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Fernanda Guedes[1], Alexandre Szklo[1], Pedro Rochedo[1], Frédéric Lantz[2], Leticia Magalar[1], Eveline Maria Vásquez Arroyo[1]

[1]*Energy Planning Program, Graduate School of Engineering, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco C, Sala 211, Cidade Universitária, Ilha do Fundão, 21941-972 Rio de Janeiro, RJ, Brazil*

[2]*IFP School, 232 Avenue Napoléon Bonaparte, 92852 Rueil-Malmaison, France*

Abstract

Oil refineries are major CO_2 emitters and are usually located in water-stress sites. While some CO_2 mitigation options can reduce water withdrawals, others can increase it, and still others are neutral. By simulating two parametric models, one for all Brazilian refineries, and the other locally detailing the water balance of the country´s largest refinery, this study aimed to quantify the impacts of CO_2 mitigation options on the water use of oil refineries. Findings show that, at 25 and 100 US$/t$CO_2$, Brazilian refineries can abate CO_2 emissions by 10% and 26%, respectively, compared to current emissions. A relevant share of this abatement derives from the implementation of carbon capture facilities in fluid catalytic cracking and hydrogen generation units. However, these CC facilities offset the co-benefits of other CO_2 mitigation options that can reduce steam and cold water requirements in refineries. In fact, for the largest Brazilian oil refinery, the implementation of all mitigation measures had almost no effect on its water balance. This means that CO_2 abatement in refineries has no significant impact on water consumption (no negative trade-off). However, this also means that the water stress in oil refineries should be dealt with with measures not directly linked to CO_2 abatement (no significant co-benefits).

Keywords: Climate-energy-water nexus; oil refineries; Brazil.

1. Introduction

Two of the UN Sustainable Development Goals (SDGs) focus on achieving physical and economic access to energy and water in quantity and quality. SDG7 aims to provide affordable, secure, sustainable and modern energy for all; furthermore, SDG6 aims to provide available and sustainable management of water and sanitation for all (UN, 2016). Energy and water are key elements closely linked to all other sectors within an economy. They also interact closely in many aspects (BIGGS et al., 2015). In this way, achieving the goal of a natural resource will influence the fulfillment of the other goal. For instance, water is needed at all stages of energy production, while water management, treatment and transportation require energy. Moreover, global climate change can add a significant amount of uncertainty to these complex inter-relations. Changes in climate variables, such as precipitation and temperature, can affect water and energy resources, increasing their vulnerabilities. Also, the strategies to tackle climate change by reducing (mitigating) greenhouse-gas (GHG) emissions can affect the water-energy nexus (HOWELLS et al., 2013).

For instance, coal-fired thermoelectric plants need water resources, mainly for cooling processes. For these plants, a promising GHG mitigation option could be the installation of amine-based carbon capture (CC) systems (ROCHEDO and SZKLO, 2013). However, CC would also increase both water withdrawal and consumption by the thermoelectric plant by more than 100%, which may intensify its vulnerability and affect the water supply to other users downstream from the power plant (ZHAI and RUBIN, 2011; MERSCHMANN et al., 2012). In the case of the production of liquid biofuels, the nexus goes beyond the energy conversion facility, which may also be affected by CO_2 mitigation options, and mostly refers to the biomass production, which usually represents a significant share of water consumption (irrigation) in countries such as Brazil (IEA, 2016). Interestingly enough, the increase of biomass productivity arising from irrigation is an emblematic case of the tradeoff between GHG mitigation and water.

At the end, given all these complex and interconnected relationships, an integrated analysis is needed to evaluate the nexus between energy-water under the challenges associated with climate change (HOWELLS et al., 2013). In addition, each energy sector needs a proper analysis to quantify this nexus. For this study, this analysis is performed at both country and local level. On one hand, the country level provides the basic answer for the primary research question of this study, which is: do CO_2 mitigation options affect the water consumption of an oil refinery system (or even: what could the nexus be between the carbon mitigation cost curve and the water consumption in refineries)? On the other hand, the detailed local level analysis, whose focus is on a specific oil refinery, allows the answering of the secondary question of this study, which is: do the impacts of climate mitigation options on water consumption affect the water supply-demand balance of an oil refinery? Only local level analyses can solve this secondary question, since it requires the proper evaluation of water sources (water supply) and sinks (water users).

In fact, oil refining is an energy-intensive activity, whose greenhouse gas (GHG) emissions are closely related to the combustion and chemical conversion of fossil fuels. The fuel combustion in oil refineries is related to the generation of direct heat, process steam and even electricity, all in stationary sources. The refineries´ technological schemes are complex (GOMES et al., 2009; COELHO and SZKLO, 2015), depending on the characteristics of the feedstocks, the units' capacities, the production profile of the oil products (quantities and specifications), and the choice of technologies to be used (CASTELO BRANCO et al., 2011). For instance, refineries that process heavy crude oils to output light products present process schemes that use more final energy, and in turn emit more GHG (EPA, 2010). In addition, the more stringent the oil derivative specifications, the greater the energy and water consumption of the refining process, due to the need of severe hydro-treatment units, which use the hydrogen produced in units emitting CO_2 from the steam reforming of light hydrocarbons (SZKLO and SCHAEFFER, 2007; CONCAWE, 2012; SUN et al., 2018). In 2012, oil refineries accounted for 2.7% of US, 3.2% of European Union and 2.0% of Brazil CO_2 emissions (MCTI, 2013; PETROBRAS, 2013; EPA, 2014).

Nevertheless, the vast majority of the research associated with the nexus between energy and climate in oil refineries has focused on the trade-off between fuel specifications and CO_2 emissions (CONCAWE, 2000; CHAN, 2006; SZKLO AND SCHAEFFER, 2007; JOHANSSON et al., 2012; CONCAWE, 2012). In the case of the nexus between energy and water, there are some studies on the relationship between water consumption and energy use in oil refineries (HIGHTOWER and PIERCE, 2008; IPIECA, 2010; HWANG and MOORE, 2011; PAN et al., 2012; MUGHEES and AL-AHMAD, 2014; SUN et al., 2018). Previous research has also focused on the implementation of CO_2 capture in oil refineries and its abatement cost, as ROCHEDO et al. (2016) have done, but it has failed to explore the water nexus with CO_2 mitigation options in oil refineries.

At the end, few attempts have been made to quantify the relationship between climate (CO_2 emission mitigation) and water-energy use in oil refineries. **Table 1** provides a brief summary of the opportunities for CO_2 abatement measures in oil refineries' processing units, and their likely impact on water consumption. It highlights the signs of the impacts that are quantified later in this study (positive and negative signs) through the use of simulation tools for all Brazilian refineries and for a specific refinery in detail.

Table 1 – Qualitative Impacts on Water Consumption of CO_2 Mitigation Options in Oil Refineries

Process Unit	Heat Integration	Reduce Boiler Blowdown/Water Treatment	Improved Maintenance/Steam Lines & Traps	Reduce Stand-by Boiler Requirements	Increase Steam Line Insulation	Recover Blowdown Steam	CC
ADU	-	-	-	-	-		
VDU	-	-	-	-	-		
CRU		-		-		-	
HDT	-	-	-	-	-	-	

RFCC	-	-		
FCC	-	-		+
DCU	-	-	-	
HGU				+

Note: The positive sign means that the measure has a positive impact on water consumption, ie it helps to reduce this consumption. On the other hand, the negative sign has a negative impact, indicating an increase in water consumption with the application of the measure.

ADU – atmospheric distillation unit; VDU – vacuum distillation unit; CRU – catalytic reforming unit; HDT – hydrotreatment unit; RFCC – resid fluid catalytic cracking; FCC – fluid catalytic cracking; DCU – delayed coking unit; HGU – hydrogen generation unit; CC: CO_2 capture

Source: WORREL and GALITSKY (2003); WORREL and GALITSKY (2005); CONCAWE (2008); BERGH, 2012; MORROW III et al. (2013)

Regarding water use, oil refining requires considerable amounts of water, which vary significantly between refineries, depending on the process configuration (WU and CHIU, 2011; SUN et al., 2018), the petroleum specification (e.g., density, sulphur content, total acid number) (SUN et al., 2018), and the products' requirements. Within this context, in Brazilian refineries, water requirements deserve attention due to the processing of heavy-to-medium crude oils, as well as to the increasingly stringent specifications of fuels that require the implementation of hydrotreatment units, associated with the water-intensive steam reforming process (CASTELO BRANCO et al., 2010; SZKLO, ULLER and BONFÁ, 2012; BARROS and SZKLO, 2015) [1].

In addition, in Brazil, water availability is not evenly distributed. While the northern region holds more than 80% of all water availability, the basins located in large urban centers, in the Brazilian southeast, for example, are currently facing low water availability coupled with high withdrawals. As shown in **Figure 1**, most Brazilian refineries are already dealing with water stress, measured in relation to the level of water criticality of watersheds. This index measures the ratio between water withdrawals for consumptive uses (irrigation, water supply, urban and industrial) and the water availability of each sub-basin expressed through the value of average flow with permanence of 95%. In fact, REPLAN, REVAP, RLAM and REDUC, which account

[1] In 2018, the Brazilian oil refining industry consisted of 17 refineries in operation, with a total installed nominal capacity of 2.2 Mbbl/day (ANP, 2018). Most Brazilian refineries were built before the 1980s with the objective of meeting the demand for gasoline and fuel oil in major urban centers (also close to Brazil's coast). However, due to the increasing diesel demand after the 1980s (BORBA et al., 2017), as well as the ramp up of medium-to-heavy crude oil production in Brazilian offshore basins in the 1980s and 1990s (HALLACK et al., 2017), the refining schemes of existing refineries were altered to convert the heaviest fractions of crude into medium cuts – e.g., by adding delayed coking units and severe hydrotreatment processes (which remove nitrogen compounds, high sulfur compounds and aromatic rings) (SZKLO and SCHAEFFER, 2007; SZKLO et al., 2012).

for 54% of Brazil's refining capacity, are located in areas classified as having critical water availability.

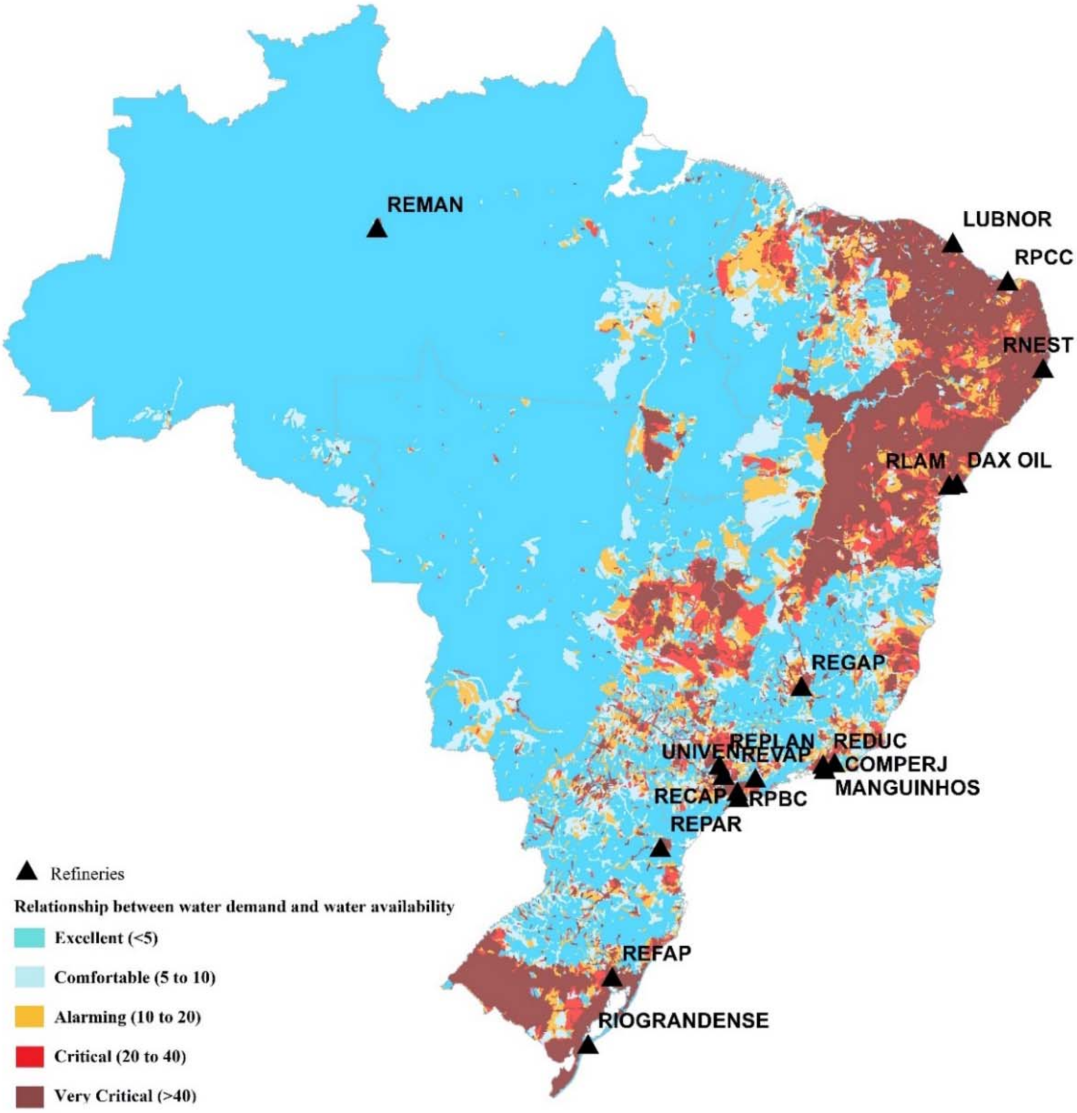


Figure 1 - Refineries locations and water criticality indicator of sub-basins in Brazil

Source: Based on ANA (2017)

To sum up, oil refineries are major CO_2 emitters and are usually located in sites with already critical availability supply of water. This is the case for Brazil, but it can be seen worldwide (OIL and GAS JOURNAL, 2018). Some CO_2 emission mitigation measures can positively or negatively influence both withdrawal and water consumption at refineries. Within this context, this study aims to quantify the extent to which these measures can impact refineries' water use. First, by developing an energy, CO_2, H_2, water balance simulator for Brazilian oil refineries, and applying it to different scenarios of CO_2 mitigation, this study evaluates the CO_2 mitigation-energy-water nexus at the country level. Then, this study analyzes the water supply of the hydrographic basin in which the largest Brazilian refinery, REPLAN, is located and how it behaves over time. This detailed analysis, at a local level, not only quantifies the water withdrawal impacts of CO_2 mitigation options, but also identifies whether or not these impacts could be overcome by the current water supply of this specific refinery.

The next section presents the methodology used to carry out the analysis, as well as a brief description of the simulation tools applied. Section 3 discusses the results obtained. Lastly, the final remarks of the study, highlighting also its limitations, are presented.

2. Methods

2.1. Methodological Procedure

The methodological procedure applied by this study consisted of the following steps. The first step is the definition of GHG mitigation measures in oil refineries, according to the scientific literature and the experience of the authors regarding Brazil's oil refineries[2]. Then, the study simulates the baseline case for estimating the scenario without CO_2 mitigation, and simulates the impacts of introducing CO_2 price scenarios into oil refineries, in terms of CO_2 emissions, final energy use and water consumption. This provides the carbon mitigation cost curve, and also helps to identify (quantify) the impacts of GHG mitigation options on the water consumption for all Brazilian refineries. However, this step is not able to detail the water supply balance at a local level. Therefore, using the mitigation cost curve for Brazilian refineries (mentioned above), the proposed procedure includes a last step for detailing the case of the largest Brazilian oil refinery, REPLAN. This step not only quantifies the water consumption impacts of CO_2 mitigation options, but also identifies whether these impacts could be overcome by the current water supply of REPLAN. In summary, the steps include:

1. To assess the CO_2 mitigation options focusing on the saving potential for the consumption of fuels, steam, electricity and H_2.
2. To estimate the energy and mass balances for a baseline case, including final energy consumption, CO_2 emissions and water requirements. This case does not consider the application of CO_2 emission mitigation options (e.g., fuel switch, fuel saving and carbon capture). This study applies an energy and mass balance simulator – the so-called

[2] See, for instance, GUEDES (2015).

"CAESAR – Carbon and Energy Strategy for Refineries" tool, which is briefly described here, and better described in the Supplementary Material.

3. To run CAESAR with CO_2 emission prices[3] of 25, 50, 100 and 200 US$/t$CO_2$. In this case, the CO_2 emissions mitigation options are selected according to their marginal abatement cost – that is, technological options with costs lower than or equal to the exogenously established CO_2 price are automatically selected by the simulation tool, allowing the construction of a CO_2 average abatement cost curve for all Brazilian oil refineries. The Supplementary Material provides the basic equation associated with the estimation of the abatement cost.
4. To develop a case study for REPLAN, the largest Brazilian refinery in terms of processing capacity, thus quantifying the water stress in detail, or locally. This allows investigating whether mitigation measures that were selected in step 3 can be adopted in cases where a greater water withdrawal is required. This case study is performed using the software tool Water Evaluation and Planning – WEAP (see section 2.2. and Supplementary Material).

2.2. CAESAR tool – Carbon and Energy Strategy Analysis for Refineries

The tool used for evaluating all Brazilian refineries, without detailing the water supply-demand balance at a local level, is the simulator CAESAR – Carbon and Energy Strategy Analysis for Refineries. It was originally developed by TOLMASQUIM and SZKLO (2000), later being used by the Brazilian Government in its Long-Term Energy Plan 2030 (EPE, 2007). Finally, it was updated by GUEDES (2015) and by VÁSQUEZ-ARROYO (2018) and MAGALAR (2018) for incorporating water balances.

The simulation is performed within Excel (visual basic), and relies on refining schemes, including the following units' energy and mass balances: atmospheric distillation, vacuum distillation, alkylation, atmospheric residue delayed coking, vacuum residue delayed coking, propane desasphalter, catalytic reformer, fluid catalytic cracker, hydrocracker, residue fluid catalytic cracker, hydrotreaters (naphtha, diesel, kerosene and instable products), hydrotreatment of finished gasoline, lube unit, and hydrogen generation unit. The processing units' capacities are determined, as well as the processed feedstocks, specific utilities consumption (steam, fuel and hydrogen) and specific water consumption. The outputs of the tool consist of the final energy consumption, CO_2 emissions, oil product output, and refineries' water consumption and withdrawal.

[3] They represent an established price to be paid for a given amount of CO_2 emitted.

Therefore, CAESAR is a bottom-up model mostly based on the simulation of the mass (water, H_2) and energy balances of Brazilian oil refineries. It has an additional feature for optimizing the energy consumption aimed at minimizing the cost of operation of oil refineries. The model also includes a list of CO_2 mitigation options, which are detailed according to the processing units in which they can be implemented, their potential for saving fuel and/or electricity, their investment, operation and maintenance costs, and their penetration rates. In total, 204 options of technologies are available in CAESAR (see Supplementary Material for detailed data).

For the carbon price scenarios, CO_2 emission prices were exogenously introduced into the simulator, which also affected the optimization problem that finds the least-cost fuel mix of refineries. Prices of 25, 50, 100 and 200 US\$/tCO_2 were considered, thus building five different scenarios for the current configuration of Brazilian oil refineries. As 204 CO_2 emission mitigation options are available in the simulator, their abatement costs range from negative values, which represent "non-regret" measures, to values above 100 US\$/tCO_2. The highest cost measures would hardly come into effect without economic incentives or more robust technological learning.

Therefore, depending on the CO_2 emission price applied, the tool automatically selects different GHG mitigation options from the set list available, affecting the final energy use, CO_2 emissions and water consumption. The Supplementary Material includes the basic data of the model and a description of how to run it.

2.3. WEAP

Before using the tool WEAP, REPLAN mass and energy balances were simulated in the above-described tool, CAESAR. This aimed to quantify the impacts of CO_2 emission mitigation options on the water required by REPLAN. Then, the results of water withdrawals obtained in CAESAR were inserted as input into the WEAP tool. This is a tool for integrated water resources management (IWRM) developed by the Stockholm Environmental Institute (SEI). WEAP integrates physical hydrological processes with water withdrawal management and infrastructure, as well as environmental and economic aspects of water planning. Its simulations are based on scenarios that can be analyzed according to different trends in hydrology, water use and demand, demography, technology, operating rules and water management policies (SIEBER and PURKEY, 2015).

The WEAP analysis consists of, firstly, configuring the time horizon, catchment areas, system components and configuration of the problem to be evaluated. Then, the model is used to simulate alternative scenarios to assess the impact of different water supply and demand management options, as well as evaluate the water availability within a region of study.

The model simulates the use of water in hydrological basins by using a linear programming algorithm, which aims to maximize the water delivered to demand sites, according to a set of priorities defined by the user. When water is limited, the algorithm is formulated to progressively constrain water allocation to the lowest priority demand sites. More details of the model can be found in SIEBER and PURKEY, 2015. See the Supplementary Material for further details on how WEAP is calibrated and used by this study.

2.4. Input Data

2.4.1. Brazilian Case Study in CAESAR

The analysis performed by this study was based on the current Brazilian oil refinery system, thus, no greenfield refinery was constructed in the simulation. The mass and energy balances rely on the breakdown in processing units, which have specific characteristics. The capacity of these units is shown in **Table 2**. The average utilization factor of the atmospheric distillation unit was set as 70%, following MME (2018).

Table 2 - Brazilian Process Unit Capacities as of December 2017

Unit	Capacity (barrels/d)
ADU	2,138,000
VDU	804,740
FCC	378,729
RFCC	123,158
ALK	6,290
DCU	115,319
CRU	2,386
HDS G	3,054
HDT N	10,528
HDT Q	28,125
HDT D	200,041
HDT I	11,698
LUB	20,009
HGU	126

ADU – atmospheric distillation unit; VDU – vacuum distillation unit; ; FCC – fluid catalytic cracking; RFCC – resid fluid catalytic cracking; ALK – alkylation unit; DCU – delayed coking unit; CRU – catalytic reforming unit; HDS G– gasoline hydrodesulphurization unit; HDT N – naphtha hydrotreatment unit; HDT Q – kerosene hydrotreatment unit; HDT D – diesel hydrotreatment unit; HDT I – severe hydrotreatment unit; LUB – lubricants unit; HGU – hydrogen generation unit (in this case, the capacity is given in MMcfd)

Source: OIL AND GAS JOURNAL (2018)

Table 3 shows the estimates for Brazilian refineries' typical utility consumption (negative values mean a net production of the utility by the unit). Although there are variations in the specific energy consumption of utilities for the same unit, depending on the supplier of the technology, local characteristics or even different design considerations, the values adopted in CAESAR seek to represent a typical Brazilian unit.

Table 3 - Process Units' Utilities Specific Energy Consumption

Unit	HP Steam	MP Steam	LP Steam	Electricity	Fuel	Coke	H_2 Consumption	H_2 Production	BFW	CW
	kg/bbl	kg/bbl	kg/bbl	kWh/bbl	MJ/bbl	MJ/bbl	m³/bbl	m³/bbl	m³/bbl	m³/bbl
ADU	0.00	11.00	0.00	0.60	127.00	0.00	0.00	0.00	0.02	0.35
VDU	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.35
FCC	-16.00	20.00	-3.60	8.80	0.00	368.00	0.00	0.00	0.07	1.00
RFCC	-18.00	0.00	0.00	1.00	0.00	368.00	0.00	0.00	0.07	1.00
ALQ	0.00	90.00	0.00	9.00	0.00	0.00	0.00	0.00	0.05	7.00
CRU	-15.60	0.00	0.00	10.00	382.00	0.00	-48.00	0.00	0.02	1.74
DCU	0.00	-18.40	0.00	3.60	126.00	0.00	0.00	0.00	0.06	2.03
HDSG	3.00	0.00	0.00	2.00	105.00	0.00	4.00	0.00	0.04	0.96
HDTN	3.00	0.00	0.00	2.00	105.00	0.00	7.00	0.00	0.01	0.19
HDTQ	4.00	0.00	0.00	3.00	158.00	0.00	7.00	0.00	0.18	0.49
HDTD	4.00	0.00	0.00	3.00	158.00	0.00	7.00	0.00	0.04	0.73
HDTI	5.00	0.00	0.00	6.00	211.00	0.00	17.00	0.00	0.05	0.71
LUB	0.00	1.60	5.60	1.60	135.00	0.00	0.00	0.00	0.05	1.00
HGU	0.00	0.00	0.00	0.00	2.55	0.00	0.00	0.16	0.00	0.00

HP – high pressure; MP – medium pressure; LP – low pressure; BFW – boiler feed water; CW – cooling water

Source: Based on HYDROCARBON PROCESSING (2008); MEYERS (2004); GARY AND HANDWERK (2001); STANISLAUS et al. (2010)

For Brazilian oil refineries, as of 2017, coefficients of water withdrawals per process unit were determined, as indicated in **Table 4**. The coefficients consist of low-pressure steam (LP Steam), medium-pressure steam (MP Steam) and high-pressure steam (HP Steam), related to the process units. The water balance also includes the water consumed in the cooling system (CW – cooling water) and the volume of demineralized water used in the boiler (BFW – boiler feed water) per barrel of oil processed. **Figure 2** shows the basic water balance applied in the simulation tool.

Table 4 - Water Use Coefficients per Process Unit

	CW (m³/bbl)	BFW (m³/bbl)	LP Steam (kg/bbl)	MP Steam (kg/bbl)	HP Steam (kg/bbl)
ADU	0.3	0.02	-	11.0	-
VDU	0.3	0.05	-	-	-
FCC	1.0	0.07	3.6	20.0	16.0
RFCC	1.0	0.07	-	-	18.0
ALQ	7.0	0.05	-	90.0	-
CRU	1.7	0.02	-	-	15.6
DCU	2.0	0.06	-	18.4	-
HDS G	1.0	0.04	-	-	3.0
HDT N	0.2	0.01	-	-	3.0
HDT Q	0.5	0.18	-	-	4.0
HDT D	0.7	0.04	-	-	4.0
HDT I	0.7	0.05	-	-	5.0
LUB	1.0	0.05	-	-	-
HGU	-	-	-	-	-

HP – high pressure; MP – medium pressure; LP – low pressure; BFW – boiler feed water; CW – cooling water

Source: VÁSQUEZ ARROYO et al. (2016)

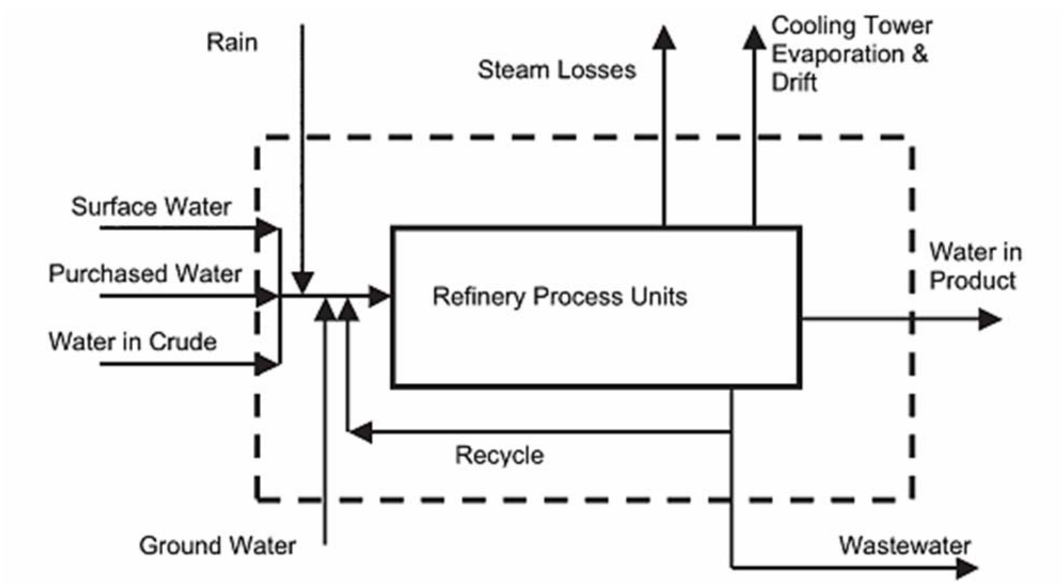


Figure 2 - Water balance in CAESAR

Source: Based on IPIECA (2010)

After obtaining the steam demand, CW and BFW, parameters were adopted to estimate the water consumed by the refinery, based on ANZE (2013). They are composed of the make-up water used in the cooling towers, the make-up water for the boilers and the water used by the processes (water incorporated into products, for instance, in the production of H_2, because of steam reforming and water gas shift, during chemical reactions). A value of 1.7% was considered for the cooling system's total circulating water, according to typical Brazilian oil refineries' concentration ratios (MAGALAR, 2018). For the boiler water make-up, a value of 49.7% was applied to the sum of the amount of water used in the boilers (BFW) and the total amount of steam consumed in process units. Steam consumed is defined as lost steam that did not return as condensate. For this, a value of 33% of all generated steam was used (VÁSQUEZ ARROYO et al., 2016). Equation (1) summarizes these assumptions and the water balance.

$$Demand = (0.017 \times \sum_i CW_i) + \{0.497 \times \sum_i BFW_i + [0.33 \times \sum_i Steam_i]\} \quad (1)$$

Where "CW_i" represents the cooling system's circulating water of each process unit "i"; "BFW_i" is the amount of water used in boilers of each process unit "i"; "$Steam_i$" is steam consumed in each process unit "i".

2.4.2. REPLAN Case Study in WEAP

REPLAN is the largest Brazilian refinery in terms of processing capacity (66 thousand m³/day) (ANP, 2018). This refinery is located in Paulínia in the state of São Paulo and is placed in the Piracicaba, Capivari and Jundiaí River Basin (PCJ), which is classified as "critical" in relation to water availability (MAGALAR, 2018).

In this study, the water availability of Jaguari basin was calculated by simulating a water balance between the inflows and outflows of its drainage area over time. The Jaguari River basin was chosen due to the catchment point of REPLAN being located in this river. In addition, the basin of the Camanduacaia, Ribeirão do Pinhal rivers was integrated into the case study because these rivers are tributaries of the Jaguari River.

The water balance method chosen by this study was the simplified coefficient Method - Rainfall Runoff, in which water requirements are calculated based on evapotranspiration and precipitation data. Twenty-six rainfall stations were evaluated within the three catchment areas: Jaguari River catchment and its tributary rivers, Camanducaia and Pinhal. The data loaded after treatment of the missing data and outliers was the monthly average rainfall. In order to use the mean value of evapotranspiration for each catchment area, the monthly average of all municipalities in each area was calculated. For more details of data, see Supplementary Material.

The water outputs considered in this study are the projected demands for public supply, industry, irrigation and for animal husbandry. These demands were identified and projected to the year 2040 to assess the extent to which water availability changes as a function of the multiple uses of water within the PCJ basin and whether the REPLAN could be impacted.

The demand for water for urban supply was calculated using a coefficient of water demand per inhabitant per day that was adjusted to account for the water losses in distribution. The same coefficient was used for the projection of water demand for future public supply. The method used for the estimation of the population of each city is described in the Supplementary Material.

Water consumption for animal husbandry was calculated from data on the number of animals per city and then calculated the product of the effective number of herds by a per capita coefficient of daily water consumption known as equivalent cattle for water demand. In order to estimate the industrial demand, the volume of water granted by industry in the water agency was consulted.

The demand for irrigation is calculated by multiplying the area under cultivation by the difference between the water requirement of the crop and the precipitation occurring over the cultivated area. For this, it is necessary to know the water demand of each crop, which is calculated from the reference evapotranspiration and crop coefficient.

After all climatic parameters, data on land use and water demands are inserted into the model, the observed values of the fluviometric stations are compared with the flow data modeled by WEAP. From the observed and simulated flow data, two calibration indices are calculated, the Nash-Sutcliffe efficiency index and the BIAS index.

To evaluate the water availability of the REPLAN catchment area, a minimum ecological flow was defined. The minimum flows most commonly used in Brazil are $Q_{7,10}$[4] or Q_{95}[5], depending on the state where the drainage area is located. According to the water resources committee of the PCJ (CBH-PCJ, 2000), areas considered critical are those in which the total water demand exceeds 50% of the minimum availability $Q_{7,10}$. In addition, the water resources policy in the state of Sao Paulo determines that the volume of water withdrawal in the industrial sector

[4] Lowest flow on seven consecutive days for 10-year return period.
[5] Flow with 95% of permanence over a period.

should be reduced if the flow of the Jaguari River reaches the minimum flow established in specific gauge stations. Therefore, in the water balance simulation done by this study, the analysis tried to find out if periods of restriction of water for REPLAN could happen.

3. Results

3.1. Baseline Scenario for all Brazilian Refineries

The total consumption of utilities and fuels in existing Brazilian refineries is shown in **Table 5**. Negative values indicate exports or utility surpluses, while positive values indicate consumption of utilities.

Table 5 - Utilities Consumption

HP Steam (kt/year)	-752,5
MP Steam (kt/year)	7,340.4
LP Steam (kt/year)	-375.9
Electricity (GWh/year)	12,162.7
Fuel (TJ/year)	284,018.2
Coke (TJ/year)	58,952.6
H_2 (M Nm³/year)	6,116.5

HP – high pressure; MP – medium pressure; LP – low pressure

From the utilities consumption, it was possible to determine the fuel consumption. The refinery fuels include natural gas, refinery gas, fuel oil, naphtha and petcoke. Electricity purchased from the grid was also accounted for, either from those refineries that do not have cogeneration or from the excess demand in relation to the capacity of cogeneration units. Natural gas is used for producing hydrogen in HGUs, electricity in cogeneration units, and steam in boilers and direct heating in process units. Refinery gas and fuel oil were accounted for direct heating in process units. In general, leftover refinery gas was directed toward flare emissions accounting. Furthermore, a 100% flare combustion efficiency was assumed to be conservative on the GHG emission estimates. Finally, the consumption of petcoke was accounted for in FCC and RFCC units. **Table 6** shows the estimation of the final energy consumption for the existing Brazilian refineries.

Table 6 - Final Energy Consumption - *Baseline* (PJ/year)

Natural Gas	367.8

Refinery Gas	84.4
Fuel oil	85.4
Coke	59.0
TOTAL	596.6
Grid Eletricity (GWh/year)	7,252.7

As such, the water requirement of the existing Brazilian refineries is detailed in **Table 7**. The water intensity of 108.2 m³/bbl is compatible with the figures found in VANELLI (2004) for REVAP – Refinaria Henrique Lage; PETROBRAS (2005) and NOGUEIRA (2007) for REPLAN – Refinaria de Paulínia; SCHOR (2006) for REDUC – Refinaria Duque de Caixas; and CETESB (2011) for RPBC – Refinaria Presidente Bernardes.

Table 7 - Water Requirements - Baseline

BFW (t/h)	8,809.2
CW (t/h)	118,486.2
Steam (t/h)	3,720.4
Condensed Steam (t/h)	2,492.7
BFW spent (t/h)	10,036.9
BFW Make-up (%)	49.7
BFW Make-up (t/h)	4,988.4
CW Make-up (%)	1.7
CW Make-up (t/h)	2,014.3
Consumption (t/h)	1,610.5
Withdrawal (t/h)	7,002.6
Consumption (m³/bbl)	24.9
Withdrawal (m³/bbl)	108.2
Consumption (km³/year)	14107.9
Withdrawal (km³/year)	61351.7

BFW – Boiler feed water; CW – Cooling water

It was also possible to estimate the CO_2 emissions of Brazilian refineries as of 2017, through the multiplication of the emission factors reported by IPCC (2006) of the respective fuels used by Brazilian refineries (**Table 8**). For electricity's CO_2 emissions, the average Brazilian grid emission factor for 2017 was considered, equal to 92.7 tCO_2/GWh (MCTIC, 2018).

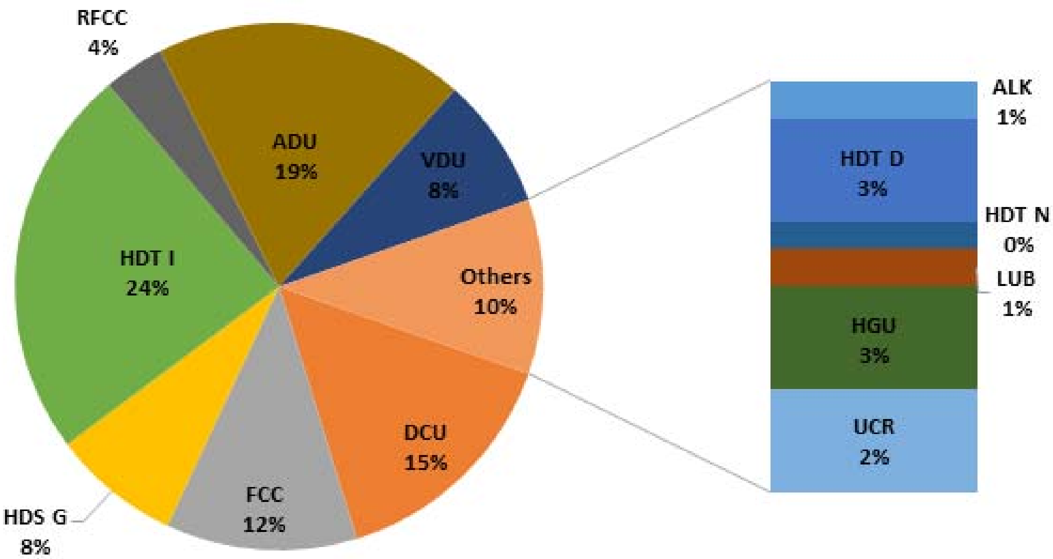
Table 8 - CO_2 Emissions ($MtCO_2$/year) - Baseline

Natural Gas	20.6
Refinery Gas	4.9
Fuel Oil	6.6
Coke	5.7
Grid Electricity	0.4

TOTAL	38.2

By dividing the total emissions by the processed feed, this study estimated an emission intensity of 0.4 tCO_2/t oil, which is compatible with the 2012 data presented by the Brazilian oil company that owns most of the country's refineries (PETROBRAS, 2013)[6]. Just for comparison, worldwide several works in the literature present CO_2 emission intensities of oil refineries hovering between 0.1 and 0.4 tCO_2/t of oil processed, with an average of 0.22 (CONCAWE, 2008; IEAGHG, 2008; STRAELEN et al., 2010; DNV, 2010). For example, the US has an average emission of 0.33 tCO2/t of processed oil, while the European Union has an average value of 0.27 (EPA, 2014).

Finally, concerning the relationship between CO_2 emissions and water withdrawals, the estimative for the baseline scenario is 0.62 tCO_2/m^3. **Figure 3** and **Figure 4** present, for this scenario, the most representative units in terms of water consumption and CO_2 emissions, respectively.



[6] Equal to 0.45 tCO_2/ t of oil processed in 2012. Of course, this intensity may vary slightly among years given the focus of the ADU campaign (in our study we focused on diesel), the possible maintenance of downstream units, which can affect the utilization factor of oil refineries (we used the ADU average utilization factor of 2017, equal to 70%), and the crudes processed in the refineries. In our study, we have considered the ramp-up of a lighter and sweeter feed that has been made available in Brazil in the last five years, from pre-salt fields. That is why we run the model with 4% of the feed from paraffinic oils from Saudi Arabia; 2% from ultra-light African crudes; 32% from Brazilian heavy crudes, and the remaining 62% from medium-to-slightly light Brazilian crudes, mostly from pre-salt fields. Therefore, the feedstock blend has become lighter than it was in 2012.

Figure 3 - Water consumption per processing unit in the baseline scenario

ADU – atmospheric distillation unit; VDU – vacuum distillation unit; ; FCC – fluid catalytic cracking; RFCC – resid fluid catalytic cracking; ALK – alkylation unit; DCU – delayed coking unit; CRU – catalytic reforming unit; HDS G – gasoline hydrodesulphurization unit; HDT N – naphtha hydrotreatment unit; HDT Q – kerosene hydrotreatment unit; HDT D – diesel hydrotreatment unit; HDT I – severe hydrotreatment unit; LUB – lubricants unit; HGU – hydrogen generation unit

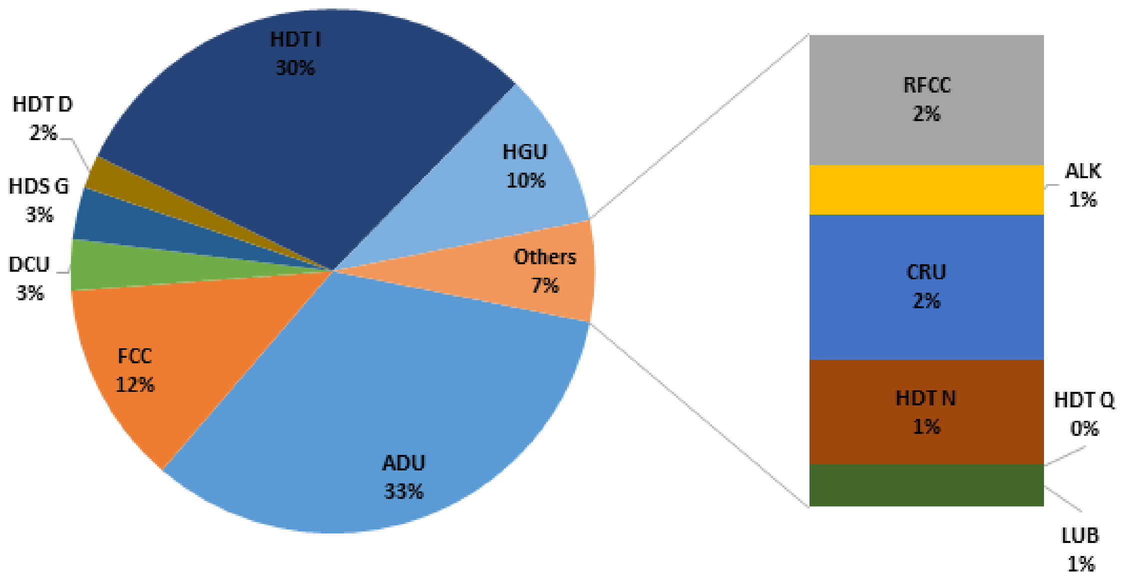


Figure 4 - CO_2 emissions per processing unit in the baseline scenario

ADU – atmospheric distillation unit; VDU – vacuum distillation unit; ; FCC – fluid catalytic cracking; RFCC – resid fluid catalytic cracking; ALK – alkylation unit; DCU – delayed coking unit; CRU – catalytic reforming unit; HDS G – gasoline hydrodesulphurization unit; HDT N – naphtha hydrotreatment unit; HDT Q – kerosene hydrotreatment unit; HDT D – diesel hydrotreatment unit; HDT I – severe hydrotreatment unit; LUB – lubricants unit; HGU – hydrogen generation unit

According to SZKLO and SCHAEFFER (2007), most CO_2 emissions from Brazilian refineries come from burning fuels. Interestingly, the fuel consumption of refineries in absolute terms concentrates on few processes, which are not the most energy intensive (in terms of energy consumption per barrel) but process large volumes of feedstock. Typically, atmospheric and vacuum distillation units account for 35-40% of a refinery's final energy use (API, 2000) because any barrel of oil entering a refinery passes through the topping separation units. This explains their share of CO_2 emissions. Also, for global refining, between 16% and 20% of the total are non-energy emissions associated with the chemical reactions of hydrogen production and cracking of the FCC (SZKLO AND SCHAEFFER, 2007). This average figure agrees with our findings for Brazil. Finally, severe hydrotreatment (for unstable and unfinished distillates) results in both higher water consumption and CO_2 emissions due to the severity (temperature higher than 450°C, H_2 partial pressure up to 21 MPa, and low liquid hourly space velocity[7] and hydrogen pressure) under which reactions must happen (GARY et al, 2007; STANISLAU et al, 2010).

3.2. CO_2 Price Scenarios for all Brazilian Refineries

As described above, four CO_2 price scenarios were simulated in CAESAR. According to the levelized cost of mitigation options on the database of the tool, different options were selected for each scenario. Moreover, the fuel mix also changed to minimize operational costs considering the CO_2 prices (and the emission factors of each possible fuel to be used). **Table 9** summarizes the results for different CO_2 prices, and **Figure 5** shows CO_2 emissions and water requirements for different CO_2 emission prices scenarios.

Table 9 – Summary of Results

Final Energy Use (PJ/year)	**CO_2 Emission Price (US$/t$CO_2$)**				
	Baseline	**25**	**50**	**100**	**200**
Natural Gas	367.84	367.84	367.84	367.84	367.84
Refinery Gas	84.39	84.39	84.39	84.39	84.39
Fuel oil	85.26	78.76	78.22	71.32	62.05
Coke	58.95	58.95	58.95	58.95	58.95
TOTAL	596.40	589.94	589.40	582.50	573.23
Grid Eletricity (GWh/year)	7252.71	7393.02	7199.61	7772.97	7643.62
Water requirements					
Consumption (km^3/year)	14107.86	14143.04	14143.04	14154.36	14154.36
Withdrawal (km^3/year)	61351.69	62191.48	62191.48	62228.12	62228.12
CO_2 emissions (MtCO_2/year)	38.20	34.43	34.38	28.18	27.46

[7] This is expressed in m^3 of fresh feed per m^3 of catalyst per hour. The inverse of LHSV is generally called residence time (STANISLAU et al, 2010).

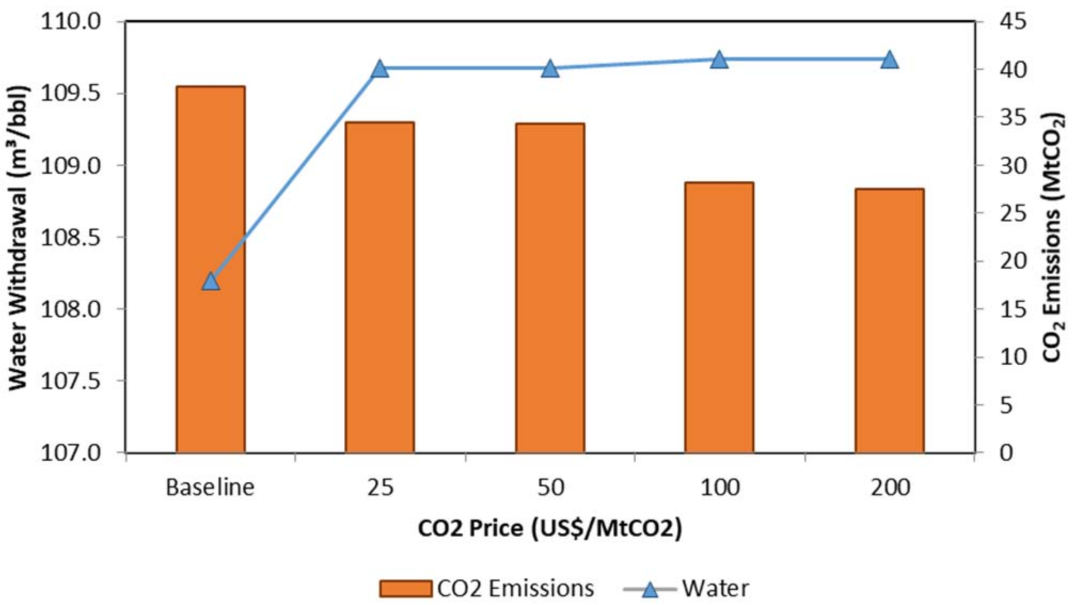


Figure 5 - Water withdrawal *versus* CO_2 emissions

The most significant CO_2 emission abatement occurs at 25 and 100 US$/t$CO_2$, 10% and 26%, respectively, compared to the baseline. This is explained by the total abatement potential of the technologies found in the cost ranges 0-25 US$/t$CO_2$ and 50-100 US$/t$CO_2$, equal to 143.5 and 205.7 MtCO_2 (see Supplementary Material). In respect to water requirements, a slight change of less than 1% occurs between the baseline scenario and 25 US$/t$CO_2$ scenario. In other scenarios, the water withdrawals remain practically stable, with a small change, less than 0.5% in the 100US$/t$CO_2$ scenario. To better illustrate the relationship between the abatement costs and the accumulated abatement potential, the abatement cost curve (**Figure 6**) was produced, including the 204 technologies considered in the study.

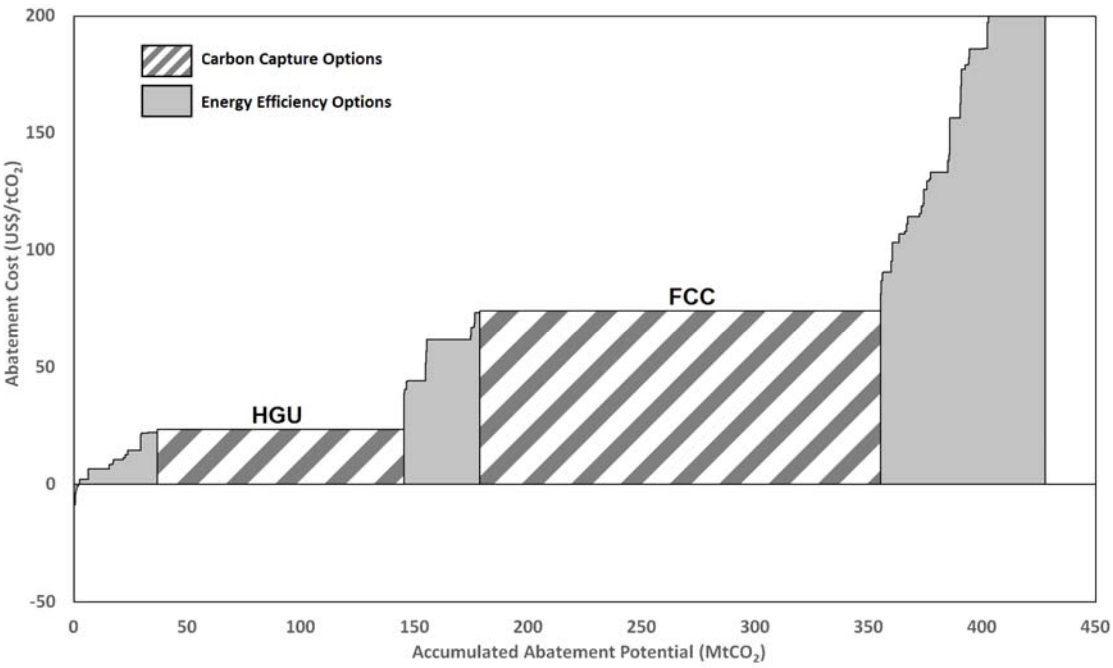


Figure 6 - Abatement cost curve for Brazilian refineries

Note: HGU – Hydrogen generation unit; FCC – Fluidized catalytic cracking.

The graph performs a static analysis of the accumulated abatement potential of the mitigation options. For instance, it demonstrates that at a cost of \$200/tCO_2, it would be possible to implement a series of measures that have a cumulative abatement potential of 423.78 MtCO_2. The two striped areas marked on the graph represent the CC technologies, while the gray-colored areas represent the other mitigation options. The first one, with an accumulated abatement potential of 145.5 MtCO_2, refers to the HGU capture with SMR/MDEA, while the second one, with 355.3 MtCO_2 of accumulated abatement potential, represents the FCC capture with Oxyfiring. These carbon capture technologies represent 65.7% of the total accumulated abatement cost, given the cracking pattern of Brazilian refineries and the recent regulations that tightened diesel and gasoline specifications in the country.

In the end, the findings of this study show that the co-benefits of GHG abatement measures that also reduce steam consumption (e.g., reduction of heat storage between ADU and VDU, steam fouling reduction in ADU, installation of vacuum pumps to replace steam injectors in ADU, increase AGR solvent concentration in HDS G, replace steam drive for electric in HDT N, and installation of CO-kiln in regenerative tower HRSG in FCC), which were chosen[8] by our

[8] Steam fouling reduction in ADU and vacuum pumps to replace steam injectors in ADU are installed at 25 US\$/tCO_2. Increase AGR solvent concentration in HDS G is chosen at 50 US\$/tCO_2. Replace steam drive for electric in HDT N is chosen at 100 US\$/tCO_2. CO-kiln in regenerative tower HRSG in FCC is installed at 200 US\$/tCO_2 tax.

simulations, were offset by the water consumption increase related to CC options, especially in HGU. In summary, at a national level and on average, CO_2 mitigation impacts on water use by oil refineries in Brazil are neutral. **Figure 7** illustrates how steam consumption reduction from some mitigation measures is overcome by the increase required with CC implementation.

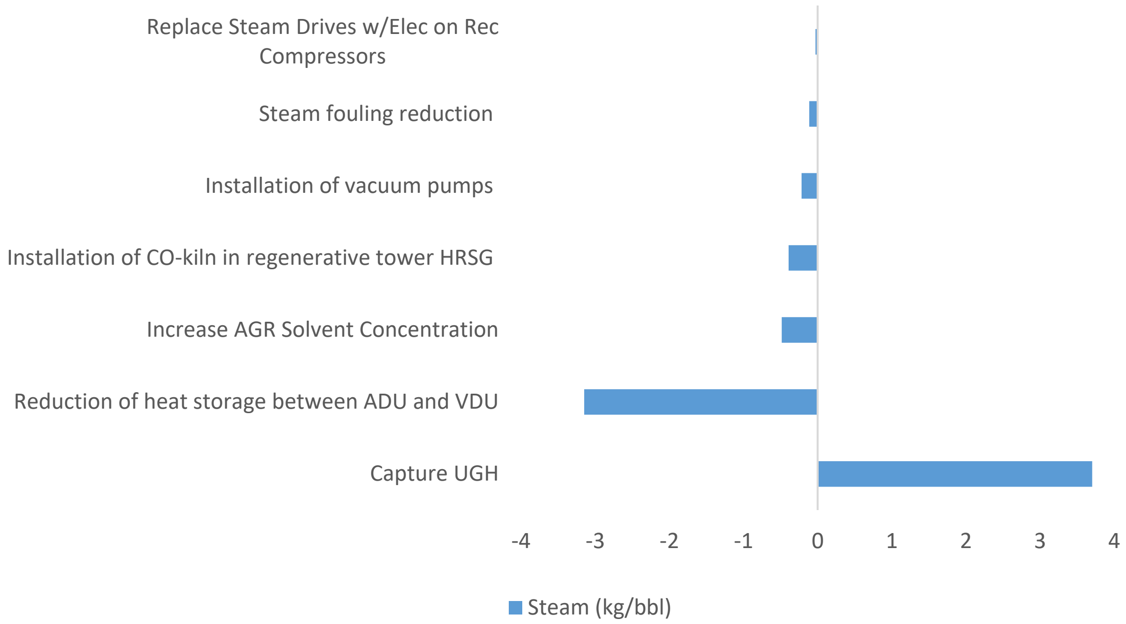


Figure 7 – Steam requirements impacts of CO_2 mitigation options

3.3. Case Study: REPLAN

At a local level, for the largest Brazilian oil refinery, the water balance undertaken showed that, although there was no unmet water demand at the REPLAN's catchment point, the conflict between the multiple water users in the basin should intensify. This is due to the trend in the river flow being progressively closer to the critical threshold of 50% of the minimum availability ($Q_{7,10}$). In addition, it was observed that the point of flow observation at Jaguari River faces instants when the flow must be restricted. This means that REPLAN may sometimes suffer impacts on its operation due to a 30% reduction in the volume of water it receives from the Jaguari River.

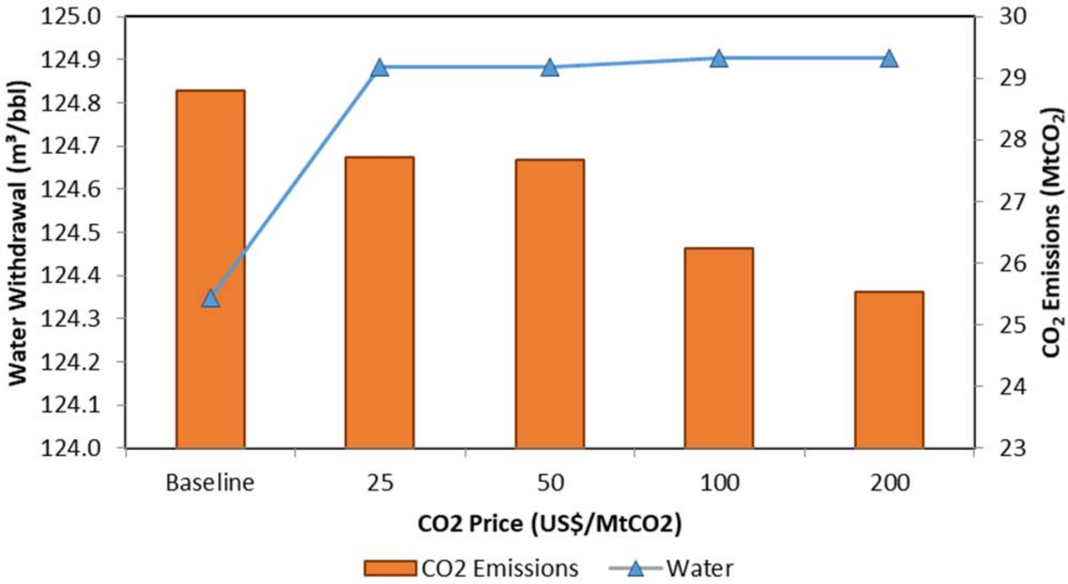


Figure 8 - Water withdrawal versus CO_2 abatement in REPLAN

Figure 8 shows an increase in water withdrawal in all scenarios. Although some mitigation measures reduce steam consumption, in the refinery's overall water balance, this reduction is offset by the increase in the demand for boiler feed water and for cooling. Mitigation measures costing up to US$ 25/MtCO_2 were the ones that most demanded water due to the increase in boiler feed water need, which was 1.4% more than in the baseline scenario. In addition, the slight increase that occurred between scenarios US$ 50/MtCO_2 and 100 was due to the implementation of CC, which increased the demand for cooling water.

Nevertheless, as a final balance, a reduction of less than 1% was obtained when implementing all CO_2 mitigation measures in REPLAN. This means that, contrary to what happens in other energy sectors (ZHAI and RUBIN, 2011; MERSCHMANN et al., 2012), the implementation of CO_2 abatement in oil refineries has no significant impact on water consumption (no negative trade-off). However, this also means that the water stress in oil refineries should be dealt with measures not directly linked to CO_2 abatement (no significant co-benefits). This is valid both at local and country levels.

4. Final Remarks

This study developed an energy, CO_2, H_2, water balance simulator for Brazilian oil refineries, and applied it to different scenarios of CO_2 mitigation (at 25, 50, 100 and 200 US$/t$CO_2$) aiming at investigating the climate-energy-water nexus. A Baseline scenario, i.e., a scenario without CO_2 prices was also elaborated. Results for both scenarios included final energy consumption, CO_2 emissions and water requirements. The most significant reductions in CO_2 emissions were due to the implementation of the carbon capture. However, this option offsets the co-benefits of CO_2 abatement measures that reduced the water requirements of Brazilian oil refineries, especially those already located in areas under water supply stress, such as the largest refinery in Brazil (REPLAN), whose water balance with carbon mitigation options was detailed in this study.

Nevertheless, as this study focused on the impacts of CO_2 mitigation options on water requirements, it was not able to follow the reverse path of the nexus: from climate to water availability. This means that climate change can affect the water availability to oil refineries (water supply, instead of water demand side). Hence, future studies could focus on this issue, also including the analysis of alternatives to regularize river flows to deal with climate impacts on water supply. Another idea could be optimizing refineries for minimizing water consumption (or withdrawals).

It is also worth noting that this study tried to validate the findings of the tools used by comparing them to real data from Brazil. However, an important issue for the simulation tool is to calibrate the feedstock blend to be run, and the focus of the refinery operation. As of today, although the Brazilian refinery system, on average, focuses on diesel optimization (e.g. when establishing the distillation cuts), single refineries can present a different feature (e.g. focusing on lube oils or petrochemicals). Similarly, the yearly focus of the average refinery operation on diesel does not mean that this is valid for all days of the year.

Finally, although the 204 CO_2 mitigation options considered by this study represent an extensive list of measures, there are always new possibilities to be assessed. For example, some studies have evaluated the use of renewable energy sources to supply the energy demand (PINSKE et al., 2012) and the hydrogen consumption (SILVA, 2017) of oil refineries.

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