



UNIVERSIDADE ESTADUAL DE CAMPINAS SISTEMA DE BIBLIOTECAS DA UNICAMP REPOSITÓRIO DA PRODUÇÃO CIENTIFICA E INTELECTUAL DA UNICAMP

Versão do arquivo anexado / Version of attached file:

Versão do Editor / Published Version

Mais informações no site da editora / Further information on publisher's website: https://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322016000400835

DOI: 10.1590/0104-6632.20160334s20140149

Direitos autorais / Publisher's copyright statement:

©2016 by Springer. All rights reserved.

DIRETORIA DE TRATAMENTO DA INFORMAÇÃO

Cidade Universitária Zeferino Vaz Barão Geraldo CEP 13083-970 – Campinas SP Fone: (19) 3521-6493 http://www.repositorio.unicamp.br Vol. 33, No. 04, pp. 835 - 850, October - December, 2016 dx.doi.org/10.1590/0104-6632.20160334s20140149

ASSESSMENT OF CO₂ EMISSION MITIGATION FOR A BRAZILIAN OIL REFINERY

W. N. Chan^{1,2*}, A. Walter¹, M. I. Sugiyama², G. C. Borges²

 ¹Universidade Estadual de Campinas (UNICAMP), Campinas - SP, Brasil.
 ²Petróleo Brasileiro S.A. (PETROBRAS), Refinaria de Paulínia, Rodovia Professor Zeferino Vaz, km 132, CEP: 13147-900, Paulínia - SP, Brasil.
 Phone: + (55) (19) 2116 6236; Fax: + (55) (19) 2116 6800 E-mail: wnchan@uol.com.br

(Submitted: November 3, 2014; Revised: June 26, 2015; Accepted: July 8, 2015)

Abstract - Currently the oil refining sector is responsible for approximately 5% of the total Brazilian energy related CO_2 emissions. Possibilities to reduce CO_2 emissions and related costs at the largest Brazilian refinery have been estimated. The abatement costs related to energy saving options are negative, meaning that feasibility exists without specific income due to emission reductions. The assessment shows that short-term mitigation options, i.e., fuel substitution and energy efficiency measures, could reduce CO_2 emissions by 6% of the total current refinery emissions. It is further shown that carbon capture and storage offers the greatest potential for more significant emission reductions in the longer term (up to 43%), but costs in the range of 64 to162 US\$/t CO_2 , depending on the CO_2 emission source (regenerators of FCC units or hydrogen production units) and the CO_2 capture technology considered (oxyfuel combustion or post-combustion). Effects of uncertainties in key parameters on abatement costs are also evaluated via sensitivity analysis.

Keywords: Carbon dioxide emissions; Mitigation; Energy efficiency; Carbon Capture and Storage (CCS); Oil refinery; Marginal abatement cost.

INTRODUCTION

Currently Brazil does not have a quantitative obligation of emission reduction of Greenhouse Gases (GHG) under the United Nations Framework Convention on Climate Change. However, according to the National Policy on Climate Change, adopted in 2009, Brazil has set the voluntary goal of reducing GHG emissions by at least 36% (compared to a business-as-usual baseline) by 2020 (Interministerial Committee on Climate Change, 2008).

In addition to the national regulatory framework, some Brazilian states, like São Paulo and Rio de Janeiro, have created their own State Policy on Climate Change. São Paulo State has established the global reduction target of 20% of the emissions of carbon dioxide by 2020 relative to 2005 levels (São Paulo, 2009).

*To whom correspondence should be addressed

Brazil is now emerging as a leading force in the oil sector. Over the last three decades, PETROBRAS – the national oil company – has made a series of large offshore discoveries, becoming a world leader in deepwater technology (IEA, 2013a). Furthermore, the Brazilian refineries have been modified to meet the goals of reducing the sulfur content of diesel and gasoline and of increasing the conversion of heavy crudes into high-quality medium and light products. So far the bulk of investments has been on adapting existing units and to install deep conversion (delayed coking) and hydrotreatment units (Castelo Branco *et al.*, 2011).

In this sense, Brazilian refineries must be prepared to cope with new challenges to sustain competitiveness, such as: increases in oil prices and the need for processing poor quality crudes; increasing demand and new demand patterns for petroleum products, including petrochemicals; new Brazilian stringent environmental regulations related to clean fuels; launching of new production technologies (e.g., heavy ends upgrading, product quality improvement, efficient fuel usage, refinery emission control strategies) embedded into more complex refining schemes and subject to increasing complexity of the logistic hardware that interconnects crude oil terminals, refineries, and distribution centers (Joly, 2012).

Worldwide the oil refining sector is a major energy user and thus a relevant CO_2 emitter. This sector currently is responsible for approximately 6% of the total European industrial CO_2 emissions, i.e. 3-4% of all anthropogenic emissions in Europe (CONCAWE, 2011). In 2011, the Brazilian refining sector was responsible for 5% of the total amount of 409 million tonnes (Mt) of Brazilian energy-related CO_2 emissions (PETROBRAS, 2014a; IEA, 2013a).

Currently Brazil has 12 refineries, mainly concentrated in the southeast region of the country, with a total refining capacity of 2.1 million barrels per day (bpd) (PETROBRAS, 2014a). Replan (Paulínia Refinery) is the largest national refinery with a crude oil throughput of 430,000 bpd.

Emissions from Brazilian petroleum refineries have increased from 18.2 Mt CO_2e in 2005 to 25 Mt CO_2e in 2013 (Chan, 2006; PETROBRAS, 2014a). This trend has primarily been driven by continuing growth in the demands for cleaner fuels (diesel and gasoline), resulting in higher total energy consumption in refining.

This so-called "petroleum refining paradox" implies that efforts to produce cleaner fuels, which would contribute to reduce emissions of sulfur and nitrogen oxides in the transport sector, result in increased CO₂ emissions from the refineries (Chan, 2006; Szklo and Schaeffer, 2007; Johansson *et al.*, 2012). Thus, it is important to consider strategies to reduce CO_2 emissions associated with the petroleum conversion process.

 CO_2 emissions at refineries can be reduced through a number of routes, but there are three main categories that are considered as key mitigation options (IPCC, 2007):

Energy efficiency;

• Low-carbon energy sources (such as natural gas and renewable energy);

• Carbon Capture and Storage (CCS).

To understand the dynamics of CO_2 emission reductions and how oil companies will define their mitigation choices, it is important to study the abatement costs of possible mitigation options of CO_2 emissions at refineries. The aim of the present study is to elaborate an assessment of CO_2 mitigation options and their costs for Replan, using the concept of Marginal Abatement Cost (MAC).

CHARACTERIZATION OF REFINERY CO₂ EMISSIONS

Worldwide, the refining sector ranks third among stationary CO_2 producers, after the power production sector and the cement industry (Gale, 2005). A refinery may use 1.5% up to 8% of its feed as fuel, depending on the complexity of the refinery. For a large-scale 300,000 bpd refinery, this will lead to CO_2 emissions ranging from 0.8 up to 4.2 MtCO₂/year (Gary *et al.*, 2007).

Oil refineries require energy to convert crude oil into marketable products. Along the process CO_2 emissions are due both to fuel burning to supply energy for the refining processes and to the production of the hydrogen required by the conversion processes. For a typical complex refinery, the key sources of CO_2 are presented in Table 1.

Source	Description	% of total refinery emissions
Furnaces and boilers	Heat required for the separation of liquid feed and to provide heat of reaction to refinery processes, such as reforming and cracking	30-60
Utilities	CO_2 from the production of electricity and steam at a refinery	20-50
Fluid catalytic cracker	Process used to upgrade a low hydrogen feed to more valuable products	20-35
Hydrogen production	Hydrogen is required for numerous processes and most refineries produce it on-site via steam methane reforming or with a gasifier	5-20

Power plants have flue gas emitted from a single stack (or possibly two or three stacks for the very large ones). Conversely, refineries can typically have 20 to 30 different CO₂ emission sources (process heaters), ranging widely in size, location, flue gas concentration and types of contaminants. These sources generally emit to the atmosphere through individual stacks, which are scattered throughout the refinery site. Furthermore, with the exception of some hydrogen plants, CO₂ is emitted in flue gases and off-gases with fairly low CO₂ concentrations, on the order of 3-12 %v/v (CONCAWE, 2011).

These characteristics potentially make end-ofpipe recovery of CO_2 logistically and technically difficult, as well as expensive. Considering that the dimension of a large complex refinery may be over 5 km², gathering these sources into a centralized capture facility requires considerable investment in large cross-section ducting and induced draft fans, with additional energy requirements, often in situations where space is severely restricted (Straelen *et al.*, 2010).

On the other hand, in the catalyst regeneration of Fluid Catalytic Cracking (FCC), the coke produced during cracking of the oil feed is burned to generate heat of reaction. In this process, the surplus heat can be used to generate steam and electricity. Because nearly pure carbon is being burned the concentration of CO₂ in the flue gases is relatively high (about 20 %v/v). In this case, CO₂ capture is technically feasible, especially if oxi-firing is considered (CONCAWE, 2011). More details about CO₂ capture options will be discussed below.

In addition to combustion, refineries generate CO₂ through decarbonisation of hydrocarbon molecules to produce the hydrogen needed for hydrotreating light and medium distillates. By far the most widely used process for hydrogen production is methane steam reforming. The average emission is about 10 tonnes of CO₂ per tonne of hydrogen produced (Hydrocarbon Publishing Company, 2010). Following the steam reforming reactions, CO₂ needs to be removed from the CO₂/H₂ mixture to produce the high purity hydrogen stream normally required for downstream processes. CO₂ removal can be effected by chemical absorption in a solvent (usually an amine) or by the more energy efficient physical adsorption route (Pressure Swing Adsorption). In the former case a high purity CO₂ stream is produced (up to 99%) that would just need drying and compression to be transported to a storage site. In the latter case the waste stream contains a mixture of CO₂, H₂, CO and hydrocarbon where the CO₂ concentration is in the 50% v/v range so that further

separation would be required to prepare a CO₂ stream suitable for transport and storage (CONCAWE, 2011).

CO₂ MITIGATION MEASURES FOR THE OIL REFINING INDUSTRY

The contribution of oil refineries to the reduction of CO_2 emissions based on the previously mentioned mitigation strategies is discussed in this section.

Energy Efficiency Opportunities

Recently, several studies have been published on the opportunities for energy efficiency and CO_2 mitigation in the oil refining industry (Petrick and Pellegrino, 1999; Worrell and Galitsky, 2005; Szklo and Schaeffer, 2007; Hydrocarbon Publishing Company, 2010). The opportunities vary from specific actions in unit operations to site-wide energy measures such as process integration.

Worrell and Galitsky (2005) estimate an energy saving economic potential of 10-20% for most U.S. refineries. For the Brazilian oil refineries, Szklo and Schaeffer (2007) have estimated the potential for energy savings with a focus on two alternatives: the reduction of primary energy use and the implementation of non-hydrogen consuming technologies for sulphur removal. They estimate a near-to-medium term energy saving potential ranging from 10% to 20%.

Large energy savings can be achieved by means of heat integration and most studies have been conducted on parts of the refinery process (Plesu *et al.*, 2003; Valino *et al.*, 2008; Bulasara *et al.*, 2009). Brown (1999) reported that typical energy savings from total site analyses are in the 20-30% range, and the results are limited to 10-15% as long as economic feasibility is considered.

According to Szklo and Schaeffer (2007), waste heat recovery is one of the most important options in the short-to-medium run, while fouling mitigation and new refining processes are promising technologies in the medium-to-long run.

However, in the short term thermal energy management still remains the major option for saving fuels in Brazilian existing refineries. Indeed, the Brazilian refineries have an impressive fuel saving potential as can be noted by the average Solomon Energy Intensity Index (EII), which was 110 in 2009, compared to the 2008 World's Best EII of 73.5 (Corrêa, 2010; Proops, 2010). The Solomon EII is used to evaluate the energy efficiency of refineries around the world, by comparing a given refinery with a reference plant with the same level of technological complexity (the reference refinery is normalized as 100). An index higher than 100 indicates that the given refinery has a primary energy consumption higher than the reference one (Castelo Branco *et al.*, 2011).

In theory, energy efficiency can provide low-cost or even payout opportunities for GHG emissions reduction. On the other hand, energy efficiency has for a very long time been a priority at the refineries, however constrained by managerial issues. Many measures with great energy saving potentials have already been implemented at the refineries (Holmgren and Sternhufvud, 2008; Nordrum *et al.*, 2011). It should be noted that further improvements in energy efficiency vary significantly across individual refineries (Johansson *et al.*, 2012). In many cases the feasibility is low due to the high capital costs for waste heat recovery and to the low reductions in emissions (Nordrum *et al.*, 2011).

However, in practice, there are some limitations to the implementation of energy efficiency measures that result in postponing these projects: (1) lifetime of existing equipment; (2) reliability of existing equipment and (3) major changes can only be executed during maintenance turnarounds.

Switching to Low-Carbon Energy Sources

The potential for fuel shift at refineries is related to substituting liquid fuels that are used in furnaces or boilers for fuels with lower carbon content, such as natural gas.

The bulk of the fuel used in a refinery is a byproduct of the refining process (refinery gas) and is composed of light hydrocarbons (mostly methane and ethane). However, these top fractions are not sufficient to cover the whole energy demand and the balance (about 23%, on average, in European Union refineries) has traditionally been met by low-value liquid residues, for example heavy fuel oil. Refineries can use these liquid fuels for other purposes and instead import natural gas (CONCAWE, 2008).

The estimates of CO_2 emission reductions due to fuel substitution are based on the assumption that refineries close to natural gas grids could displace all liquid fuels (Johansson *et al.*, 2012). For example, Elkamel *et al.* (2008) showed that 30% of the CO_2 emissions could be reduced by switching all liquid fuels for natural gas.

Carbon Capture and Storage

Energy efficiency is the main opportunity to reduce CO_2 emissions, but even an efficient refinery continues to demand energy to a large extent, therefore emitting considerable amounts of CO₂. Thus, an option to further reduce these emissions is through CCS (Straelen *et al.*, 2010). In general, the largest potential reductions of CO₂ emissions in the refining industry are related to CCS (Johansson *et al.*, 2012).

According to Freund (2005), three routes are recognized for the capture of CO_2 :

• Post-combustion capture: is an end-of-pipe solution, where CO₂ is removed from the flue gas before the flue gas is emitted to the atmosphere via the stack;

• Oxyfuel combustion capture: in this case, pure oxygen rather than air is used for combustion. This eliminates nitrogen from flue gases. In refineries, burners may be oxy-fired. Also the operation of FCC on oxygen is under study;

• Pre-combustion capture: is a process where the hydrocarbon fuel is pretreated to produce a CO_2 and H_2 stream from which CO_2 can be separated. Gasifiers with pre-combustion capture would be used to supply the refinery's utilities.

To date, the focus has been on post-combustion and oxyfuel combustion capture. Regarding oxyfuel the motivation is that it generates a cleaner CO_2 stream and less heat is required. However, the oxyfuel process requires oxygen, the producing process of which is very energy demanding (large electricity requirement for oxygen generation is due to the Air Separation Unit (ASU) via cryogenic distillation), besides the fact that the reconstruction of furnaces and/or boilers is also necessary. On the contrary, no reconstruction of existing equipment is necessary for post-combustion CO_2 capture (Johansson, 2013).

Whatever the option selected, CO_2 capture would result in high cost and significant additional energy consumption and CO_2 emissions (CONCAWE, 2011). Indeed, it is important to consider the energy consumption by CO_2 capture systems, but what is even more important is to know how this energy is provided, and the impacts in terms of costs and CO_2 emissions. The capture technology will impose more or less energy consumption as steam or electricity. The Air Separation Unit (ASU) consumes almost exclusively electricity, while chemical absorption consumes mostly steam (Saggese, 2012).

In recent years, the reduction of CO_2 emissions in refining via CCS has been addressed in publications. For example, Reddy and Vyas (2009) investigated CO_2 recovery from pressure swing adsorption off gas (hydrogen production). An important contribution of Statoil Hydro is the deployment of a large CO_2 capture plant at their Mongstad (Norway) refinery, predicted for 2014. At full-scale the project aims to capture around 2 MtCO₂/year of the flue gases of the residue catalytic cracker and of a cogeneration plant using chemical absorption with monoethanolamine (Statoil, 2009). A pilot test of oxyfuel CO_2 capture from FCC has been performed in Brazil and confirmed no significant changes from normal operations in product profile, stability of operation and the effectiveness of coke burn. The feasibility study in the oxy-firing FCC also indicates significantly lower CO_2 capture costs compared to post-combustion capture (Mello *et al.*, 2009).

Kuramochi *et al.* (2012) compared the technoeconomic performance of several CO₂ capture techniques for selected industries, including the oil refining sector. The findings of their study indicate that CO₂ capture in oil refineries could be achieved at a cost in the range of 30 to 120 \notin /t CO₂, depending on the targets of CO₂ capturing and on the CO₂ capture technologies considered. For instance, CO₂ mitigation costs for post-combustion capture in the shortto-medium term are found to be above 100 \notin /t CO₂. Oxyfuel capture, in contrast, may provide relatively low CO₂ avoidance costs, as around 50-60 \notin /t CO₂. According to CONCAWE (2011), the cost of capturing is typically about 80% of the total CCS cost.

The specificity of oil refinery CCS projects will be mostly related to capture (CONCAWE, 2011). While it would be technically feasible to combine a number of sources and route all the flue gases to one CO_2 capture plant, this would require several kilometers of ducting (i.e., for transport) and additional blower duties (i.e., to overcome pressure drops) (Simmonds *et al.*, 2003).

Thus, such strategy would entail significant costs and require space for the infrastructure. Therefore, most studies focus on capturing CO_2 from the largest sources or from the sources with the highest CO_2 concentrations (e.g., hydrogen production). Another important aspect is to understand in what extension the refineries with capture can be integrated in a network infrastructure for transport and storage of the captured CO_2 (Johansson *et al.* 2012). In this sense, Rootzén *et al.* (2011) discuss how the geographical distribution of large CO_2 emitters and the distance to storage sites could affect the development of CO_2 transportation networks.

In summary, the implementation of CO_2 capture technologies in refineries presents some issues that must be taken into account: (1) space requirements to install the following systems: flue gas gathering, removal of sulfur and nitrogen oxides (gas scrubber), CO_2 drying and compression, off-site, additional utility production, besides the amine treatment towers (post-combustion) or the ASU (oxyfuel combustion); (2) additional water availability for the gas scrubber and for the steam generation; (3) additional wastewater treatment due to gas scrubbing and (4) additional carbon footprint associated with the extra energy consumption (steam and power generation due to firing natural gas in a combined heat and power plant). In the specific case studied in this paper, space and water availability could be constraints and further detailed feasibility analysis of CO_2 capture must take these issues into account.

Last but not least, the CO_2 capture technology struggles with several issues, especially with respect to public acceptance for onshore CO_2 storage and uncertainties about the legal framework for CO_2 capture, transportation and storage (Johansson, 2013).

METHODOLOGY

Definition of Calculation Parameters

In order to estimate the cost of each emission-reducing measure at Replan the following calculation parameters were considered.

Annual Plant Operation Time

A typical value of 8,500 hours per year (Kuramochi *et al.*, 2012) was considered.

Lifetime of Investment

The economic lifetime of the investment was assumed to be equal to the technical lifetime of the abatement measure. In this study an average lifetime of 25 years was considered.

Discount Rate

The economic assessment could vary significantly, depending on whether the perspective is the public or private sector (Gouvello *et al.*, 2010). Therefore, the average abatement cost of each mitigation option was determined on the basis of incremental costs compared with a baseline scenario at a discount rate of 10%, which is typically adopted by the private oil sector both for energy efficiency projects and for CO₂ capture projects (Melien, 2005; Kuramochi *et al.*, 2012).

Pricing Structure

In the present study, the evolution of fuel pricing is based on the New Policies Scenario, which is the central scenario of the World Energy Outlook 2013 (IEA, 2013a). The period of analysis is from 2014 up to 2020, which is the timeframe of the State of São Paulo Policy on Climate Change.

There is no global benchmark pricing for natural gas, as there is for oil (IEA, 2013a). Brazilian gas prices are aligned with the European market (FIESP, 2014). Brazilian fuel oil price is assumed to be 85% of the imported crude oil price. The forecast for electricity prices is based on the current tariffs of electricity (AES Eletropaulo, 2014) and on the evolution of the marginal cost shown in the Brazilian Plan of Energy Expansion (Brasil, 2013).

The energy prices considered in this study are presented in Table 2.

Emission Factors

The considered CO_2 emission factors are shown in Table 3.

Cost Estimates

This study used an incremental cost approach, based on Gouvello *et al.* (2010), to calculate the abatement costs. The cost of each emission-reducing measure (including new technologies, fuel switches and efficiency improvements) was estimated by comparing the cost difference between two options: the option to implement the abatement technology and the option not to implement it (reference scenario) as described in Equation (1).

$$AC = \frac{C^{abatement} - C^{reference}}{E^{reference} - E^{abatement}}$$
(1)

where,

 $AC = Abatement \text{ cost of } CO_2 \text{ mitigation measure}$

 $C^{abatement}$ = Net annual cost of the abatement technology

 $C^{reference}$ = Net annual cost of the technology in the reference scenario

 $E^{abatement} = Annual CO_2$ emission with the abatement technology

 $E^{reference}$ = Annual CO₂ emission with the technology in the reference scenario

The net annual cost of each option includes costs for the investment, fuel, operation and maintenance, besides the revenue generated by the technology as described in Equation (2).

C = INV.r.
$$\frac{(1+r)^{t}}{(1+r)^{t}-1}$$
 + OMC + FC - REV (2)

where,

C = Net annual cost of the abatement technology or of the technology used in the reference scenario

INV = Total investment or capital cost of the abatement technology or of the technology used in the reference scenario

OMC = Annual operations and maintenance cost of the abatement technology or of the technology used in the reference scenario

FC = Annual fuel cost of the abatement technology or of the technology used in the reference scenario

REV = Annual revenue generated by the abatement technology or by the technology used in the reference scenario

r = Discount rate

t = Lifetime of the technology.

Fuel	Price Unit	2014	2015	2016	2017	2018	2019	2020
Crude oil	US\$/barrel	110.00	110.50	111.00	111.50	112.00	112.50	113.00
Heavy fuel oil	US\$/barrel	93.50	93.93	94.35	94.78	95.20	95.63	96.05
Natural gas	US\$/MBtu	11.7	11.8	11.8	11.8	11.9	11.9	11.9
Electricity	US\$/MWh	79.37	74.49	59.22	55.56	58.61	56.78	54.95

Table 2: Considered energy prices (IEA, 2013a; AES Eletropaulo, 2014; Brasil, 2013).

	Unit	Nominal value
Heavy fuel oil	t CO ₂ /GJ	0.079^{a}
Natural gas	t CO ₂ /GJ	0.056 ^b
Electricity grid	t CO ₂ /MWh	0.5932 ^c

Notes:

^a The value is due to fuel burning in boilers and furnaces and is based on typical values of heavy fuel oil processed at Replan: carbon content

= 87%; lower heating value = 40,260 kJ/kg; density = 0.995 t/m^3 (Chan, 2006)

^b The value is due to fuel burning in boilers and furnaces and is based on typical values of natural gas consumed at Replan: carbon content = 73%; lower heating value = 47,730 kJ/kg (Chan, 2006)

^c The value is due to production of electricity and corresponds to the annual (2013) average value of CO₂ emission factor based on a marginal operation of Brazilian electricity system (Brasil, 2014)

For a given technology over the study period (2014-2020), annual abatement costs are weighted with the corresponding annual CO_2 mitigation to calculate the average annual abatement cost.

By definition, the MAC is the cost of reducing a unit of emissions regarding the current situation (Holmgren and Sternhufvud, 2008). A MAC curve can be shown as a graph that indicates the cost of each mitigating technology as a function of the potential for emission reduction (in general in million or billion tonnes of CO₂). Therefore, a baseline (reference scenario) with no CO₂ constraint has to be defined in order to assess the marginal cost against this baseline. The MAC curve is constructed by assuming that the measures will be implemented in cost order, ranked from the cheapest to the most expensive. MAC curves are easy to understand: if a particular abatement level is targeted, one knows what measures need to be implemented in order to achieve the goal. In summary, MAC curves typically show the technological potential of abatement measures (Kesicki, 2011).

CASE STUDY: CO₂ EMISSIONS MITIGATION AT REPLAN

With a crude oil throughput of 430,000 bpd, Replan (Paulinia Refinery) is the largest Brazilian refinery. It is located in Paulinia, State of São Paulo, and is focused on fuel production, particularly diesel. Like most large-scale petroleum refineries, Replan is a complex industrial installation including a variety of process units: crude and vacuum distillation (CVD), fluid catalytic cracking (FCC), catalytic reforming (CR), delayed coking (DC) and distillate hydrotreating (DHT). There are also side processes, like hydrogen generation (HG) and onsite power generation.

In this study, the assumption was considered that Replan's current figures of crude oil throughput (430,000 bpd) and total CO_2 emissions (3.8 Mt CO_2 , based on the actual set of process units of Replan) remain constant during the period of analysis (2014-2020). The technologies discussed above were evaluated for Replan.

Energy Efficiency Opportunities

Many measures aiming at energy savings have already been implemented at Replan (Chan, 2006). In this sense, opportunities for additional improvements in energy efficiency are limited. Since it is unfeasible to make a complete investigation of all remaining energy efficiency opportunities, focus was put on covering the main projects identified in an Energy Optimization Study developed by the company. Conducted in 2013 at Replan, this assessment focused on 30 opportunities for major process units and identified energy savings of 10% of the total energy used at the refinery, considering only projects with a payback of less than five years (PETROBRAS, 2014b).

Half of these 30 opportunities are more related to optimization measures focusing on higher yield of products. The most promising projects in terms of CO_2 mitigation potential are described next.

Improved Heat Integration

The heat exchanger networks of the two CVD units and of the two DC units could be improved by adding a total of eight new heat exchangers. Additionally, it is possible to send a pre-flash tower sidecut to the atmospheric tower and to recover more heat by increasing the circulation of atmospheric tower pump-around stream in the two CVD units.

Operation Improvement

Direct feeding of vacuum gas oil at 100 °C from CVD units to FCC units (without cooling and storage) could enable the use of surplus heat to preheat boiler feed-water (BFW).

Waste Heat Recovery

Each of the two former DHT units has a significant amount of heat in the reactor effluent that is rejected to cooling water. Thus, there is some available heat in this stream that could be recovered by adding two new exchangers (in each DHT unit) to preheat the BFW makeup.

Hydrogen Management

A discharge of the pressure control valve of the hydrogen system (vent gas) could be routed to the fuel gas system rather than flare.

Energy Optimization for Utility Systems

Considering the CO₂ mitigation potential, two opportunities stand out:

• Increasing steam use of the Heat Recovery Steam Generator from 80% to 100% would result in

more efficient steam production and less fuel gas consumption;

• The use of medium pressure steam to preheat BFW is an advantageous option since there is an excess of this flow in the refinery.

Onsite Power Generation

In FCC units, it is common practice to utilize expansion turbines or turbo expanders to generate electric power by recovering energy released in the catalyst regeneration process (MacLean *et al.*, 1985). At Replan one of the two FCC units has no turbo expander. So, a new turbo expander could be installed to generate 8.4 MW. However, the implementation of this measure would only be feasible by 2020 after retrofitting the FCC unit.

Cost Estimation

In the case of energy efficiency opportunities, a typical value of 2.5% of the capital cost was considered as the annual cost of operation and maintenance (O&M), except energy. The capital cost is relative to the installed equipments for each CO₂ abatement measure (acquisition, taxes and installation). The annual revenue is relative to the fuel savings, considering natural gas prices. In the case of Replan, two factors must be taken into account. The first one is that, even considering all the internally generated fuels (refinery gas, FCC coke and other waste gases), there is a permanent energy deficit and, therefore, another fuel is necessary to complement the refinery fuel demand. The second factor is the selection of the complementary fuel between fuel oil and natural gas. But, at Replan, fuel oil burning in furnaces and boilers is restricted due to environmental requirements. In other words, natural gas is the choice for use as complementary fuel (around 15-20% of internal supply). Thus, at Replan, any fuel saving results directly in a natural gas saving (i.e. natural gas is the marginal fuel). Table 4 summarizes the energy saving, the capital cost and the annual revenue for each alternative previously described (for each measure described in Table 4, the preliminary cost is based on estimated cost of major equipments (pumps, compressors, heat exchangers, vessels, etc.) considering the historical database of Petrobras. Each equipment cost should be multiplied by the Installation Factor and also the Import Factor. The Installation Factor includes shipping, foundations, piping, instrumentation, etc. Retrofittings have installation costs greater than new equipments. The Import Factor is applied to the imported equipments

and it includes import and transport costs).

Substitution of Fuel Oil by Natural Gas

At Replan the use of liquid fuels has decreased over the years due to environmental requirements. Currently, only one steam boiler is fired with 50% heavy fuel oil due to operational safety in the case of irregular fuel gas (a mixture of refinery gas and natural gas) supply to the boilers. This fuel oil consumption corresponds to 1.5% of the refinery total energy supply and the related emission is about 65,100 t CO_2 /year. Natural gas could replace the current use of heavy fuel oil, yielding a reduction of 19,000 t CO_2 /year.

Carbon Capture and Storage

Given the dominant role that fossil fuels continue to play in the energy consumption worldwide, the urgency of CCS deployment is increasing. According to IEA (2013b), it would be necessary to create a solid foundation for deployment of CCS starting by 2020.

Considering the hypothesis that Replan would have to meet targets to reduce CO_2 emissions in the short-term (for instance, due to the State of São Paulo Policy on Climate Change), prompt actions should be taken in order to implement pioneer CCS projects up to 2020.

Most studies focus on capturing CO_2 in a refinery from the largest sources, or from the sources with the highest CO_2 concentrations. In this way, CO_2 capture at Replan would be feasible for regenerators of FCC units (using oxyfuel combustion) and hydrogen production units (using post-combustion), respectively. Currently, FCC units account for emissions of 1 Mt CO_2 /year at Replan, while hydrogen production is responsible for emissions of 0.8 Mt CO_2 /year.

Cost Estimation

The cost estimation of CO_2 capture technologies for Replan is based on economic and on the performance parameters in the short-term (10 years) presented by Kuramochi *et al.* (2012), as shown in Table 5.

The capital costs for FCC units and hydrogen production at Replan are standardized for processing 1 Mt CO₂/year and 0.8 Mt CO₂/year, respectively. Regarding the reference figures (1 Mt CO₂/year for FCC units and 2 Mt CO₂/year for hydrogen production), the estimated capital costs were adjusted by applying a 0.67 cost scaling factor, according to Kuramochi *et al.* (2012).

Table 4: Capital cost and annual revenue for energy efficiency opportunities (Petrobras, 2014b).

Measure	Energy saving (GJ/h)	Capital cost (MUS\$)	Annual revenue (MUS\$/year)	
M1. Improved heat integration	157.31	11.09	15.08	
M2. Operation improvement	20.97	0.88	2.01	
M3. Waste heat recovery	35.08	1.36	3.36	
M4. Hydrogen management	16.75	0.50	1.61	
M5. Energy optimization for utility systems	126.57	0	12.13	
M6. Onsite power generation	30.27	30.70	3.92	

Table 5: Short-term performance data for oil refineries with CO₂ capture (Kuramochi et al., 2012).

Technique	Process	CO ₂ capture Rate (t/t reference			Incremental capital cost (US\$/t CO ₂	O&M cost	
		emissions)	Natural gas	Steam	Power	captured/year)	
Oxyfuel	FCC	0.94	-	-3.3	2.5	274	4%
Post-combustion	Hydrogen Production	0.85	5.7	-	-0.1	352	8%

According to Table 5, it would be feasible to capture 0.94 Mt CO_2 /year at the FCC units and 0.68 Mt CO_2 /year at the hydrogen production. The capital cost (turn-key cost; 2012 basis) was estimated as 258 MUS\$ for oxyfuel combustion capture and 239 MUS\$ for post-combustion capture.

Nowadays, in the Replan surroundings there is no infrastructure either for CO_2 transportation or CO_2 storage. Thus, the costs of transport and storage would have to be added to the cost of CO_2 capture. In order to estimate the abatement cost of the CCS technologies at Replan, it was considered that the cost of capturing is 80% of the total CCS cost (CONCAWE, 2011).

RESULTS

At this point, it is important to remember that the results should be considered as potential rather than effective CO_2 emission reductions at Replan.

The implementation of the turbo expander and of

the CCS technologies would only be feasible in 2020 and onwards. For this reason two sets of results are presented. The first set includes short-term measures (period 2014-2019) while the second one includes both short-term and mid-term measures available from 2020 onwards.

Table 6 and Figure 1 present the results of the CO₂ abatement actions in the period 2014-2019. In the period it would be possible to mitigate the emissions of 189 thousand t CO₂ per year, i.e., 5% regarding the emissions of the reference case (2013). The accumulated reductions in emissions would be 1,134 thousand t CO₂ in six years, at a cost that would vary from -144.72 to -114.04 US\$/t CO₂ (average values in the period, discounted to 2014 at 10% per year). The negative values indicate that mitigating measures are already cost-effective, just considering the benefits of energy savings and for the hypothesis taken into account. As there is no technological constraint, and all measures are already cost-effective, they could be implemented immediately.

Measure	Annual reduction potential (1000 tCO ₂ /year)	Total reduction potential (1000 tCO ₂)	Average cost 10% discount rate (US\$/t CO ₂)	
M1. Improved heat integration	75	450	-130.22	
M2. Operation improvement	10	60	-136.09	
M3. Waste heat recovery	17	102	-136.75	
M4. Hydrogen management	8	48	-138.58	
M5. Energy optimization for utility systems	60	360	-144.72	
M7. Substitution of fuel oil by natural gas	19	114	-114.04	
Total	189	1134		

Table 6: Abatement costs for CO₂ emissions at Replan (period 2014-2019).

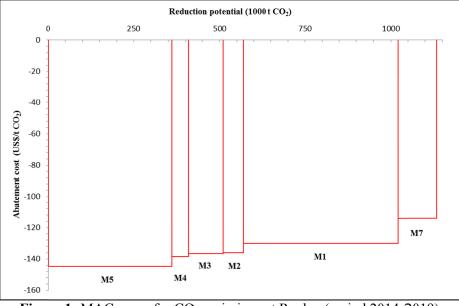


Figure 1: MAC curve for CO₂ emissions at Replan (period 2014-2019).

Table 7 and Figure 2 present the results of all CO_2 abatement actions, with nominal costs in 2020. Implementing all measures it would be possible to mitigate emissions by 1.85 Mt CO₂ per year, i.e., 48.7% regarding the emissions of the reference case (2013). Increased energy efficiency could contribute to lowering the emissions by 212 thousand tCO_2 per year. Applying a fuel shift gives an abatement potential of 19 thousand tCO_2 per year. However, the mitigation of 1.62 Mt CO_2 per year (42.6% of the emissions regarding the reference case) would be based on CCS technology and would have a significant cost (on average, about 106.78 US\$/t CO₂). The high costs due to CCS technologies and the early-stage of the technological development suggested a careful position in the decision process. For instance, if it would be possible to postpone the investments in CCS, costs could be reduced due to the learning effects.

According to Johansson *et al.* (2012), estimates of CO_2 abatement costs vary significantly depending on the abatement options considered, on local particu-

larities, and on the assumptions made, such as discount rates and fossil fuel prices. Castelo Branco *et al.* (2011) have evaluated the abatement costs in Brazilian oil refineries, assuming two discount rates. The results show relatively high abatement costs, varying in the range of 20.2-77.3 US\$/tCO₂ for thermal energy management and in the range of 115.6-210.8 US\$/tCO₂ for fouling mitigation. In contrast, the study of Stenhufvud and Holmgren (2008) reported negative costs for a number of abatement measures in Swedish refineries. In the last case, the potential of carbon abatement due to replace fuel oil for natural gas or LPG is huge. The relative fuel prices determine the feasibility of the mitigation option (Castelo Branco *et al.*, 2011).

As previously mentioned, Kuramochi *et al.* (2012) compared the techno-economic performance of several CO_2 capture techniques for the oil refining sector. For instance, costs for post-combustion capture in the short-to-medium term were found to be above 137 US\$/t CO_2 . Oxyfuel capture, in contrast, may

Measure	Annual reduction potential	Annual reduction poten t ial	Nominal cost in 2020 (US\$/t CO ₂)
	•	(% of total emissions	· -/
M1. Improved heat integration	75	2.0	-180.96
M2. Operation improvement	10	0.3	-189.05
M3. Waste heat recovery	17	0.4	-189.95
M4. Hydrogen management	8	0.2	-192.48
M5. Energy optimization for utility systems	60	1.6	-200.94
M6. Onsite power generation	42	1.1	-87.29
M7. Substitution of fuel oil by natural gas	19	0.5	-164.16
M8. CCS with oxyfuel combustion capture (FCC units)	940	24.7	64.25
M9. CCS with post-combustion capture (hydrogen production)	680	17.9	162.17
Total	1851	48.7	

Table 7: Abatement costs for CO₂ emissions at Replan (year 2020).

Brazilian Journal of Chemical Engineering

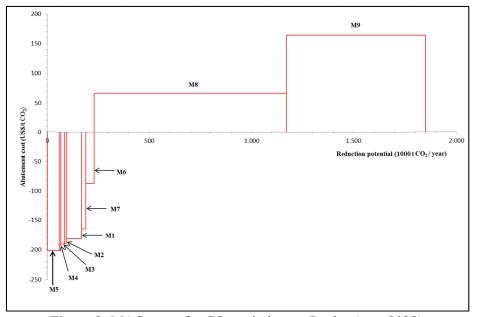


Figure 2: MAC curve for CO₂ emissions at Replan (year 2020).

provide relatively low costs, around 68-82 US\$/t CO_2 . These values are higher than those estimated for the capturing processes at Replan (130 US\$/t CO_2 and 51 US\$/t CO_2 , respectively), without transport and storage. But it is important to note that the capture costs are strongly affected by the price of the natural gas (in the post-combustion case) and the price of electricity (in the oxyfuel case).

SENSITIVITY ANALYSIS

A traditional sensitivity analysis was performed considering variations of $\pm 20\%$ in the following

parameters: energy saving, all energy prices, total investment of each technology, discount rate, lifetime and O&M cost.

For comparison the base case considered for each abatement cost is the nominal cost in 2020 (Table 7). The value ranges of the parameters are presented in Table 8. The analysis is divided into three categories: energy efficiency, fuel substitution and CCS.

In the category energy efficiency the two most representative projects were considered: (1) Improved heat integration (in order to evaluate the effect of the price of natural gas) and (2) Onsite power generation (in order to evaluate the effect of the price of electricity).

Parameter	Unit	Nominal value (base case)	Range used for sensitivity analysis (±20% nominal value)
Energy saving	GJ/h	157.31 (heat integration)	125.85 - 188.77
		30.27 (power generation)	24.22 - 36.32
Price of natural gas	US\$/MBtu	11.90	9.52 - 14.28
Price of fuel oil	US\$/ barrel	96.05	76.84 - 115.26
Price of electricity	US\$/MWh	54.95	43.96 - 65.94
Total investment (INV)	MUS\$	11.09 (heat integration)	8.87 - 13.31
		30.70 (power generation)	24.56 - 36.84
		257.56 (CCS/oxyfuel combustion)	206.05 - 309.07
		239.50 (CCS/post-combustion)	191.60 - 287.40
Discount rate	%	10	8-12
Lifetime	year	25	20 - 30
O&M cost	%INV	2.5 (heat integration)	2 - 3
		2.5 (power generation)	2 - 3
		4 (CCS/oxyfuel combustion)	3.2 - 4.8
		8 (CCS/post-combustion)	6.4 - 9.6

Table 8: Parameters considered for the sensitivity analysis.

Table 9 displays the main results of the sensitivity analysis. As an illustration, Figure 3 presents the impacts of the main parameters on the CO_2 abatement cost of the project related to CCS with oxyfuel combustion.

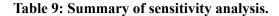
The lifetime and O&M cost have a small influence on the CO_2 abatement cost for the three considered categories (maximum variations in the range of $\pm 4\%$).

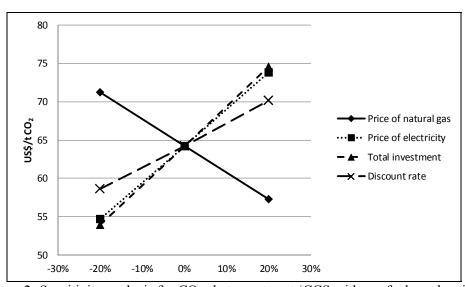
For the heat integration measure, the parameter that most impacts the abatement cost is the price of natural gas (range of $\pm 22\%$). In the case of power

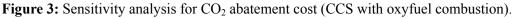
generation, the price of electricity causes the greatest impact on the abatement cost (range of $\pm 42\%$)

In the category of fuel substitution, the parameter that most impacts the abatement cost is the price of fuel oil (range of $\pm 79\%$), which is directly proportional to the price of crude oil. The price of natural gas also has a significant impact on the abatement cost (range of $\pm 59\%$). However, as the CO₂ reduction potential of fuel substitution is small, the direct impact of crude oil prices on the CO₂ abatement costs is not significant.

	Nominal value of	R	esults of Sens	sitivity Analys	sis
Measure/Parameter	abatement cost	(US\$/	t CO ₂)	% variation	
	(US\$/t CO ₂)	Minimum	Maximum	Minimum	Maximum
M1. Improved heat integration					
- Price of natural gas		-221.13	-140.79	-22.2	22.2
- Energy saving	-180.96	-184.29	-175.97	-1.8	2.8
- Total investment	-180.90	-184.96	-176.97	-2.2	2.2
- Discount rate		-183.40	-178.40	-1.3	1.4
M6. On site power generation					
- Price of electricity		-124.35	-50.24	-42.4	42.4
- Energy saving	-87.29	-103.62	-62.80	-18.7	28.1
- Total investment		-106.89	-67.70	-22.4	22.4
- Discount rate		-99.25	-74.73	-13.7	14.4
M7. Substitution of fuel oil by natural gas					
- Price of fuel oil	-164.16	-294.41	-33.91	-79.3	79.3
- Price of natural gas	-104.10	-261.57	-66.74	-59.3	59.3
M8. CCS with oxyfuel combustion capture					
- Total investment		53.96	74.54	-16.0	16.0
- Price of electricity	64.25	54.71	73.79	-14.8	14.9
- Price of natural gas	04.23	57.28	71.22	-10.9	10.9
- Discount rate		58.60	70.18	-8.8	9.2
M9. CCS with post-combustion capture					
- Total investment		145.43	178.92	-10.33	10.33
- Price of natural gas	162.17	146.11	178.24	-9.91	9.91
- Discount rate	102.17	154.91	169.80	-4.48	4.71
- Price of electricity		161.79	162.55	-0.24	0.24







Brazilian Journal of Chemical Engineering

In the case of CCS with oxyfuel combustion, the parameters that most impact the abatement cost are total investment and price of electricity (range of $\pm 15\%$). For CCS with post-combustion, the parameters that most impact the abatement cost are total investment and price of natural gas (range of $\pm 10\%$).

In summary, the parameters that most affect the abatement cost are the prices of energy, especially the price of natural gas. The price of fuel oil only has a direct influence in the case of fuel substitution, while the price of electricity influences the cases of power generation and CCS with oxyfuel combustion. Total investment and discount rate have a significant influence on the abatement cost (\pm 10% on average) only in cases of higher total investments, like the projects of power generation and CCS.

CONCLUSIONS

The results of the assessment show that continued energy efficiency improvements and fuel switching represent the most promising strategies for CO_2 emission reduction at Replan in the short-term. Most of the estimated abatement costs are negative, meaning that the measures are already cost-effective and could be implemented immediately.

Despite these options, the overall abatement potential is relatively low (6.1% of the total emissions). Although a number of energy efficiency projects were identified, the cumulative total emission reduction available through energy efficiency projects is relatively limited, since ongoing energy efficiency programs have identified and implemented nearly all opportunities.

In a long-term perspective, an additional reduction in on-site CO_2 emissions up to 42.6% could be achieved by implementing CCS technologies at Replan. The potential for CO_2 capture varies depending on the choice of capture technology (oxyfuel combustion or post-combustion) and targeted CO_2 emission source (for example, targeting only flue gases from regenerators of FCC units or targeting also flue gases from hydrogen production). Assuming that carbon capture will be implemented only in the largest sources (regenerators of FCC units), the potential for CO_2 emission reduction decreases to 24.7%.

Estimated abatement costs are very high for CCS technologies and, according to the results of sensitivity analysis, they are mostly impacted by total investment and energy prices (natural gas and electricity).

The high costs due to CCS technologies and the early-stage of the technological development suggest a careful position in the decision process, which involves the following aspects: • The definition of an optimum capture capacity at the refinery, considering gain of scale (which reduces cost) and additional piping and blower duties (which increase cost);

• The possibility to postpone the investments in CCS, resulting in reduced costs in the future due to the learning effects.

In a carbon-constrained scenario, considering the high carbon abatement costs associated with CCS projects (on average, about 107 US\$/t CO₂), private investors would certainly prefer to buy emission allowances of around 20 US\$/t CO₂, which is the 2020 price in the main carbon markets studied in the New Policies Scenario of World Energy Outlook 2013 (IEA, 2013a).

To overcome this huge difference in cost, public policies and regulatory frameworks should be deployed for promoting carbon mitigation measures in the Brazilian oil industry.

Since cost-effective and feasible options are limited for refineries, the availability of sufficient allowances and offsets is an important element if regulatory goals are to be achieved. In this way, carbon allowances could provide some synergy for the oil industry.

In the case of a Brazilian carbon-constrained scenario, an option is to consider a two-step CO_2 mitigation strategy to meet regulatory goals. CCS implementation could be postponed by a period after 2020 until the technology becomes economically viable. During this period emission allowances could be used by the refining industry.

ACKNOWLEDGEMENTS

The authors wish to thank the support and contributions of the staff of *Petróleo Brasileiro S.A.* (PETROBRAS) and the *Universidade Estadual de Campinas* (UNICAMP). This research was performed as part of a Ph.D. Thesis developed at the UNI-CAMP's Mechanical Engineering Faculty (Energy Planning Systems).

NOMENCLATURE

AC	Abatement cost of CO ₂ mitigation
	measures
ASU	Air Separation Unit
BFW	Boiler feed-water
bpd	Barrels per day
Ċ	Net annual cost of the abatement
	technology or of the technology used in
	the reference scenario

Cabatement	Net annual cost of the abatement
	technology
Creference	Net annual cost of the technology in the
	reference scenario
CCS	Carbon Capture and Storage
CO_2e	Carbon dioxide equivalent
CR	Catalytic Reforming
CVD	Crude and Vacuum Distillation
DC	Delayed Coking
DHT	Distillate Hydrotreating
Eabatement	Annual CO ₂ emission with the abatement
	technology
E ^{reference}	Annual CO ₂ emission with the technology
	in the reference scenario
EII	Energy Intensity Index
FC	Annual fuel cost of the abatement
	technology or of the technology used in
	the reference scenario
FCC	Fluid Catalytic Cracking
GHG	Greenhouse Gases
HG	Hydrogen Generating
INV	Total investment of the abatement
	technology or of the technology used in
	the reference scenario
MAC	Marginal Abatement Cost
MBtu	Million British thermal units
Mt	Million tonnes
MUS\$	Million dollars
O&M	Operation and Maintenance
OMC	Annual operations and maintenance cost
	of the abatement technology or of the
	technology used in the reference scenario
r	Discount rate
REV	Annual revenue generated by the
	abatement technology or by the
	technology used in the reference scenario
t	Lifetime of the technology

REFERENCES

- AES Eletropaulo, Tarifa de energia elétrica. AES Eletropaulo, São Paulo (2014). Available at: https://www.aeseletropaulo.com.br/poder-publico/prazose-tarifas/conteudo/tarifa-de-energia-eletrica. (Accessed: August 12, 2014). (In Portuguese).
- Brasil, Ministério de Minas e Energia, Empresa de Pesquisa Energética, Plano Decenal de Expansão de Energia 2022. MME/EPE, Brasília (2013). (In Portuguese).
- Brasil, Ministério da Ciência, Tecnologia e Inovação, Fatores de Emissão de CO₂ pela geração de energia elétrica no Sistema Interligado Nacional do Brasil. MCTI, Brasília (2014). Available at:

<http://www.mct.gov.br/index.php/content/view/7 2764.html>. (Accessed: August 11, 2014). (In Portuguese).

- Brown S. M., The drive for refinery energy efficiency. Petroleum Technology Quarterly Refining, Autumn, 45-55 (1999).
- Bulasara, V. K., Uppaluri, R. and Ghoshal, A. K., Revamp study of crude distillation unit heat exchanger network: Energy integration potential of delayed coking unit free hot streams. Applied Thermal Engineering, 29, 2271-2279 (2009).
- Castelo Branco, D. A., Szklo, A., Gomes, G., Borba,
 B. S. M. C. and Schaeffer, R., Abatement costs of CO₂ emission in the Brazilian oil refining sector.
 Applied Energy, 88, (11), 3782-3790 (2011).
- Chan, W. N., Quantificação e redução de emissões de gases de efeito estufa em uma refinaria de petróleo. Master Thesis, Universidade Estadual de Campinas (2006). (In Portuguese).
- CONCAWE, Impact of product quality and demand evolution on EU refineries at the 2020 horizon.
 CO₂ emission trend and mitigation options. Report No. 8/08. CONCAWE, Brussels, (2008).
 Available at: http://www.concawe.be/content/default.asp?
 PageID=577>. (Accessed: August 11, 2014).
- CONCAWE, The potential for application of CO₂ capture and storage in EU oil refineries. Report No. 7/11. CONCAWE, Brussels, (2011). https://www.concawe.eu/content/default.asp?PageID=56 9>. (Accessed: June 11, 2014).
- Corrêa, E. C., Energy Performance Management in PETROBRAS Refineries. In: V Latin American Carbon Forum, Santo Domingo, Dominican Republic (2010).
- Elkamel, A., Ba-Shammakh, M., Douglas, P. and Croiset, E., An Optimization approach for integrating planning and CO₂ emission reduction in the petroleum refining industry. Ind. Eng. Chem. Res., 47(3), 760-776 (2008).
- FIESP, Federação das Indústrias do Estado de São Paulo, Especialistas defendem gás natural a preço justo durante 14º Encontro Internacional de Energia da Fiesp. FIESP, São Paulo (2014). Available at: http://www.fiesp.com.br/noticias/especialistasdefendem-gas-natural-a-preco-justo-durante-14oencontro-internacional-de-energia-da-fiesp/. (Accessed: June 4, 2014). (In Portuguese).
- Freund, P., Chapter 1, Introduction, Carbon Dioxide Capture and Storage. Intergovernmental Panel on Climate Change. Cambridge University Press, New York, (2005).
- Gale, J., Chapter 2, Sources of CO₂. Carbon Dioxide Capture and Storage. Intergovernmental Panel on

Climate Change. Cambridge University Press, New York, (2005).

- Gary, J. H., Handwerk, G. E., Kaiser, M. J., Petroleum Refining: Technology and Economics. Fifth Edition, CRC Press, Boca Raton (2007).
- Global CCS Institute, Projects. Global CCS Institute, Docklands (2014). Available at: http://www.globalccsinstitute.com/projects/browse. (Accessed: August 22, 2014).
- Gouvello, C., Soares Filho, B. S., Schaeffer, R., Alves, F. J., Alves, J. W. S., Brazil Low-Carbon: Country Case Study. The World Bank, Washington DC (2010).
- Holmgren, K. and Sternhufvud, C., CO₂-emission reduction costs for petroleum refineries in Sweden. Journal of Cleaner Product, 16(3), 385-394 (2008).
- Hydrocarbon Publishing Company, Refinery CO₂ Management Strategies. Hydrocarbon Publishing Company, Southeastern (2010).
- IEA, International Energy Agency, World Energy Outlook 2013. OECD/IEA, Paris, (2013a).
- IEA, International Energy Agency, Technology Roadmap: Carbon capture and storage 2013. OECD/IEA, Paris (2013b). Available at: http://www.iea.org/publications/freepublications/publications/freepublications/publication/technology-roadmap-carbon-capture-and-storage-2013.html>. (Accessed: August 3, 2014.)
- Interministerial Committee on Climate Change, National plan on climate change. Government of Brazil, Brasília (2008). Available at: http://www.mma.gov.br/estruturas/208/_arquivos/nation al plan 208.pdf>. (Accessed: June 29, 2014).
- IPCC, Intergovernmental Panel on Climate Change, Climate Change 2007: Synthesis Report. IPCC, Geneva (2007).
- Johansson, D., Rootzén, J., Berntsson, T. and Johnsson, F., Assessment of strategies for CO₂ abatement in the European petroleum refining industry. Energy, 42, 375-386 (2012).
- Johansson, D., System studies of different CO₂ mitigation options in the oil refining industry: Postcombustion CO₂ capture and biomass gasification. Ph.D. Thesis, Chalmers University of Technology (2013).
- Joly, M., Refinery production planning and scheduling: The refining core business. Brazilian Journal of Chemical Engineering, 29(2), 371-384 (2012).
- Kesicki, F., Marginal abatement cost curves for policy making – expert-based vs. model-derived curves. UCL Energy Institute, London (2011). Available at: http://www.homepages.ucl.ac.uk/ ~ucft347/Kesicki_MACC.pdf>. (Accessed: July 08, 2014).

- Kuramochi, T., Ramírez, A., Turkenburg, W. and Faaij, A., Comparative assessment of CO₂ capture technologies for carbon-intensive industrial processes. Progress in Energy and Combustion Science, 38(1), 87-112 (2012).
- MacLean, J. P., Bittensky, J. S., Colvert, J. H., Process for improving power recovery from regeneration gas under turndown conditions. United States Patent No. 4, 539, 303 (1985).
- Melien, T., Economic and Cost Analysis for CO₂ Capture Costs in the CO₂ Capture Project Scenarios. Carbon Dioxide Capture for Storage in Deep Geologic Formations. Chapter 3, Elsevier Science, Amsterdam (2005).
- Mello, L. F., Pimenta, R. D. M., Moure, G. T., Pravia, O. R. C., Gearhart, L., Milios, P. B., Melien, T., A technical and economical evaluation of CO₂ capture from FCC units. Energy Procedia, 1, 117-124 (2009).
- Nordrum, S., Lieberman, D., Colombo, M., Gorski A. and Webb, C., Assessment of greenhouse gas mitigation options and costs for California petroleum industry facilities: The shape of things to come. Energy Procedia, 4, 5729-5737 (2011).
- Petrick, M. and Pellegrino, J., The potential for reducing energy consumption in the refining industry. Report No. ANL/ESD/TM-158. Argonne National Laboratory, Lemont (1999).
- PETROBRAS, Petróleo Brasileiro S.A., Sustainability report 2013. PETROBRAS, Rio de Janeiro (2014a). Available at: http://www.petrobras.com.br/en/society-and-environment/sustainability-report/. (Accessed: June 27, 2014).
- PETROBRAS, Petróleo Brasileiro S.A., Replan Refinery Energy Study. Technical Report, PETRO-BRAS, Paulínia (2014b).
- Plesu, V., Bumbac, G., Iancu, P., Ivanescu, I. and Popescu, D. C., Thermal coupling between crude distillation and delayed coking units. Applied Thermal Engineering, 23, 1857-1869 (2003).
- Proops, K. R., EII Analysis Methodology: Gap Analysis vs World's Best EII. HSB Solomon Associates LLC, Dallas (2010). Available at: http://solomononline.com/documents/Whitepapers/EII_AM_WWW.pdf>. (Accessed: September 12, 2013).
- Reddy, S., Vyas, S., Recovery of carbon dioxide and hydrogen from PSA tail gas. Energy Procedia, 1(1), 149-154 (2009).
- Rootzén, J., Kjärstad, J. and Johnsson, F., Prospects for CO₂ capture in European industry. Management of Environmental Quality, 22(1), 18-32 (2011).
- Saggese, D., Integrated Assessment of CO₂ Emissions in European and Brazilian Oil Refining. IFP Energies Nouvelles, Paris (2012).

- São Paulo, Política Estadual de Mudanças Climáticas. LEI Nº 13.798, de 9 de novembro de 2009. Diário Oficial do Estado de São Paulo, 119(209), 1-20 (2009). (In Portuguese).
- Simmonds, M., Hurst, P., Wilkinson, M. B., Watt, C. and Roberts, C. A., A study of very large scale post combustion CO₂ capture at a refining & petrochemical complex. Greenhouse Gas Control Technologies, 1, 39-45 (2003).
- Statoil, CO₂ Masterplan Mongstad (English Summary). Statoil, Stavanger (2009). Available at: http://www.statoil.com/no/newsandmedia/news/2009/downloads/masterplan%20mongstad%20english%20summary.pdf>. (Accessed: August 22, 2014).
- Straelen, J., Geuzebroek, F., Goodchild, N., Protopapas, G., Mahony, L., CO₂ capture for refineries, a practical approach. International Journal of Greenhouse Gas Control, 4, 316-320 (2010).
- Szklo, A. S., Schaeffer, R., Fuel specification, energy consumption and CO₂ emission in oil refineries. Energy, 32(7), 1075-1092 (2007).
- Valino, C. M., Irizar, I. C., Bascones, A. A., Heins, A., Toccaceli, S., Improving crude unit heat integration. Petroleum Technology Quarterly, 13(2), 107-111 (2008).
- Worrell, E., Galitsky, C., Energy Efficiency Improvement and Cost Saving Opportunities for Petroleum Refineries. Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley (2005).