first two criteria of Markewitz et al. (2012). Willingness to pay is a criterion based on the product market price and represents how much the CO_2 is valued. Ease of implementation is a commercial criterion and represents the difficulties in entring in a market. Side effects and co-benefits evaluates other effects as either positives (or negatives), such as reduced air pollution or increase in fossil fuels consumption. This study recommends investments in eight products of four clusters: (i) Building materials (concrete and carbonate aggregates), (ii) Chemical intermediates (methanol, syngas, and formic acid), (iii) Fuels (liquid fuels, methane) and (iv) Polymers (polyols and polycarbonates).

Otto et al. (2015) studied 123 CO_2 utilization reactions, 23 to produce bulk chemicals (more than 10 kt/y) and 100 to produce fine chemicals (less than 10 kt/y). For bulk chemicals, the criteria were: specific mass of CO_2 as a feedstock (mass of CO_2 necessary to produce one kg of a product), CO_2 avoidance potential (mass of CO_2 necessary to produce one kg of a product multiplied by the global production), relative added value (difference between the value of the product and the prices of the reagents), independence from fossil reactants (if no carbon from fossil is used). Using these criteria, 6 bulk chemicals were chosen (formic acid, oxalic acid, formaldehyde, methanol, urea and DME). For

fine chemicals, with similar criteria, the products selected were methylurethane, 3-oxo-pentanedioic acid, 2-imidazolidinone, ethylurethane, 2-oxazolidone and isopropyl isocyanate.

This work propose a method that aims to analyze the Brazilian market for potential products from CO_2 chemical conversion, as well as to predict the behavior of this market in 2030. The selected products are used in a methodological framework for a region prioritization at a national level. This method may be easily applied for other countries through market analysis.

2. METHODS

The proposed method comprises four steps. (1) Defining criteria to evaluate the products, grouped into technological, environmental and economical criteria; (2) Collecting data for each product; (3) Generating the decision matrix and carrying out a sensitivity analysis; (4) Carring out a top-down approach methodology including opportunity identification, resulting in cluster identification and region prioritization for Brazil.

2.1. Multiple Criteria Decision Analysis Assessment

Multiple criteria decision analysis (MCDA) refers to making preference decisions (e.g., evaluation and selection) over the available alternatives characterized by multiple, usually conflicting, attributes.

MCDA is a branch of operations research and deals with planning scientific and computational apparatuses to address a limited number of choices under a limited number of criteria by a unique or a group of decision makers.

There is a wide variety of approaches, for example analytic hierarchy process (AHP) (Saaty, 1977), Preference Ranking Organization Method for Enrichment Evaluations (PROMETHEE) (Brans and Vincke, 1985), Technique for Order Preference by Similarity to an Ideal Solution (TOPSIS) (Behzadian et al., 2012; Hwang and Yoon, 2012) and the simple additive weighted (SAW) method (Kirkwood and Corner, 1993) which have been successfully utilized in dealing with MCDA problems.

The latter two approaches were used in different case studies to select the most promising products for further/deeper study. The TOPSIS method designates alternatives that simultaneously have the shortest distance from the positive ideal solution (maximization of benefit criteria) and the farthest distance from the negative-ideal solution (maximization of cost criteria). More details about the method can be found in the work by Hwang and Yoon (2012). The SAW method is simpler as compared to TOPSIS, performing only the summation of the products of weight and the normalized value of each alternative.

The calculations of the TOPSIS method was performed using the python module Scikit-Criteria (Scikit-Criteria, RRID:SCR_017084) v0.2.10 (Cabral et al., 2016) running on python v2.7.15; for the SAW method, simple spreadsheets and MATLAB R2015a were used.

2.2. Criteria Description

The option of using CO_2 for chemical conversion has thermodynamic and intrinsic kinetic restrictions. Estimating their real potential will require a thorough comparative analysis of proposed and existing processes to determine whether or not the proposed conceptual plant reduces CO_2 emissions (directly or indirectly), and whether there is a sale of the obtained chemicals (Peters et al., 2011).

The evaluation of rejection or acceptance of the proposal will produce reliable results only if significant number of parameters is used; for this situation, ten criteria were employed. The criteria were grouped into technical, environmental and economic.

2.2.1. Technical Group

For the technical group, the standard enthalpy of reaction (ΔH^o_{rxn}) and the Technical Readiness Level (TRL) were evaluated.

Equation (1) was used to calculate the enthalpy of reaction. This was done by executing basic algebraic operations based on chemical equations of reactions taking into account the values of enthalpies of formation of the gas phase

$$\Delta H^o_{rxn} = \sum_{products} \nu_i \left(\Delta_f H^o_{298,g}\right)_i - \sum_{reactants} \nu_i \left(\Delta_f H^o_{298,g}\right)_i \quad (1)$$

The enthalpy of reaction can be determined by scaling each species enthalpy of formation [obtained from the literature - NIST (2018) or NIST-TDE inside Aspen Plus commercial simulator] by its stoichiometric coefficient ν_i. In this study, only direct conversion routes to the products were considered, i.e., the CO_2 reacts with one or more reactants to directly form the products under assessment.

TRL is a systematic metric/measurement system that determines the maturity of a specific technology. The methodology was proposed by NASA and, due to its simplicity and versatility, it expanded to other domains as well (European Commission, 2013).

In this case, the TRL scale measures the development of technology from its basic concept (TRL 1) to being available at commercial/industrial scale (TRL 9), reaching the physical scale of deployment or its maximum technical maturity. Each step in between represents the increase in the level of maturity of the technology.

The TRL assessment refers to the innovative route for each product, not the conventional one. The TRL applied to this study ranges from basic and applied research, proof of concept and laboratory testing (stages 1–5), to prototyping, piloting and final development (stages 6–8), to full- scale deployment/market introduction (9).

Several products manufactured using CO_2 as a feedstock have been studied and produced. An overview of the set of compounds and their technological path can be found in international reports (Parsons Brinckerhoff, 2011; Bocin-dumitriu et al., 2013; CO_2 Sciences and The Global CO_2 Initiative, 2016; Zimmermann and Schomäcker, 2017; Zimmermann et al., 2017), which are used to assign TRL to the chemicals described in section 2.3.

2.2.2. Environmental Group

For the environmental group, the willingness to pay (WP), scientific relevance, side effects and benefits and utilization ratio were evaluated.

The side effects and benefits and WP were proposed by Dairanieh (2016) to evaluate CO_2 products. The first criterion of this group (side effects and benefits) is related to the increased production of fossil fuels and the avoidance of a hazard route. The second criterion, despite being based on the economics of the target market, it is set in the environmental group because it represents the unit cost/price point of CO_2 supply at which the product is competitive for that use ($/tonne of CO_2).

The scientific relevance is a criterion proposed by Otto et al. (2015), defined as the number of related references of a certain chemical (SCI-Finder database). According to the author, this criterion discerns rare application chemicals from diverse application chemicals. The former belong either to basic research or speciality chemicals; the latter can be use of a wide variety of applications as a feedstock, which are more attractive from an ecological and economic point of view. The number of citations was gathered in October and November 2018.

The utilization ratio is the amount fixed, which takes into consideration the mass of carbon dioxide, the mass of product and their respective stoichiometric coefficient (CO_2 and reference product) as shown in Equation (2).

$$\frac{m_{CO_2}}{m_p} = \frac{\left|\nu_{CO_2}\right| \cdot M_{CO_2}}{\left|\nu_p\right| \cdot M_p} \tag{2}$$

Where m_{CO_2} is the mass of CO_2, m_P is the mass of product, ν_{CO_2} is the stoichiometric coefficient for CO_2, while ν_p is for product, M_{CO_2} is the molecular weight of CO_2 and M_p is the molecular weight of the product.

2.2.3. Economic Group

The economic group represents the market-related criteria (demand and price). The imports and exports (amount and price) of the compounds were taken into account. The data for the value (in millions of US$) were stated in *Free On Board* (FOB) value, which means that the exporter is responsible for the merchandise until it is inside the ship, for transportation, at the port indicated by the buyer.

The values of imports and exports for 2030 were forecast and the harmonized mean of values from 2015–2018 and 2030 for each chemical were used in the decision matrix.

The annual data were collected from the official website of foreign trade statistics of the Brazilian government (AliceWeb, 2018).

2.2.4. Forecast Method

Time series analysis is a tool for forecasting future values, based on past and present events (Wei, 2006). There are several forecasting alternative methodologies classified in automatic and non-automatic approach. While the latter required prior exploratory data analysis for each case, the former does it automatically.

Papacharalampous et al. (2018) explore the capability of seven different forecast methods used to predict monthly temperature and precipitation. The methods are a naïve, random walk (with drift), ARFIMA (AutoRegressive Fractionally Integrated Moving Average), BATS (Box–Cox transform, ARMA errors, Trend, and Seasonal components), simple exponential smoothing, Theta and Prophet. Their results indicate that the last five models performed better than the first two and the Prophet method is competitive.

In this work, the facebook prophet model (Taylor and Letham, 2017b) was used. It was introduced in 2017, inspired by a nature of time series forecast by the company. The package is available at an R library named 'prophet' (Taylor and Letham, 2017a). The procedure used by prophet is additive regression model with the main components: a linear growth curve trend, yearly seasonal components modeled using the Fourier series.

The 2030 values were forecast for each product using the data available from 2000 to 2018. The time series analysis was based on its past values using prophet package (Prophet, RRID:SCR_017083) version 0.5 on R [version 3.6.0 (2019-04-26)].

2.3. Data Collection

A database of 13 chemicals was selected from the open literature as products from CO_2 conversion (Aresta et al., 1996, 2013, 2015; Song, 2006; Aresta and Dibenedetto, 2007; Aresta, 2010; Styring et al., 2011; Otto et al., 2015), for which was possible to retrieve their data related to Brazilian Statistics.

The chemical compounds used in this assessment are listed: (1) Acetaldehyde; (2) Acetic Acid; (3) Acetone; (4) Benzoic Acid; (5) Formaldehyde; (6) Formic Acid; (7) Methacrylic Acid; (8) Methanol; (9) Oxalic Acid; (10) Polycarbonates; (11) Propanol; (12) Salicylic Acid; and (13) Urea.

2.4. Weighting Method

The weight for each criterion can be assigned to two group categories: subjective and objective weights. Subjective weights are determined based on the preference of the decision maker [e.g., AHP method (Saaty, 1977), weighted least squares method (Chu et al., 1979), Delphi method (Hwang and Lin, 2012) and equal weights]. Objective methods determine weights by solving mathematical models and do not account for the decision maker preference [e.g., Shannon entropy method (Shannon, 1948; Zeleny, 2012) and multiple objective programming (Choo and Wedley, 1985)].

For solving problems, the expertise of a decision maker ought to be calculated; in this case, subjective weighting is preferable. However, when reliable subjective weights are difficult, objective weighting must be selected.

The Shannon information entropy measures the predicted value of the information contained in a message, usually in units of bits, nats or bans. The value is the average unpredictability in a random variable, equivalent to its information essence. In the MCDA context, the entropy method is an objective method to assign weights depending on the decision matrix (Shannon, 1948; Zeleny, 2012). The relative weight of criterion *j* is calculated in

relation to the amount of information supplied by the intrinsic set of alternatives.

The concept of entropy in an information channel was proposed by Shannon (1948) and the procedure defines a series of steps:

(a) Normalization of data.
In order to remove anomalies with different measurements units and scales, the normalization procedure is carried out. Considering $p_{ij} = \frac{x_{ij}}{\sum_{j=1}^{m} x_{ij}}$, $j = 1, \cdots, m$, $i = 1, \cdots, n$, where p_{ij} is the normalized data and x_{ij} is the raw data (i alternative on j criterion).

(b) Calculation of the entropy
Entropy E_j for criterion j is calculated according to Equation 3

$$E_i = -E_0 \cdot \sum_{j=1} \left(p_{ij} \cdot \ln(p_{ij})\right) \qquad i = 1, \cdot, n \tag{3}$$

The entropy constant E_0 was calculated as $\ln(m)^{-1}$.

(c) Calculation of Diversity Criterion
The diversity criterion is then calculated using Equation 4, which represents the degree of diversification.

$$D_j = 1 - E_j \tag{4}$$

(d) Computation of normalized weight
Finally, the degree of importance is calculated according to Equation (5)

$$w_j = \frac{D_j}{\sum D_j} \tag{5}$$

The closer the entropy of a criterion is to 1, the less important the criterion is. Shannon entropy measures the amount of uncertainty with a probability distribution in terms of entropy taking into account the complete set of information available.

Along with Shannon entropy, subjective weighting was also employed in the case studies described in section 2.5.

2.5. Sensitivity Analysis

In order to evaluate the use of a MCDA method (either TOPSIS or SAW) and the weighting system (either objective or subjective), a sensitivity analysis was carried out.

Table 1 shows the case studies involved in the sensitivity analysis.

As a result, the most promising products will appear more often in the first places.

2.6. Opportunity Identification Approach

A top-down methodology approach developed by Patricio et al. (2017a,b) consisting of three consecutive steps was adapted and used to identify opportunities for CCU at national level. In the first step, technologies that use CO_2 in Brazil were identified. The second step is the geographical location of thermoelectric power plant (Natural Gas-based). The third step is matching the sources with the potential receiver, based only on geographic parameters.

TABLE 1 | Different case studies involved in the sensitivity analysis.

Case	Weight	Method
Case 1	Shannon entropy	TOPSIS
Case 2	Equal weight[a]	TOPSIS
Case 3	Technical criteria[b]	TOPSIS
Case 4	Economical criteria[b]	TOPSIS
Case 5	Environmental criteria[b]	TOPSIS
Case 6	Shannon entropy	SAW
Case 7	Equal weight[a]	SAW
Case 8	Technical criteria[b]	SAW
Case 9	Economical criteria[b]	SAW
Case 10	Environmental criteria[b]	SAW

[a] *All criteria received the same weight.*
[b] *Weights for the criterion that belongs to this group were the double when compared to the other groups.*

2.6.1. Emission Calculations

In order to evaluate the CO_2 emissions of a Power Plant, the net capacity factor and the power capacity are used to calculate the energy generated in a year, according to Equation 6 (Ruggero, 2017; U.S.NRC, 2018).

$$E_a = F_c \cdot C \cdot 8760 \tag{6}$$

Where E_a is the annually produced energy, F_c is the capacity factor and C is the power plant installed capacity.

The capacity factor is the ratio of the actual output over a period. The data used in these calculations was based on a statistics of the Brazilian Government (MME - Ministério de Minas e Energia, 2017) for the year 2016, for the public generation of energy based on natural gas. The average F_C of 2016 was 0.43, a much lower indicator than in 2015 (0.72), but still higher than in 2011 (0.26). According to Araújo et al. (2017), the installed capacity of a power plant is directly proportional to its CO_2 emission (517 g CO_2/kWe-h), these values are then used.

3. RESULTS AND DISCUSSIONS

3.1. Forecast Results

A time series forecasting model is designed to handle the common features of the business time series of imports and exports. The investigation of the predictability of imports and exports of 13 chemical products was performed from 2000 to 2018 to forecast 2030 values.

Figures 3A,B present statistical data on the Brazilian trade balance of the last 4 years, in terms of imports absolute volume and value in US dollars, respectively, as well as the projection of these values for 2030. It is worth mentioning that no more CO_2 conversion products were analyzed, due to the difficulty in finding theirs NCM in the Brazilian trade system.

The annual absolute quantity imported (kton) is highlighted by the large average amount of urea, methanol and acetic acid imported (8574, 4168.7, 1383.4 kton, respectively for 2030) in this period, with tendency to increase in the evaluated period.

Next, come acetone and formic acid, showing forecast tendency to increase. Acetone was forecast to increase the

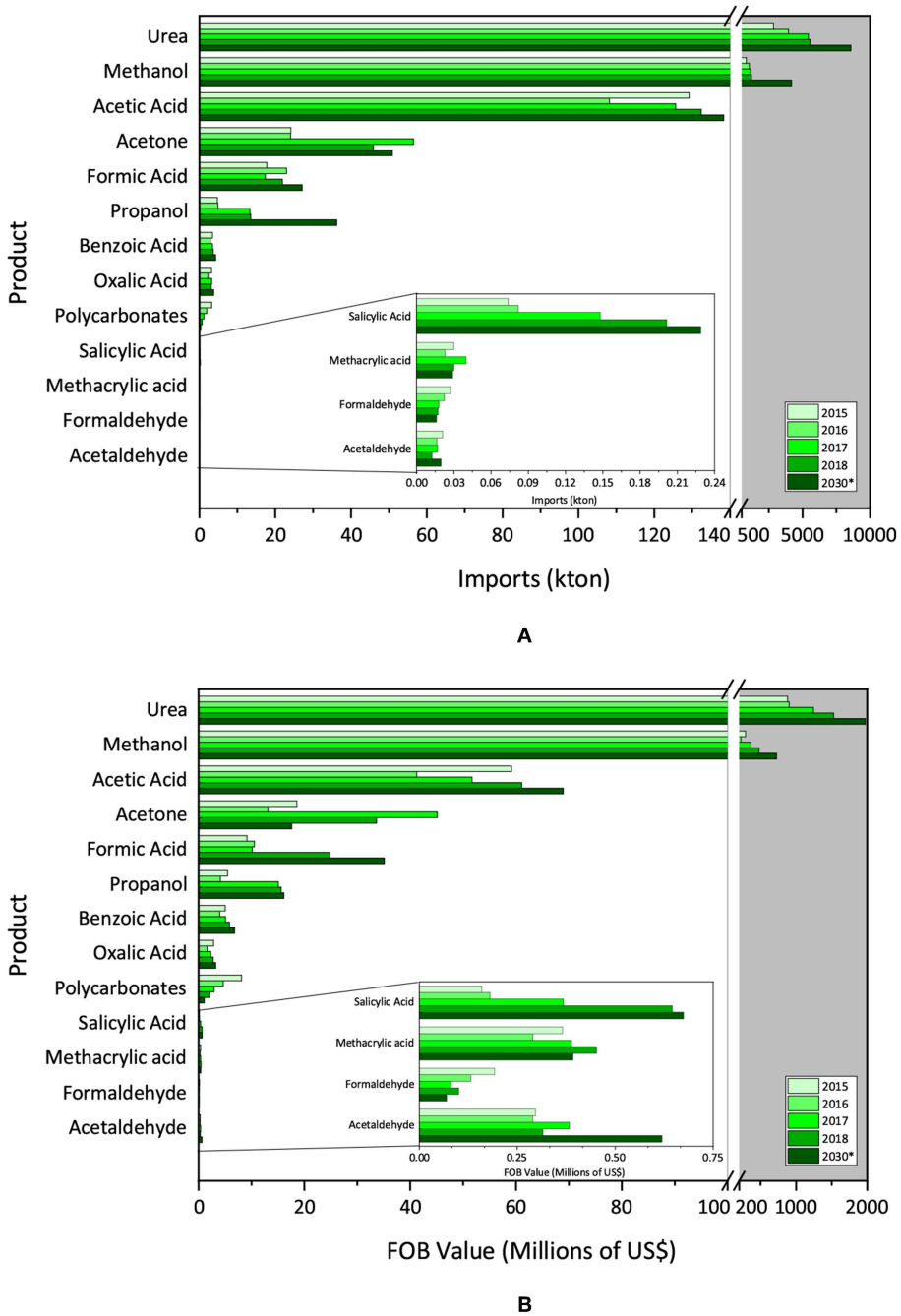

FIGURE 3 | (A) Brazilian importation data (absolute volume) and **(B)** Brazilian importation data (FOB value).

imported absolute amount (from 45.9 kton in 2018 to 50.9 kton in 2030) and formic acid was forecast to increase 23.93% from 2018 to 2030. The other products exhibited imports smaller than 5 kton/year each (except for propanol in 2018 with 13.5 kton).

Regarding the value generated in the transactions, **Figure 3B** depicts the imports in millions of US$. Urea, methanol and acetic acid were the products with the highest value. However, the values for acetic acid are followed more closely by acetone, formic acid and acrylic acid, which have higher added value. Comparing 2030 to 2018, there is an increasing trend of import costs for methanol, acetic acid and urea, while a decrease for acetone.

It is possible to calculate the prices for imports and exports, taking into account the FOB value divided by the absolute amount for each chemical product (see **Table 2** for details).

TABLE 2 | Multi-criteria performance matrix for assessing CO_2 products.

Products	Economic criterium				Technical criterium		Environmental criterium			
	Imports[a] (kg/y)	Imports price[a] (US$/kg)	Exports[a] (kg/y)	Exports price[a] (US$/kg)	ΔH^0_{rxn} [b] (kcal/mol)	TRL (–)	WP (US$/tonne$_{CO_2}$)	Sci. Rel. (%)	Effects[c] (–)	Utilization ratio ($kg_{CO_2}/kg_{prod.}$)
Acetaldehyde	16,680	20.62	21	2.09	14.14	2	225	90	0	0.999
Acetic acid	125,856,438	0.44	483	1.74	8.60	1	225	100	0	0.733
Acetone	35,168,454	0.58	1,522,373	0.73	20.23	2	225	100	0	0.758
Benzoic acid	3,484,402	1.50	5,539	5.24	4.08	2	225	90	0	0.360
Formaldehyde	19,425	5.34	565,624	0.50	10.28	1	225	100	1	1.465
Formic acid	20,856,261	0.67	241	1.62	3.57	5	225	90	1	0.956
Methacrylic acid	29,398	12.38	3,867,793	3.48	2.39	1	225	90	0	0.511
Methanol	1,229,493,061	0.26	63	3.63	−11.84	5	28	100	1	1.374
Oxalic acid	3,020,134	0.80	2516	3.41	17.25	1	225	90	1	0.978
Polycarbonates	87,3880	2.63	43	0.96	−4.10[d]	3	225	90	2	0.489
Propanol	8,422,607	0.83	2,856	1.80	−37.24	2	225	90	0	0.732
Salicylic acid	119,416	2.54	2,442,643	2.05	−0.22	7	225	90	0	0.319
Urea	4,609,107,497	0.25	17,087,027	0.34	1.91	7	28	100	1	0.733

[a] *The values correspond to the harmonized average of the period 2015–2018 and 2030 (the latter year was estimated in this study—see section 2.2.4), without outliers.*

[b] *The enthalpy of reaction is for the direct route only.*

[c] *The criteria named Effects refers to side effects and benefits (avoid hazard route - 1, avoid use of fossil fuels - 1).*

[d] *The functional group ROC(O)OR' is a key constituent of organic products comprising molecules with one carbonate unit and polycarbonates with numerous carbonate moieties. Important representatives with one carbonate unit are dimethyl carbonate: its captive consumption for using in the production of polycarbonates is 46 kt/y, approximately 50% of the world production (Artz et al., 2018). Therefore, the direct route was estimated for dimethyl carbonate.*

The situation changes when the prices are taken into account; the most expensive imported product is acetaldehyde, followed by methacrylic acid. Formaldehyde presented an oscillation during the evaluated period from 7.03 US$/kg in 2015 to 5.83 US$/kg in 2018. Polycarbonates were imported for an average price of 2.60 US$/kg, similar to salicylic acid (2.51 US$/kg).

Figure 4A reveals the annual absolute exported quantity (kton), while **Figure 4B** shows the involved costs.

Figure 4A points out the high average amount of methacrylic acid, salycilic acid and urea exported, followed by acetone, acetic acid and formaldehyde, all tending to increase exports in 2030, as compared with 2018, except for methacrylic acid.

Figure 4B displays the expected behavior of the exportation costs involved for products. Due to the higher market value, the export profit of methacrylic acid exceed that of urea. In 2030, as compared with 2018, profits appear to be higher for methacrylic acid and urea, and smaller for salicylic acid and acetone.

Anomalous data did not have a great impact on the forecast, due to the robustness of the time series analysis method. According to Papacharalampous et al. (2018), comparing different forecast methods, prophet exhibited the smallest median RMSE for the temperature forecasts, while offering 13–32% (depending on the examined set of time series) more accurate results than naïve. In their case, the model is competitive to the ARFIMA, BATS, simple exponential smoothing and Theta models.

3.2. Multi-Criteria Performance Matrix

Estimating the use of CO_2 for chemical conversion by their real potential will require a full comparative analysis of the proposed processes to determine whether or not the process is feasible, and whether there is a market for the given products. In order to select the most promising products for further study, a multi-criteria performance table (**Table 2**) was constructed encompassing the criteria and alternatives.

Table 2 presents the performance of the alternatives (chemical compounds) in each criterion. Regarding the technical criteria, enthalpy of the direct reaction, acetone and formaldehyde are the most endothermic, while propanol and methanol the most exothermic. The maturity of urea and salicylic acid reflect the commercial production of this chemicals, on the other hand oxalic acid, methacrylic acid and acetic acid are in the early stages of research and development.

In the environmental group, the utilization ratio criteria that represents the amount of CO_2 fixed in the molecule, showed higher values for formaldehyde and methanol and lower values for salicylic acid and benzoic acid. There is no wide amplitude in scientific relevance and in effects, and two broad group of chemicals were identified through the criterion willingness to pay (represented by the numbers 225 or 28).

The economic group (imports and exports) showed a similar behavior compared with described in the forecast predictions.

3.3. Sensitivity Results

The 10 cases described in section 2.5 used either the TOPSIS or SAW method for evaluation. Regarding the weighting method, either a subjective method or an objective method was employed.

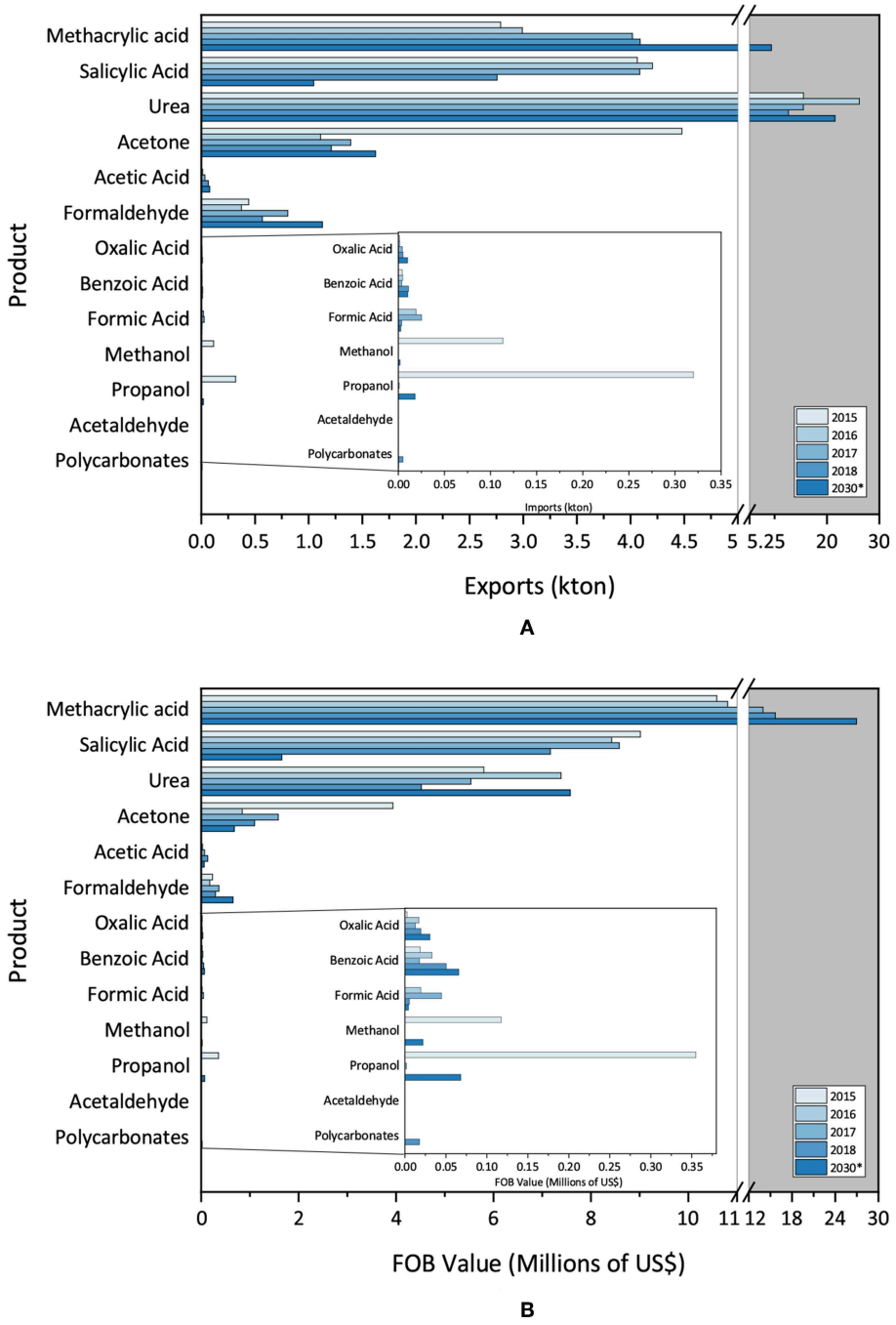

FIGURE 4 | (A) Brazilian exportation data (absolute volume) and **(B)** Brazilian exportation data (FOB value).

The Shannon Entropy equation was used for the objective weighting method in order to express the relative intensities of criterion importance and to determine the objective weights. **Table 3** presents the results of the proposed approach for weight elicitation.

Table 3 describes the criteria used and their relative importance. The exports amount, exports price and enthalpy of the reaction are cost-type criteria, indicating that the performance of every alternative must be as minimum as possible.

The enthalpy of a reaction and the willingness to pay showed the highest values for entropy indicating a minor importance when compared with other criterion. Scientific relevance and imports price showed higher relative importance.

Figure 5 presents the results of the sensitivity analysis. The classification in every case is assigned in the horizontal

TABLE 3 | Shannon entropy weights (used in cases 1 and 6).

Criteria (*i*)	Type	Min/Max	Entropy (E_i)	Diversity (D_i)	Normalized Weight (w_i)
Imports (kg/y)	Benefit	Max	0.875	0.125	0.066
Imports price (US$/kg)	Benefit	Max	0.613	0.387	0.203
Exports (kg/y)	Cost	Min	0.875	0.125	0.065
Exports price (US$/kg)	Cost	Min	0.872	0.128	0.067
ΔH^{o}_{rxn} (kcal/mol)	Cost	Min	0.960	0.040	0.021
TRL (–)	Benefit	Max	0.761	0.239	0.125
WP (US$/tonne$_{CO_2}$)	Benefit	Max	0.935	0.065	0.034
Sci. Relevance (Benefits (–)	Benefit	Max	0.681	0.319	0.167
Utilization ratio (kg$_{CO_2}$/kg$_{prod.}$)	Benefit	Max	0.891	0.109	0.057

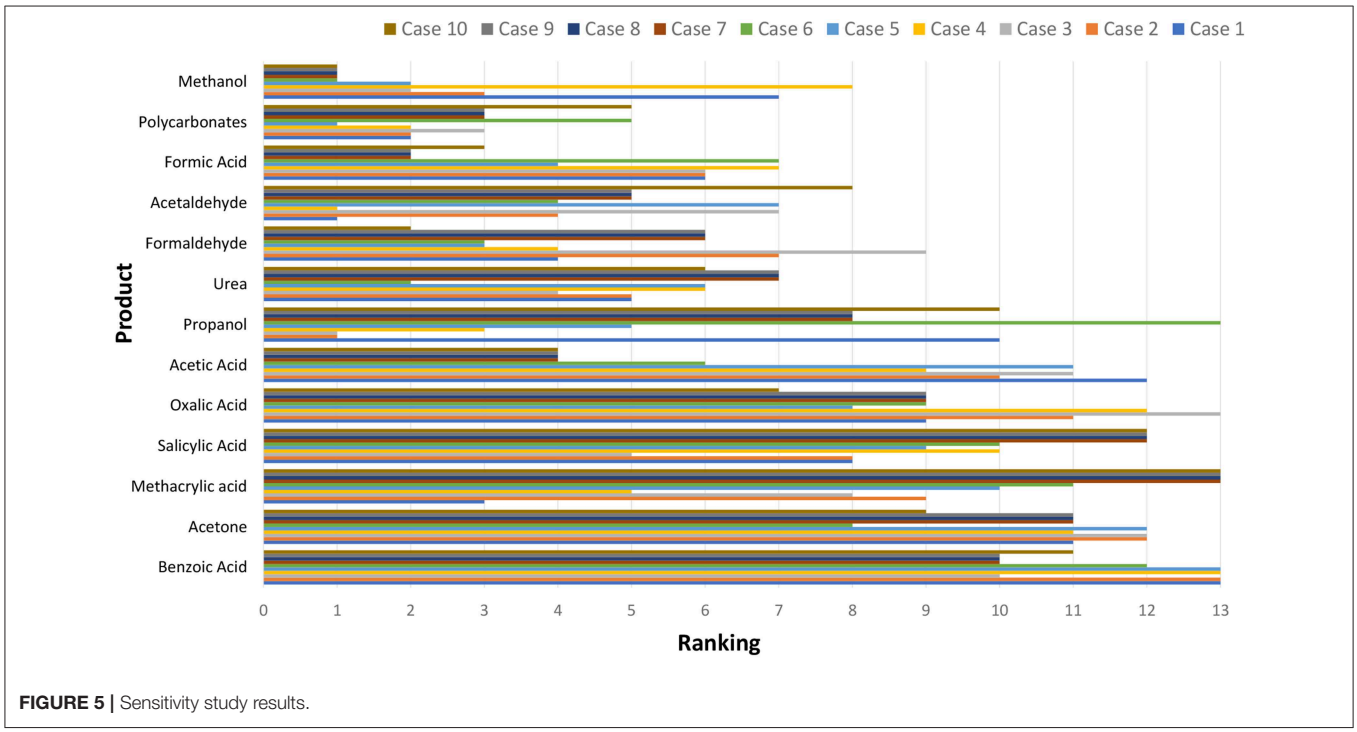

FIGURE 5 | Sensitivity study results.

axis. The weighting method affects the final classification, and a sensitivity analysis could thus potentially incorporate this influence.

Methanol, polycarbonates, formic acid and acetaldehyde appear more often in the top positions. Therefore, their further study and implementation in Brazil is recommended, considering the evaluated criteria and the range of chemical products assessed.

The method proposed was robust for selecting the most promising products; the weights assigned or calculated were taken into consideration, however it was specific designed for the Brazilian context. The implementation of the method in other countries can assessed easly, it only required a detailed study of the local market and appropriate weight elicitation.

3.4. Opportunity Identification Results

Based on Equation (6), the CO_2 amount emitted annually by the 20 Brazilian Power Plants with the highest installed capacity was calculated. **Figure 6** shows the more emitters power plants in Brazil, as well as their respective locations.

The power plants with the highest CO_2 emissions are present in the southeast region. Therefore, there is a greater supply of CO_2 in this region, which could support the installation of new plants of CO_2 conversion processes

Figure 7 presents the location and capacity of the Brazilian Natural gas based Power Plants.

São Paulo and Rio de Janeiro are the most promising regions in terms of CO_2 availability and infrastructure identified as clusters in **Figure 7** were the most interesting spots. However, the third step of the methodology is the match with the local needs.

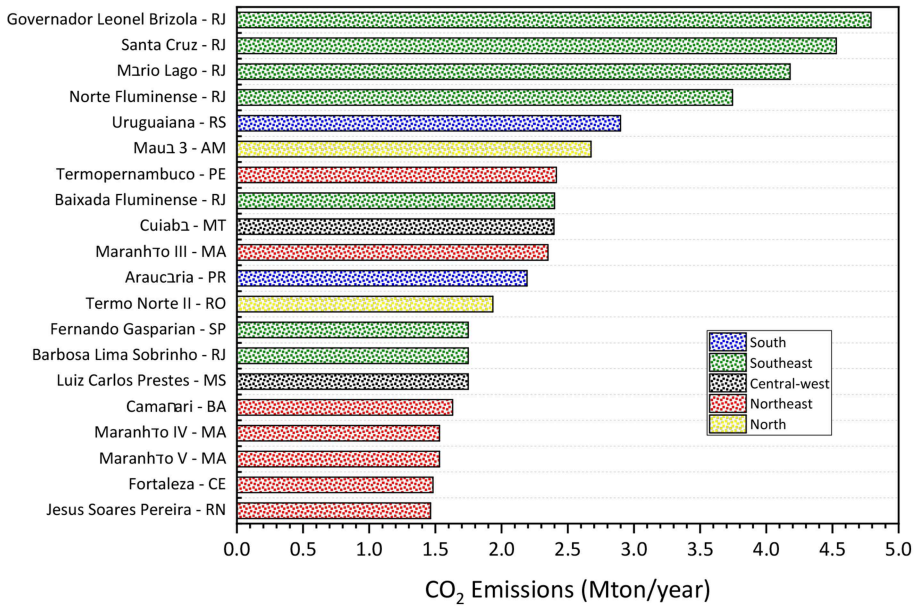

FIGURE 6 | Annual emissions of 20 Brazilian Power Plant (natural gas) with higher installed capacity (RJ, Rio de Janeiro; RS, Rio Grande do Sul; AM, Amazonas; PE, Pernambuco; MT, Mato Grosso; MA, Maranhão; PR, Paraná; RO, Rondônia; SP, São Paulo; MS, Mato Grosso do Sul; BA, Bahia; CE, Ceará; RN, Rio Grande do Norte).

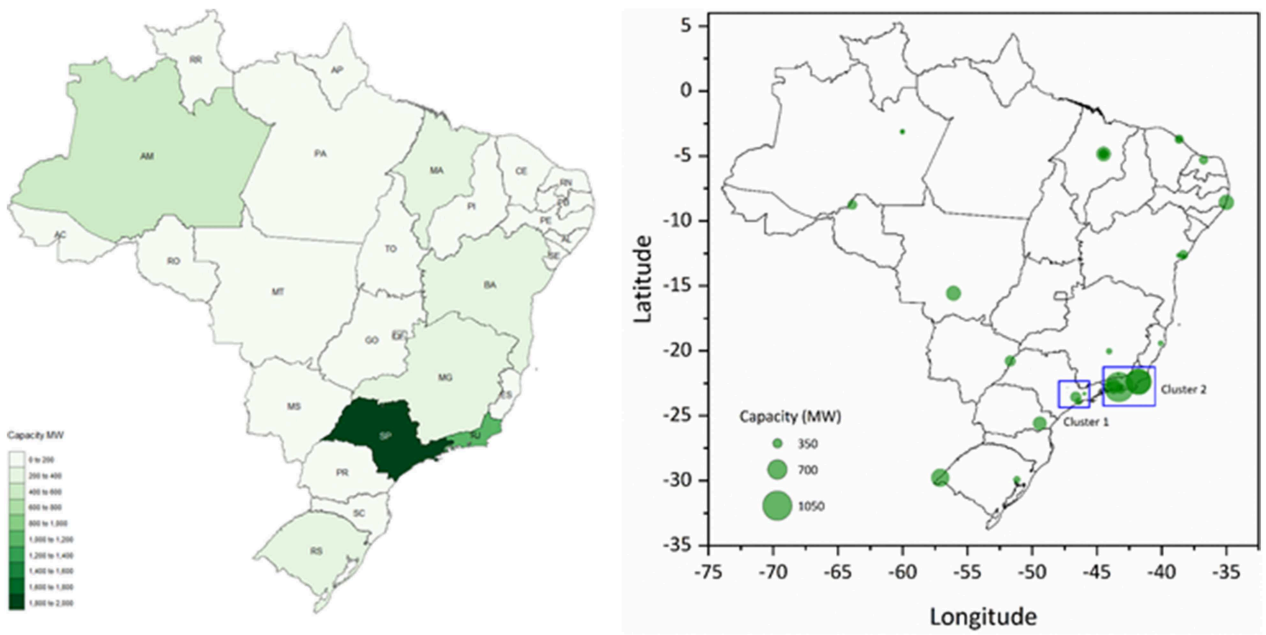

FIGURE 7 | Location and capacity of Power Plant (Natural Gas-based).

The final step is to identify the need in a specific State for a specific product. According to the sensitivity analysis, the most promising products were considered.

The stratification based on States rather than cities is due to the fiscal confidentiality, therefore it is not possible to access individual company data. It is important to emphasize that the exportation by State definition consider the producer of the chemical, independently the headquarters cities of the producer. The data can be also related to the entry port.

The data contained in **Figures 8B–11B** concern about the imports, separated by country of production and Brazilian state of consumption. The country refers to the location of

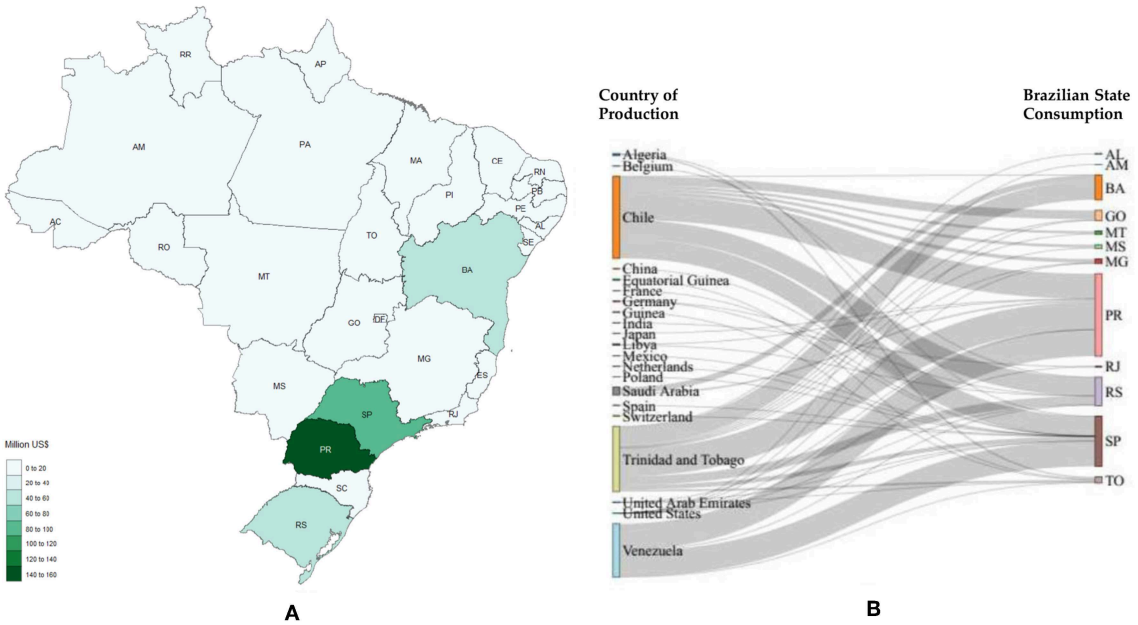

FIGURE 8 | Methanol imports. **(A)** Local needs considering 2017; **(B)** Stratification for 2017, countries on the left represent the origin of the product studied and the states on the right represent the destination (AL, Alagoas; AM, Amazonas; BA, Bahia; GO, Goiás; MT, Mato Grosso; MS, Mato Grosso do Sul; MG, Minas Gerais; PR, Paraná; RJ, Rio de Janeiro; RS, Rio Grande do Sul; SP, São Paulo; TO, Tocantins).

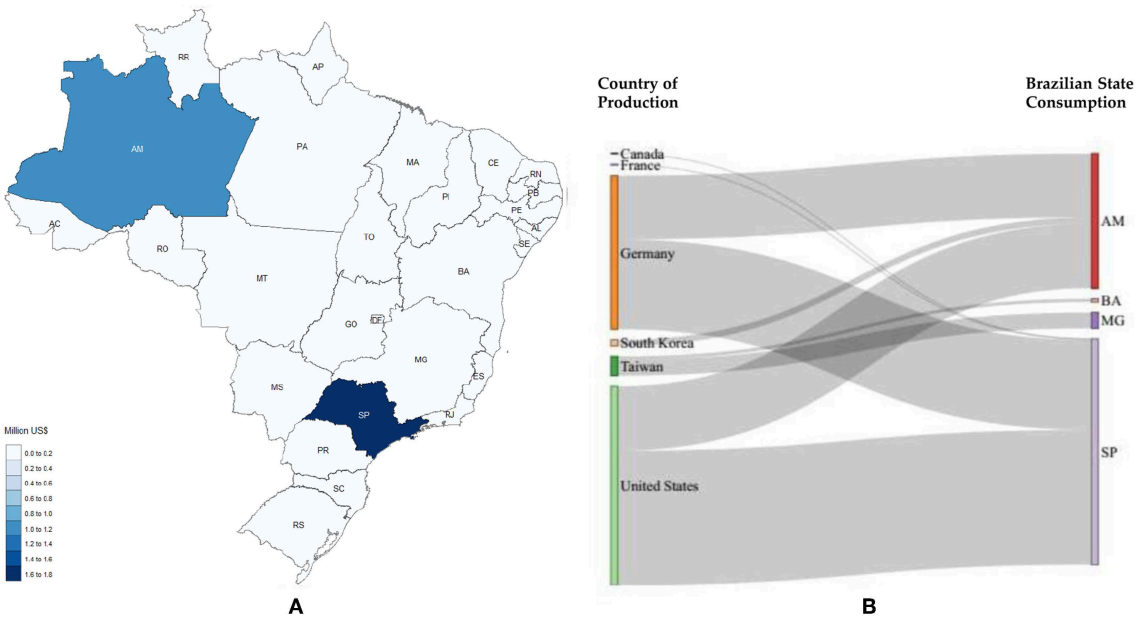

FIGURE 9 | Polycarbonate imports. **(A)** Local needs considering 2017; **(B)** Stratification for 2017, countries on the left represent the origin of the product studied and the states on the right represent the destination (AM, Amazonas; BA, Bahia; MG, Minas Gerais; SP, São Paulo).

the last registry of the product before enter in Brazil, not necessarily the producer location. The State refers to the Brazil entry location, not necessarily the final destination of the chemical's consumption.

The valuation of the potential utilization per State is helpful for guiding decision makers and policy makers to invest in CDU.

Figures 8–11 depict the imports in 2017 for methanol, polycarbonates, formic acid and acetaldehyde, respectively.

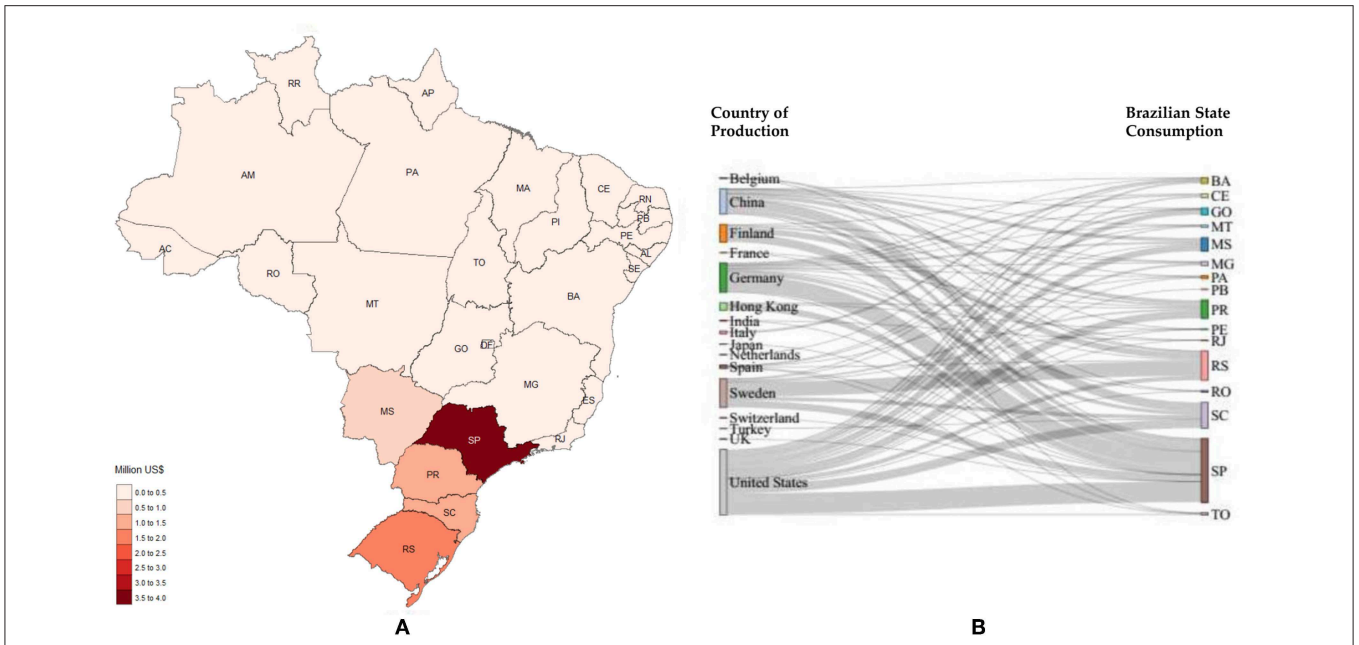

FIGURE 10 | Formic Acid imports. **(A)** Local needs considering 2017; **(B)** Stratification for 2017, countries on the left represent the origin of the product studied and the states on the right represent the destination (BA, Bahia; CE, Ceará; GO, Goiás; MT, Mato Grosso; MS, Mato Grosso do Sul; MG, Minas Gerais; PA, Pará; PB, Paraíba; PR, Paraná; PE, Pernambuco; RJ, Rio de Janeiro; RS, Rio Grande do Sul; RO, Rondônia; SC, Santa Catarina; SP, São Paulo; TO, Tocantins).

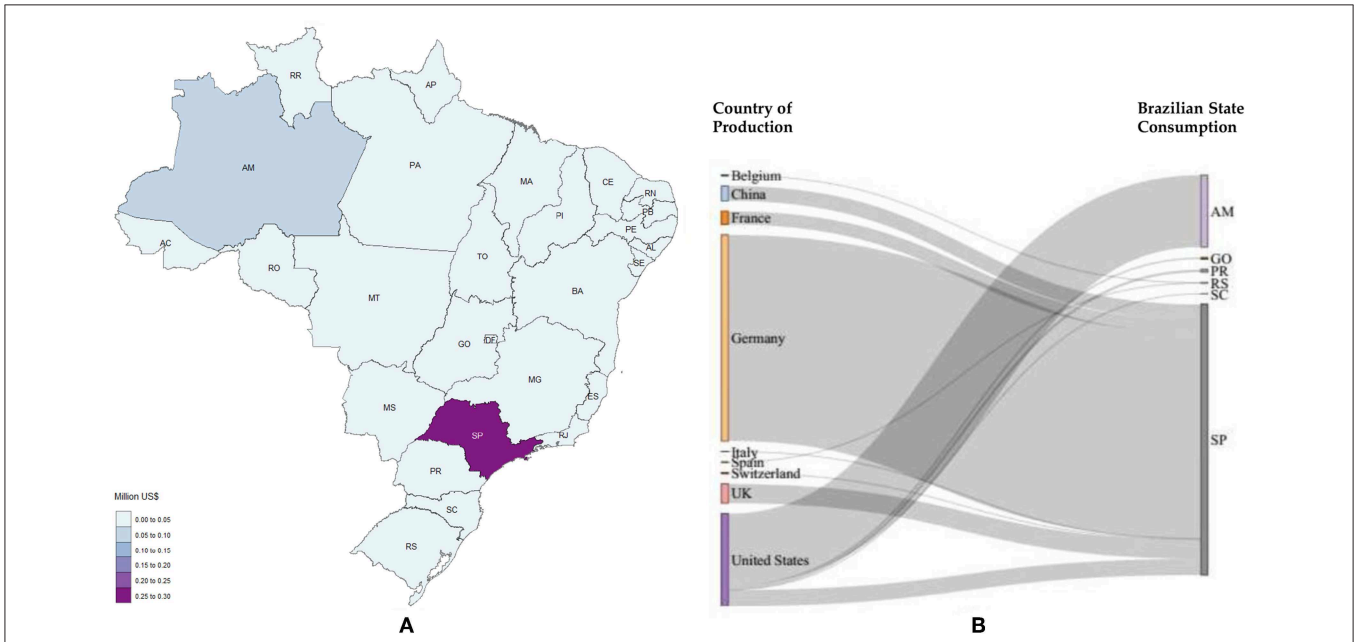

FIGURE 11 | Acetaldehyde imports. **(A)** Local needs considering 2017; **(B)** Stratification for 2017, countries on the left represent the origin of the product studied and the states on the right represent the destination (AM, Amazonas; GO, Goiás; PR, Paraná; RS, Rio Grande do Sul; SC, Santa Catarina; SP, São Paulo).

From **Figure 8** Paraná is the State that most imported methanol in 2017, followed by São Paulo, Rio Grande do Sul and Bahia. Paraná imported almost 40% more than São Paulo; moreover, Rio Grande do Sul and Bahia imported similar values of methanol (48.7 and 42.3 million US$, respectively).

According to **Figure 9** São Paulo and Amazonas are the States with the highest imports, 1.73 and 1.03 million US$, respectively. Polycarbonates were imported mainly from the United States and Germany.

Regarding formic acid, São Paulo leads the importation with 3.57 million US$, followed by Rio Grande do Sul (1.64 million US$), Santa Catarina (1.44 million US$) and Paraná (1.03 million US$) (**Figure 10**).

For acetaldehyde, São Paulo heads the imports followed by Amazonas. Paraná, Goiás, Rio Grande do Sul and Santa Catarina also import the product, yet less than 0.003 million US$ (2800 US$) in 2017 (**Figure 11**).

Lastly, potential technologies can be assessed in São Paulo, Paraná, Rio Grande do Sul, Bahia and Santa Catarina States, where the demand is high and they are identified as favorable regions for developing CCU schemes. It also portrays and evaluates the commercial movement of Brazil with the other nations of the world, encompassing sales and purchases made externally

São Paulo showed high availability and demand, therefore it is indicated as location for implementation of CDU schemes.

4. CONCLUSION

The proposed method was robust for selecting the most promising products for CO_2 conversion. The concern regarding CO_2 emissions from Brazilian power plants motivated their mapping, as well the performance of a local market analysis for potential products from CO_2 chemical conversion.

Methanol, polycarbonates, formic acid and acetaldehyde were the most promising products for implementation in Brazil. The research pointed out that the power plants of higher capacity and, consequently, the greatest CO_2 emitters, are present in São Paulo and Rio de Janeiro. São Paulo showed higher demand of the assessed products and also CO_2 availability, indicating the location where a new CDU plant could potentially be installed.

Most of the current CO_2 technologies are in the research and development phase and there are already several collaborative works among researchers, startups and corporations in Europe and North America indicating a great potential for similar activities in Brazil. This work will contribute to this development.

DATA AVAILABILITY

All datasets generated for this study are included in the manuscript and/or the **Supplementary Files**.

AUTHOR CONTRIBUTIONS

RA confirms that all listed authors (KP, AR, AB, and CN) were involved in data acquisition, writing, proofreading, and processing of this research article.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenrg.2019.00075/full#supplementary-material

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