Comparison of carbon balance measuring tools in an enhanced oil recovery project based on the carbon dioxide from the ammonia production process streams

Miguel Angel Morales Mora¹, Froebel Carlos Pretelín Vergara C.², Sergio Alejandro Martínez Delgadillo³ and Miguel Antonio Leiva⁴

Abstract

A number of studies addressing the environmental impact of deploying carbon capture utilization and storage are focused on sources of CO₂ in the power sector. However, there is a lack of environmental studies on the use of CO₂ from process stream within the oil and gas industries. The carbon balance of an enhanced oil recovery project for the specific case of using CO₂ process stream of ammonia production from emission factors and regional databases in the Mexican oil and gas sector was assessed. Two independent tools to assess life cycle assessment according to guidelines ISO 14040/14044 were utilized: (i) use of Umberto software to quantify the environmental impact with ReCiPe model midpoint; and, (ii) The American Petroleum Institute method through the use of emissions factor for each source and emission gas of the activity/facility in a spread sheet. The results of the tools were compared and the dissimilarities analysed. The emissions profiles from all direct and indirect activities associated with the enhanced oil recovery system were compared with a “cradle-to-grave” model. The functional unit is one barrel of crude oil extracted and consumed. Global warming as the environmental indicator of both tools was used. Additionally, the energy balance of the project was estimated. The global warming impact of the enhanced oil recovery system was 0.51 tCO_{2e}/barrel (bbl) using the American Petroleum Institute tool, whilst the emissions using Umberto software were 0.54 tCO_{2e}/bbl. Also, for each MJ of energy produced a value of 72 tCO_{2e}/MJ oil and of 66 tCO_{2e}/MJ oil, were obtained. This study demonstrates that both tools delivered an accurate estimation of the greenhouse gas emissions in the enhanced oil recovery system for the oil and gas industries. However, American Petroleum Institute has the advantage that the calculations can be performed ‘manually’ in a spread sheet using emissions factor adjusted to the facilities and Country. Regarding the results of both tools, this work shows that American Petroleum Institute results have proven to be an efficient tool for practitioners and researchers that intend to analyse the greenhouse gas emission of carbon capture utilization and storage systems to estimate, with accuracy, the global warming impact.

Key words: Ammonia production, cradle to grave model, carbon balance, global warming impact

1. Introduction

The number of studies addressing the environmental impact of deploying carbon capture and utilization (CCU) and/or carbon capture and storage (CCS) is rather limited and focuses on sources of CO₂ from the power sector (Corten et al., 2013). Moreover, CCS from industrial applications has so far received little attention, despite International Energy Agency-United Nations Industrial Development Organization, IEA-UNIDO (2011) highlighting that CO₂ emissions should be reduced up to 4.0 gigatonnes (Gt) annually by 2050. The CCS studies suggest that the global warming (GW) resulting from power plants needs to be reduced (Leung et al., 2014).

Many studies marginally discuss different aspects (Cuellar-Franca and Azapagic, 2015) when assessing the environmental performance of power plants with CCS and CCU, despite the difficulty in directly comparing the relative importance of upstream (e.g. coal mining, coal transport, monoethanolamine production), as mentioned by Corsten et al. (2013), and downstream emissions (e.g. CO₂ capture). This emphasises the need for optimal designs in all the value chains. Nevertheless, as the available recent literature aiming to address the life cycle assessment (LCA) of CCS focuses on different technologies, as well as system boundaries; database sources, transparency in the data reported and specific assumptions are not clearly evident in the studies. This makes it even more difficult to draw robust conclusions on the potential environmental impact of CCS and CCU. Marx et al. (2011) gave a synthesis report about LCA-CCS evaluations, in which some shortcomings in the studies' underlying assumptions and methodologies were found. Petrakopoulou and Tsatsaronis (2014) established that the principal aim of CCUS technology is how their environmental impact can be reduced and energy efficiency maximized. Consequently, a valuable way to assess the LCA of enhanced oil recovery operations is to review the carbon emissions profile for the whole operation, and compare this with projects of CO₂ storage profile.

This subject is important since frequently the LCA practitioner will not find one obvious choice among a number of different databases or calculation methods, and the question, therefore naturally arises: "Does my choice of method or database have any influence on the conclusions?". Based on simulation results and process configuration of the CCS system, the LCA method has been applied to evaluate the environmental impact of the system taking into account the complete life cycle from raw material to CO₂ injection or refinery product combustion from commercial software (von der Assen, et al., 2014). In addition, the life cycle inventory (LCI) calculations could involve either the whole system boundary or not, and include different raw materials (coal and natural gas) or only main stages of the LCA, i.e. a gross inventory, without going into the details of each stage from extraction of raw material to use. Therefore, system boundary or expanded system boundaries and their stages are neither clearly specified nor detailed, generating different results of net emission per barrel of oil in the enhanced oil recovery (EOR) system (Cuellar-Franca and Azapagic, 2015). Specific to the oil and gas industries, there is a lack of direct measurements, or offshore/onshore monitoring of emission gases is rare, and so for most sources only the activity data, such as fuel consumption or the rate of a process activity are available. When direct measurement systems are not in place, the calculation of emissions can be made from an activity factor (Stewart and Haszeldine, 2014).

The most commonly practiced CCS approach, in terms of CO₂ sequestered, is CO₂-enhanced oil recovery (CO₂-EOR). The CO₂ injection from natural sources for EOR has been applied commercially since the early 1970s in the United States for oil recovery, typically in no longer productive mature fields. However, today EOR operations are carried out with the aim of maximizing oil output with the minimum CO₂ injection (International Energy Agency, EIA, 2015).

According to Leach et al. (2011), approximately 30-40% of the CO₂ injected during a single injection usually remains trapped in the reservoir. This value is similar to that reported in the first CO₂-EOR case study in Mexico performed at the Artesa reservoir in the Chiapas and Tabasco states, where 40% of CO₂ injected was stored (Leon-Garcia et al. 2015).

As with any secondary recovery methods, additional energy is consumed in the CO₂ capture, resulting in a higher environmental impact per MWh than without CO₂ capture (Petrakopoulou and Tsatsaronis, 2014). The production of additional oil will be CO₂-EOR that, when combusted will generate additional CO₂ emissions (Jaramillo et al. 2009). Along with this, there is a discussion as to whether these technologies can provide products that sequester the CO₂ for a long or short period (Electric Power Research Institute, EPRI, 2013), how much CO₂ is really sequestered by each technology, and if CCS should be considered as a mitigation technology (Armstrong and Styring, 2015). Thus, climate change mitigation and long-term CO₂ storage goals are not principal drivers for EOR projects (IEA, 2015). EOR also sequesters CO₂ in the process with potential climate benefits. An important portion of the injected CO₂ remains in place, a technology that has been proved in USA (Dai et al., 2014a) and Canada with the world's first commercial scale post-combustion coal fired carbon capture and storage in the Saskatchewan Project (Stéphanne, 2014). All studies show a substantial reduction of greenhouse gas (GHG) emissions from power production, in the order of 40-97% (Corsten et al., 2013). According to Cuellar-Franca and Azapagic (2015), the reduction in the global warming potential (GWP) is sensitive to CO₂ capture and allocation methods as well as the assumptions for heat recovery from the system.

IEA-UNIDO (2011) published a Technology Roadmap CCS in industrial applications providing an outlook of industrial CCS up to 2050, where high-purity CO₂ sources like ethylene oxide and ammonia production were included in this roadmap.

The 2014 global status of CSS projects states that four projects are in operation from CO₂ fertilizer plants: three for EOR and one as geological storage, with a contribution of 4.5–5.1 MtCO₂/year (Global CCS Institute, 2015). These values represent a marginal fraction of the total anthropogenic emission (32,000 Mt CO₂/y) by this sector (Armstrong and Styring, 2015). In 2014, the start up operation of the commercial North Burbank Unit (NBU), in Kansas-Oklahoma USA, CCU and the CCS (EOR) from a fertilizer-urea plant (National Energy Technology Laboratory, NETL, 2015) were included.

The United States Environmental Protection Agency (USEPA) lists 22 ammonia manufacturers in the United States. Eighteen of these are capturing CO₂ as a by-product and selling it as an industrial product to the market (USEPA, 2015). NETL (2013a) published a report on alternative sources of CO₂, documenting a cradle-to-gate footprint per unit of CO₂ produced from ammonia production. This study has not found cradle-to-grave life cycle results published on EOR production from CO₂ by ammonia plants. There are not many references in the literature describing the use of LCA-CCS studies in petrochemical processes or the oil refinery (Nagashima et al., 2011).

Consequently, this work was motivated by the need within the oil and gas sectors, to analyse and compare the results of other methodological models, to identify environmental “hot spots” in the LCI calculations of the CCUS-LCA studies. This study might therefore suggest potential improvement actions to enable a reduction in the environmental impact of the upstream and downstream processes of the oil and gas industries, as well as to assist LCA practitioners to compare the results when they use the CCUS system using regional or local databases.

1.1. Overview of CCUS in Mexico

The Mexican Government recently published the CCUS Technology Roadmap recognizing the need for CCS to aid in reaching the CO₂ reduction goal in view of the fast growth in electricity demand in the country (Energy Secretariat, SENER, 2014). According to this study, it is estimated that Mexico has a theoretical capacity for storing 100 Gt of CO₂. If it were considered that the CO₂ annual emissions in Mexico in 2012 represented an equivalent of 0.74 Gt, then the maximum storage capacity in the country would be reached in 135 years.

A recent update of the 2013 GHG inventory showed that emissions from the oil and gas sectors in Mexico accounted for 12% of total GHG emissions at the national level, i.e. 80,455 Gt CO₂e/y (Secretariat of Environment and Natural Resources-National Institute of Ecology and Climate Change, SEMARNAT-INECC, 2016). Of this, 20% is generated in the states of Veracruz and Tabasco, where mature fields are located and would require large amounts of CO₂ for EOR. For instance, it is estimated that the bigger Mexican oil fields candidates for EOR would need up to 50 million metric tons of CO₂ per year in the Gulf of Mexico (Lacy et al., 2012). Petróleos Mexicanos (PEMEX) Sustainability Report, (2014), affirms that 14.7 million metric tons CO₂/year were emitted from fuel combustions, 1.4 million metric tons CO₂/year were produced by venting gas from three ammonia plants' processes, and 0.9 million metric tons CO₂/year from one hydrogen plant in the Southeast of Mexico (Southeast of the states of Veracruz and Tabasco) (Figure 1).

Specifically, the Cinco Presidentes Oil asset (CPOA) with a 0.085 million barrel (bbl) a day production of domestic oil (20-35°API) (PEMEX, 2015) has been classified as an inclusion zone (D) for the geologic storage of CO₂ (Dávila et al., 2010). In the case of employing CO₂ for EOR, the ammonia plant from Cosoleacaque Petrochemical Complex (CPC) has the advantage of being located only 50-70 km from the CPOA. It is the closest CO₂ source for implementing the technology of EOR in Mexico, with a total 2P volume (Proven and probable reserves) of 249.9 billion barrels of oil reserves, with 565 wells in operation (National Hydrocarbons Commission, CNH, 2016).

INSERT FIGURE 1 HERE

The Brillante oil field is a young field, having been in operation for three years, located within the CPOA (Table 1) with a production of less than 3,000 bbl/d of 35°API (Arteaga-Cardona et al., 2015).

INSERT TABLE 1 HERE

1.2. CO₂ source: Ammonia process from CPC

Ammonia production depends on natural gas (NG) both as a feedstock and as a fuel. Haas and van Dijk (2010) estimated the average energy consumption for ammonia (NH₃) production in Europe to be around 34.7 GJ/t with 1.5 tons of CO₂/t of ammonia emitted to the atmosphere during production. Williams and Al-Ansari (2007) determined a global average energy consumption of 36.9×10^3 MJ/t. Makhoul et al. (2015) estimated a Cumulative Energy Requirement (CER) of 51.945×10^3 MJ/t of ammonia and 1.44 t CO_{2eq}/t of ammonia for an ammonia plant taking into account the CO₂ in the flue gas in Algeria.

In Mexico, the NG comes from an offshore platform located in the Southeast of the Gulf of Mexico at 500 km distance from the CPC. For synthetic ammonia production there are six principal process steps from NG feedstock (Figure 2). The primary reforming step converts methane (CH₄) to CO₂, carbon monoxide (CO), and hydrogen (H₂) in the presence of a catalyst. Only 30 to 40 per cent of the CH₄ feedstock to the primary reformer is converted to CO and CO₂ in this step of the process. The secondary reforming step converts the remaining CH₄ feedstock to CO and CO₂. The CO from the secondary reforming step (representing approximately 15 per cent of the process gas) is converted to CO₂ in the presence of a catalyst, water, and air in the shift conversion step. CO₂ is removed from the process gas by the shift conversion process; the hydrogen is combined with the nitrogen (N₂) gas in the process gas during the ammonia synthesis step to produce ammonia. The CO₂ is incorporated to a waste gas stream with other process impurities and absorbed by a scrubber solution (Overcash et al., 2007).

The CO₂ emissions from four ammonia plants (AP) of the CPC, producing 480,000 tNH₃/y and 497,000 tCO₂/y as by-product with 98% purity, were considered as supply for the EOR project in this study. Currently, the CO₂ produced is employed to produce urea and for the beverage industry. Of the remainder currently emitted into the atmosphere (Figure 2), PEMEX plans to use 834 t/d of this CO₂ for EOR in the Brillante field (Arteaga-Cardona et al., 2015).

INSERT FIGURE 2 HERE

A considerably lower energy is required to separate and capture the CO₂ from ammonia production. For instance, AP from CPC is 1.35 MJ/kgCO₂, which is lower than in the power sector (2.8 to 4.2 MJ/kgCO₂) CO₂ capture technologies (Luis, 2015). The CO₂ is removed in a tower with several beds through absorption (pre-combustion) employing 30% solutions of potassium carbonate (K₂CO₃), using heat integration in their facilities. The AP from CPC has an emission factor of 1.4 metric tons CO₂/metric ton NH₃. Therefore, the use of CO₂ that is currently vent into the atmosphere by the ammonia plant and close to mature oil fields as the CPOA, could substantially improve the environmental profile of the plant and energy of the EOR project.

2. Materials and methods

The CCUS technology was considered here as an end-of-life process, so that it can be integrated to any industrial plant that is an anthropogenic source of CO₂. Therefore, the product category was defined either as a system of technologies that integrate the CO₂-EOR project's three stages: carbon dioxide (CO₂) capture (pre-combustion), transport (CO₂) and

storage (oil and gas reservoirs) or as utilization (EOR) services (Strazza et al., 2013), using process streams from the AP as a source of CO₂.

2.1 Objective and scope of study

The objective of this study was to assess the impact of GHG emissions and energy balance of the Brillante CO₂-EOR project, located in the CPOA in the southeast of Mexico, using CO₂ process streams from ammonia production, and to compare the single environmental impact: resulting global warming (GW) contrast. Two independent tools to assess life cycle analysis (LCA) according to ISO 14040/14044 guidelines were compared: Umberto software (US) versus American Petroleum Institute (API) calculations through a spreadsheet, with EF adjusted to Mexico. Additionally, to identify environmental hotspots and to suggest potential improvement actions that would reduce the environmental impact of the CCUS system.

The study considered the stages from the extraction of natural gas as feedstock for producing ammonia, to the combustion of the refined petroleum. The studied system operates at six subsystems involving different industrial sites, separated by nearly 500 km which requires the transport of gas and oil by pipeline (Figure 3).

INSERT FIGURE 3 HERE

2.1.1 System boundary

To facilitate the identification of impact sources, the system was divided into six subsystems: (i) gas extraction, (ii) gas processing (iii) ammonia production, (iv) EOR operation, (v) refining process and (vi) refinery product's combustion (Table 2). Figure 4 shows the system boundary for the whole Brillante CO₂-EOR system. The GHG emissions associated with the life cycle of the project include the emissions from the offshore based oil producing platform (Cantarell), located in the southeast marine region in the Gulf of Mexico, to the Refinery product's combustion (e.g. gasoline) i.e. "cradle-to-grave" model (Figure 4). Material and energy flow network of process system is shown in Supporting Information (SI) Figure SI-1.

INSERT TABLE 2 HERE

Expanded system boundary and displacement was used to sum the GHG emissions for both methodologies according to table 2 and figure 4, and also for the ammonia product and CO₂ as by-product generated in accordance with ISO standards 14040-14044 (ISO, 2006 a, b).

INSERT FIGURE 4 HERE

The boundaries excluded transport of refined petroleum products from the refinery to the consumer, since emissions from transporting these products represent less than 1% of the lifecycle emissions, Wang et al. (2008). In addition, this study also omits the associated

emissions for the infrastructure necessary for the construction of the CO₂-EOR because Brillante field already exists.

2.1.2 Functional unit (FU)

Considering that the purpose of the Brillante CO₂-EOR project is to capture CO₂ and employ it in the oil recovery process, for both methodologies, the FU was defined as one barrel of crude oil extracted and consumed.

2.2 Life cycle inventory (LCI)

In order to build and compare the LCIs with both tools, this study was conducted in accordance with ISO standards for LCA ISO 14040 and ISO 14044 (ISO, 2006 a, b).

The LCI includes direct (combustion) and indirect emissions, fugitive emissions (leaks in facilities and pipeline, oil and gas fields) and venting processes; i.e. the direct activities related to exploration, production, gas processing, transportation, distribution and refining by the oil and gas industries (Table 2).

The inventory data were collected from the PEMEX 2015 database to obtain the GHG emissions from assets over which PEMEX has 100% operational control. The characterization of GHG emissions of each stage/activity was made with an up-bottom approach. The uncertainty of the data from upstream and downstream operations to build LCI was evaluated. The data have a confidence interval of 95%. The stage of the direct emissions (combustion and indirect) corresponds to the estimated for the manufacturing processes from PEMEX data. The non-combustion emissions (gas transmission pipeline and CO₂ transport, pipeline leaks, process vents) were estimated according to the EF established by American Petroleum Institute, API (2009), as well as the API SPEC 5L: Specification for Line Pipe, for the emission factor of the CO₂ transport (API, 2011). It was considered necessary to remove 1,355 Nm³/day of natural gas for each ton of NH₃ in the CPC, which is equivalent to 0.0077 % of the total NG production at Cantarell, to establish the amount of natural gas to be subtracted from the offshore platform Cantarell for the CP CO₂-EOR project. Finally, it was necessary to do the correction for the actual composition of methane in the handled gas, and therefore CO₂ emissions were calculated by the ratio of methane (CH₄) to CO₂ in the gas produced. Table 3 shows the key input parameters utilized in the model of the CO₂-EOR project.

INSERT TABLE 3 HERE

2.2.1 Establishment and guide calculation:

a) API

The LCI emissions were calculated according to Table SI-1 (Supporting Information) and reported in CO₂-equivalent (CO_{2e}) units. Section 3-technical considerations of the Compendium of GHG methodologies for the oil and natural gas industry (Americam PI, 2009) were used to obtain the results of the GW. The calculation of emissions where direct

monitoring results are not available involves the use of an activity factor, such as fuel consumption or flow to flare/vent, and an emission factor for each source (s) and emission gas (i). By multiplying the activity factor (AF) by the emission factor (EF), the masses of emission gas can be calculated. Equation 1 results from applying Table SI-1 to obtain the GHG inventory of the six subsystems, i.e. the sum of all the emissions for a particular facility used:

$$M(i,s) = EF(i,s) \bullet AF(s) \quad \text{Equation (1)}$$

Where:

$M(i,s)$ = is the emitted mass of a particular emission gas (i) for a given source (s); $EF(i,s)$ = is the emission factor for the emission gas (i) relevant to the emission source (s); $AF(s)$ is the source (s) activity factor.

To calculate CO_{2e} , equation 2 was used and incorporated in Table SP-1.

$$CO_{2e} \text{ tonnes} = \sum_{i=1}^{\# \text{ Greenhouse Gas Species}} (\text{tonnes}_i \bullet GWP_i) \quad \text{Equation (2)}$$

Where:

CO_{2e} = carbon dioxide equivalent emissions (ton); tonnes_i = GHG emissions of pollutant i (tonnes); and GWP_i = global warming potential of pollutant i . (i.e. CO_2 , (1), CH_4 (25), N_2O (298)) (tonnes CO_{2e} per ton i).

An emission factor (default and calculated from tables of API or another source) represents an average emission rate for a given source, and is generally expressed as a mass or volume of emissions per source type or measure of activity related to the source.

As shown in Table SI-1, step 1 consists of making a list of number of facilities and type of activity GHG emissions (columns a and b), step 2 add the EF (column c) for type of activity and step 3 multiply and add up to the total emissions as CO_{2e} (column i).

b) Umberto software (US)

In the construction of LCI for US, the next step was to adjust the input/output material and then process the six subsystems in Umberto according to the EF of Table 3, as well as the composition and amount of natural gas, to estimate GHG emissions as CO_{2e} for the CO_2 -EOR project.

2.2.2 Displacement and allocation of coproduct management

Systems operations produce ammonia and CO_2 , in addition to petroleum as by-products. Thus system boundary expansions and displacements were used to allocate lifecycle GHG emissions between petroleum and ammonia (ISO, 2006b).

Given the process characteristics, in which the NG functions as feedstock and fuel, the proportion of mass for each activity was used as a method of assignment, with the aim of reflecting the value of the ammonia product and the CO_2 as subproduct. Since the production of 1 ton of ammonia requires 1,355 NM^3 of NG consumption (Feedstock + fuel), generating CO_2 as a by-product (Table 4), the amount of feedstock consumed in the

process was calculated ($749 \text{ NM}^3/\text{tNH}_3$). This value was used to determine the total amount of ammonia displaced by the system, representing the emissions credits (Figure 4).

INSERT TABLE 4 HERE

Therefore, an allocation factor of 55.2% was subtracted or considered as emissions avoided and used for displacement.

Negative emissions (credits) associated with geological sequestration of CO_2 during EOR were calculated based on storage factor reported by Hussaint et al. (2013) and corresponding to about $0.20 \text{ tCO}_2\text{e}/\text{bbl}$.

2.3. Impact assessment of API and US

The life cycle of GHG emissions was quantified using “global warming” (GW), expressed in emissions of CO_2 equivalent (CO_2e) as the environmental indicator. The life cycle is considered as the established FU for both API and US.

The mandatory and optional elements of the LCA according to ISO 14040 were used in both methodologies. The time horizon resulting from the use of primary and secondary energy from fossil fuels: (1) time horizon characterization (for calculating GWPs) and (2) time period of assessment (the period over which GHG emissions and removals from a product system) was considered (Levasseur, 2015). The main impact category analysed in this study was GW expressed in emissions of equivalent CO_2 (CO_2e) and referred to the established FU: one barrel of crude oil extracted and consumed for both tools.

API. Analytically, with the application of equations 1 and 2 in Table SI-1, the CO_2 and methane (CH_4) emissions were calculated and reported as CO_2e (see first column to the right) using 100-year GWP (Intergovernmental Panel Climate Change, IPCC, 2007) as well as for that established by API (2009) and the Project’s nine year lifetime (CCS phase) (Arteaga-Cardona et al., 2015). This time period was adopted for both tools given that CO_2 is the main contributing pollutant. It is important to manage the risk of CO_2 migration through monitoring, verifying and reporting (Bandza and Vajjhala, 2014), given the CO_2 stored by the CO_2 -EOR operation. Lastly, the aim is to confirm that combining CO_2 -EOR with storage integrity is a promising strategy for GHG reduction.

US. The environmental impacts were quantified by LCA applying Umberto Universal 5.3 software based on the ReCiPe methodology (Goedkoop et al., 2009) and Ecoinvent 2.2 database of material in Umberto. The model of ReCiPe used for this CO_2 -EOR system included the application of life-cycle of fossil fuel GHG emissions, involving six subsystems. In this sense, LCA studies have already been employed for the assessment of the CCS technology, which have used ReCiPe Method with Umberto software (Xiao et al., 2013), and Volkart et al. (2013) with SimaPro v7.3.3 software.

Finally, lifecycle GHG emissions and inputs/outputs for CO_2 -EOR as metric tons of CO_2 equivalent emissions per barrel of crude oil extracted ($\text{tCO}_2\text{e}/\text{bbl}$) for both tools in each process step, as well as net GHG emissions, are presented to ensure net emission reduction and allow the addressees to evaluate directly a set of relevant inventory data for capture and storage (EOR/CCS) activities, together with a measure of the performance of the whole process.

3. Results and discussion

3.1 Life Cycle GHG CO₂-EOR project

Table 5 shows the results of the net GHG emissions for each of the six subsystems and the sixteen steps, along with assessment of results between both tools in CO₂-EOR. For each process step, the values are reported as metric tons of CO_{2e} per barrel of oil extracted (tCO_{2e}/bbl). The total emissions represent the carbon footprint (i.e. GW) for the whole chain.

INSERT TABLE 5 HERE

The GW impact estimated by the API together with the life cycle analysed was 0.88 tCO_{2e}/bbl, only 2.0 % higher than US (0.85 tCO_{2e}/bbl). These results do not consider displacement and allocation of emissions. No significant differences between both tools by subsystems or stages were found.

In subsystem III, representing the production of ammonia and transport of CO₂ to the Brillante CO₂-EOR project, the average estimation of GW was of 0.266 tCO_{2e}/bbl, with a contribution of 30.8% of the total emissions (Table 5). These emissions would be generated by ammonia production, compression (electricity), transport and fugitive emission of the total GHG emissions. Subsystems II and V, the operation units, provided the lower emissions. The upstream emissions from the NG extraction on the offshore platform in Cantarell to NG processing were 4.4 %. This value is 126.7 times higher than that of upstream emissions reported for Natural gas NGCC CO₂-EOR, but with values almost similar to the Coal SNG plant CO₂-EOR values of 0.02 tCO_{2e}/bbl (Hussaint et al., 2013). Lacy et al. (2015) found a GWP impact for this stage of 0.139 tCO_{2e}/bbl, which included construction, operation and dismantling of pipelines and oil wells activities.

Figure 5 shows the GHG emissions by principal activities. Both LCA-US and API identify that both refinery combustion products and transformation processes represent 50.7% and 30.8% of the total GHG emission, representing 81.5 % of the net direct emissions, with similar values in both methodologies. This result was comparable to the GHG emissions of a CO₂-EOR case in the power sector, since the majority of the emissions are from combustion of refined petroleum products (Venkatesh et al., 2011). Additionally, some studies assume that EOR crude from fossil CO₂ is less CO₂ intensive than EOR crude from natural dome CO₂, albeit with the same efficiency of production regardless of CO₂ source (Cooney et al., 2015).

The remainder (18.5%) corresponds to other activities. In the upstream emissions, this study found more contrasting results for each of the methodologies used than LCA-CCS studies calculating CO₂ resulting from power generation.

INSERT FIGURE 5 HERE

The contributions by transport and compression were 2% of the net emissions, with CO₂ representing 72% and methane 28%. These values agree with those reported by Zapp et al. (2012). The length of the pipeline has the smallest effect. Spath and Mann (2004) estimated a share of transport on total GW increasing from 0.1% for 300 km to 1% for 1800 km pipeline length.

Table 6 shows that for each MJ used to produce energy from the CO₂-EOR project, 66 tCO_{2e}/MJ oil are emitted in US, whilst the API predicts that, on average the emissions were

72 tCO_{2e}/MJ oil. If it were considered that on average Mexican oils have 6,382 MJ/bbl, in this project, only 1% of the total energy generated would be required to produce one barrel. On the other hand, this result is 36.2% higher when compared to that obtained by Lacy et al. (2015) from a hypothetical CCUS case in a natural gas combined cycle power plant (NGCC). They reported values of 44.0 tCO_{2e}/MJ.

INSERT TABLE 6 HERE

It is important to point out that 1,350 MJ/tCO₂ are needed to capture one ton of CO₂ as by-product at the ammonia plant, 58% lower than that reported from thermal generation processes of electricity with CO₂ capture (Rochelle et al., 2011). As 4,632 tCO₂/d could be sent into the atmosphere in the four ammonia plants from the CPC, then primary energy is being wasted to the equivalent of 6,253,2 GJ/d, a loss of primary energy that could generate 980 bbl/d.

Table 7 provides the input/output results expressed in metric tons of CO_{2e} emissions per barrel of crude oil extracted (t/bbl) for each process step and for both tools. With the API method, the result was 0.54 tCO_{2e}/bbl, higher than that predicted by the US with 0.51 tCO_{2e}/bbl. This value is similar if compared to the natural-source and Coal SNG plant CO₂-EOR, and to the average domestic U.S. oil (Hussaint et al., 2013) lifecycle emissions factor of 0.50 ± 0.02 t/bbl (Figure 6). However, it is lower than the result of the life cycle EF of Mexican crude oil of 0.55 tCO_{2e}/bbl reported by Mangmeechai (2009), which includes extraction, transportation, and refining emissions. The slight differences between tools are in the upstream emissions. These minor differences between API and US are due to the relationships between the assumptions and boundary issues that have an impact on the magnitude of the calculated life-cycle emissions. In this regard, the same study can give differing results in likelihood because a different boundary system exists in the process, as well as the material inventory in Umberto at upstream emissions with respect to API. This comparison helps to demonstrate that the choice of boundary, assumptions or accounting methods can have an impact on the end results of the LCA studies.

INSERT TABLE 7 AND FIGURE 6 HERE

3.2 Other environmental impacts from the Brillante CO₂-EOR project

Table 8 shows the resulting life cycle assessment impact (LCIA) obtained with US for the whole project.

Fossil depletion registers a value of 4,109 kg of oil in the six subsystems. This value represents an equivalent to 0.172 TJ used energy and 5.18 m³ for water depletion along the value chain. Next to the climate change category, human toxicity is the most important environmental impact category with a value of 44.5 kg 1,4-DCB.

INSERT TABLE 8 HERE

3.3 Assessment of the energy balance

To analyse the storage factor of the Brillante CO₂-EOR project, Arteaga-Cardona et al. (2015) study results were used. Their estimations were based on CO₂ miscible flood predictive models. CO₂ injection is expected to further decrease the sharp decline in

pressure of the Brillante field, and increase oil production up to 5,900 bpd by injecting 15×10^6 cubic feet per day ($834 \text{ tCO}_2/\text{d}$), for a total of 22×10^9 standard cubic feet (Bscf) throughout the nine-year duration of the project. A cumulative oil production of 5.2 million bbl is expected, with the added benefit of sequestering approximately 50% or 1.3 Mt of the CO_2 injected to the field. This storage factor does not take into account direct and indirect emissions by the EOR operation, so this must be recalculated adjusting the retention rates, which tend to be lower than 50%. Additionally, this result is 10 to 20% higher to that reported by Leach et al. (2011), who gave a value of approximately 30-40% of the CO_2 injected during a single injection, which typically remains trapped in the reservoir. It is important to point out that retention rates within a CO_2 -EOR operation vary depending on the reservoir properties, injection strategy and oil gravity along with other factors. Therefore, according to Arteaga-Cardona et al. (2015), considering GHG emissions in the EOR operation, CO_2 -EOR Brillante project has storage factors of $203.9 \text{ kgCO}_2/\text{barrel}$ of oil produced, this being within the range of that reported in other cases of EOR operations of 170 to $300 \text{ kg CO}_2/\text{barrel}$ of oil (Stewart and Haszeldine, 2014). CO_2 recovered from the reservoir will be re-injected and not vented, meaning that 7.07 barrels oil extracted per net metric ton CO_2 are injected. This value is of interest and is in contrast to that reported by McCoy and Rubin (2008) and Hussain et al. (2013), with values of 4.6 bbl/tCO_2 or compared to the average US figure of 3.8 bbl/tCO_2 (Stewart and Haszeldine, 2014). NTEU also (2010) reported 4.35 bbl/tCO_2 for tertiary injection EOR best practices based on a water alternating gas (WAG). Therefore, an increment in the crude recovery ratio reduces the amount of CO_2 required and the corresponding CO_2 storage (Cooney et al., 2015). As it has been indicated by Dai et al. (2014b), these different results suggest that CO_2 injection/storage and oil/gas recovery rates are the major intrinsic reservoir parameters. For instance, in the case of the Artesa CO_2 -EOR project in Mexico, Leon-Garcia et al. (2015) found a value of 2.2 bbl/tCO_2 . These recovery rates are different to those of the Brillante project, despite the Artesa project being located in the same region in Tabasco State, but with different geology.

With respect to the effectiveness of CO_2 -EOR projects to store net CO_2 , if the reasoning of Faltison and Gunter (2011) regarding world oil production being controlled by demand is considered, implementing CO_2 -EOR projects will not result in incremental aggregate oil consumption emissions. Thus, this approach is made under the assumption that if oil were not produced by CO_2 -EOR, then another source would have to be developed to fill the gap. The study states that only relevant fugitive emissions that are directly associated with the CO_2 -EOR project should be included in the life cycle assessment of the project. Consequently, product refining and combustion in the system boundary of the analysis should be discounted.

From this point of view, if only subsystems III (Ammonia plant) and IV (EOR operation in CPOA) are considered, for every barrel of petroleum recovered, subtracting the geological sequestration and the displacement for ammonia production as avoided burden would, on average, produce a value of $0.03 \text{ tCO}_2/\text{bbl}$.

The Brillante CO_2 -EOR project case comes with additional useful energy (Faltison and Gunter, 2011) due to the 'additional oil', not being used. Table 9 shows that with the energy provided by the $834 \text{ tCO}_2/\text{d}$ from the ammonia plant, equivalent to 3,699 TJ, the Brillante CO_2 -EOR project would provide primary energy additional to 33,189 TJ during EOR operation. This means that with only 11.1% of energy (i.e. $834 \text{ tCO}_2/\text{d}$), the net energy generated would be 28,488 TJ, along with economic profits. Without the project,

there would continue to be a loss of energy by continual venting of CO₂ into the atmosphere, equivalent to 16,751 TJ, without taking economic profits into account. Hence, when compared with the average US figure of 3.8 bbl/tCO₂ of energy generated, which is the equivalent of 0.024 TJ/tCO₂, the Brillante CO₂-EOR project would provide 53.3% of additional energy.

INSERT TABLE 9 HERE

Table 10 shows the main key indicators of the Brillante CO₂-EOR project, which included the upstream and downstream emissions.

INSERT TABLE 10 HERE

Due to the fact that the current storage factor is very low because of their immiscibility characteristics and given that the results were obtained based on a CO₂ miscible predictive model and not by Huff & Puff tests (pilot tests in the field), verification of the operational parameters and CO₂ storage factor with an immiscible model would be worthwhile. It would be important to consider incorporating a separation and re-injection system for the CO₂ (CO₂ recycle plant), which is mixed with the oil in order to make a “closed loop” system. This approach CO₂-EOR+CCS would allow the CO₂ storage factor ratio to be increased whilst decreasing crude recovery (Cooney et al., 2015).

4. Sensitivity analysis

A sensitivity analysis (SA) was undertaken on three important assumptions used in the study. The scenarios were as follows:

SA1: Use of specific emissions values for the Brillante EOR field operations.

SA2: Changing values of geological sequestration with the change of emissions in EOR field operations.

SA3: Potential CO₂ capture flue gas from primary reformer of ammonia plant, using an old CO₂ capture unit (MEA solutions) from ammonia plant I.

The emissions from EOR field operation are important as they have a significant impact on the GW impact results in the study. Given the facilities (Table 2) and production at the Brillante field (Arteaga-Cardona et al., 2015), this study estimated, using equations 1 and 2, an emission of 0.015 tCO_{2e}/bbl for EOR field operations. This sensitivity recognizes the variations in the emissions of EOR field operations from 0.060 (see Table 3) up to 0.015 tCO_{2e}/bbl. The sensitivity is based on an emitted value that is 75% lower than the Hussaint et al. (2013) study. However, it is important to comment that this study does not take into account GHG emissions from the operation of the CO₂ recycling plant; therefore, the value used for EOR operations in Brillante must exceed 0.015 tCO_{2e}/bbl.

When post-combustion CO₂ capture through process simulations (PS) was done assuming a new emissions value for the EOR operation, the geological sequestration changed from -0.203 tCO_{2e}/bbl (base case) to -0.248 tCO_{2e}/bbl or 18.1% more of CO₂ storage.

Results show that 372,426 tons/year of CO₂ may be captured from flue gas of the primary reformer of an ammonia plant of 480,000 tons/y of capacity (Morales-Mora et al.,

2016). The emissions of the ammonia plant are 0.26 tCO_{2e}/bbl. This study carried out an LCA for this new scenario in the ammonia plant; the result of CO₂ capture shows a new value of 0.105 tCO_{2e}/bbl, i.e. a CO₂ emissions reduction of 40%. The results of these scenarios were incorporated (Table 7) to visualise the variation of new GHG emission results per barrel extracted.

Figure 7 shows the change in the GW results depending on the assumptions made for the oil field operation, geological sequestration and CO₂ capture from flue gas from the ammonia plant, and their comparison with the base case (US) and NGCC CO₂-EOR.

For scenario one (S1), the results show that the GW impacts have 7% lower emissions per barrel of oil extracted with a new value of oil field operation with respect to the base case (Ammonia plant-CO₂-EOR, see value US of table 5). However, the emissions are still 34% higher with respect to the NGCC CO₂-EOR case (Hussaint et al., 2013). The results of the sensitivity analysis for S2 show an appropriate response to the induced modifications of geological sequestration which showed the same behaviour, with a reduction of the total emissions per barrel extracted from the 17.6% for base case, but still superior at 20% to the NGCC CO₂-EOR case. The sensitivity analysis for S3 shows a positive impact as a consequence of the potential capture of 1,000 t/d of CO₂ gases from combustion of the primary reformer of the ammonia plant. This variable results from implementing post-combustion CO₂ capture from the ammonia plant. It can be observed that with a combination of the three scenarios, the CO_{2e} per barrel produces a reduction in the total CO₂ emissions on the EOR system of the order of 49% in comparison with the base case and 25.7% with respect to NGCC CO₂-EOR case. Consequently, post-combustion CO₂ capture in the ammonia plant may represent a relevant factor to consider for reducing CO_{2e} emissions and increase the energy efficiency of a CCUS system.

INSERT FIGURE 7 HERE

5. Conclusions and recommendations

Both LCA and API tools produced accurate estimations of the GHG emission in the EOR system for the oil and gas industries. The differences between both tools were in the upstream emissions (subsystem I and II), with a ratio of 0.42 to 3.5, which are not relevant since these subsystems contribute only eight per cent of the total emissions. At the downstream emissions (Subsystem III to VI), no differences were found in the results for both methodologies with a ratio close to 1. This lack of difference between the US and API is owed to the adjustment to the conditions of the EF of the oil and gas sectors for Mexico Ecoinven in Umberto materials and processes.

Both tools appear to be clear, fast and comprehensive for the purpose of LCA-CCS studies, which can be used within the particularities of the oil and gas industries in Mexico. The API used to estimate the GHG emission in the oil and gas sector projects was validated and can be applied through calculations performed 'manually' in a spreadsheet by practitioners and researchers intending to analyse the GHG emission of CCS. This comparison allows the estimation and acknowledgement of GHG emissions in the whole chain of value of the project; as well as the energy demand to produce one barrel of oil through EOR. The results of the comparison between both tools prove that API made an accurate calculation of the life cycle emissions to the EOR system when US with standard databases are not available. Overall, the use of CO₂ process stream in the petrochemical

sector for the EOR system in Mexico registered a lower environmental footprint, but slightly higher in comparison with alternative CO₂ sources for CO₂-EOR, to coal or NG combustion (Pulverized coal-fired PP, Integrated gasification CC, NGCC). The use of different boundary systems, databases, allocation of by-products, functional units (1 MWh or kWh of Electricity) and technologies for CO₂ capture in the LCA-CCS study, make it difficult to make comparisons when assessing the environmental performance from power plants versus process stream of the oil and gas sectors.

The energy balance is positive because, with CO₂-EOR, LCA from the oil and gas industries has so far received little attention, in spite of being an important tool to address and compare different technological options. From the standpoint of energy efficiency, the Brillante CO₂-EOR project provides 46% of additional primary energy, than average, of CO₂-EOR in the U.S. (3.8 bbl/tCO₂). The total CO₂ storage during the EOR operation could achieve 1.3 million tons. In spite of the limited availability of LCA literature on process streams from petrochemical or refining processes to CCS or EOR, these technologies will generate the lowest relative increase in the environmental impact categories.

Based on the results of this study, the use of manual calculations for studies on LCA-CCUS is recommended, where quick adjustments or updates at the EF regional or local level can be made at any time in the worksheets, in accordance with operative guidelines determined by the oil and gas companies in contrast to the Ecoinvent database.

Supporting Information

The Supporting Information file accompanying this paper includes a Table SI-1 with the steps for calculated CO_{2e} by API method as well as material and energy flow network of Brillante CO₂-EOR project.

Acknowledgments

The authors would like to thank the Gregory Conney and Timothy J. Skone of National Energy Technology Laboratory-LCA U.S. Department of Energy for their comments, which helped to clarify and improve the presentation of the results of this work and to Maria del C. Avalos Islas for her invaluable support and contributions to this study. Moreover, the authors would like to acknowledge Mr. Emiliano Leiva and Dr. Anya Leiva for the final writing of the text.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

- API, 2009. Compendium of Greenhouse Gas Emissions Estimation Methodologies for the Oil and Natural Gas Industry. Version 3.0, August 2009. American Petroleum Institute, Washington D.C.
- API (American Petroleum Institute), 2011. API SPEC 5L: Specification for Line Pipe. American Petroleum Institute.

- 1
- 2
- 3
- 4 Arteaga Cardona M., F. Rodríguez de la Garza, I. Báez Marín, 2015. Inyección de bióxido
- 5 de carbono en el campo Brillante [CO₂ injection in the Brillante field]. Ingeniería
- 6 Petrolera, Vol. 55 No. 10, Octubre. ISSN 0185-3899, México.
- 7
- 8 Armstrong K. and P. Styring, 2015. Assessing the potential of utilization and storage
- 9 strategies for post-combustion CO₂ emissions reductions. Front. Energy Res. Vo. 3. Art.
- 10 8.
- 11 ARI and Melzer Consulting, 2010. Optimization of CO₂ storage in CO₂-enhanced oil
- 12 recovery projects, report for the UK Department of Energy and Climate Change.
- 13 Available at: [www.adv-res.com/pdf/1006-optimization-of-co2-storage-in-co2-](http://www.adv-res.com/pdf/1006-optimization-of-co2-storage-in-co2-enhanced-oil-re.pdf)
- 14 [enhanced-oil-re.pdf](http://www.adv-res.com/pdf/1006-optimization-of-co2-storage-in-co2-enhanced-oil-re.pdf) (accessed 10.10.15).
- 15
- 16 Bandyopadhyay A. 2011. Amine versus ammonia absorption of CO₂ as a measure of
- 17 reducing GHG emission: a critical analysis. Clean Techn. Environ. Policy 13, 269–294.
- 18
- 19 Bandza A. J. and S. P. Vajjhala, 2014. Modeling the Transition from Enhanced Oil
- 20 Recovery to Geologic Carbon Sequestration. Manage. Decis. Econ. 35: 20–35.
- 21
- 22 Brandão M., & A. Levasseur, M. U. F. Kirschbaum, B. P. Weidema, A. L. Cowie, S. V.
- 23 Jørgensen, M. Z. Hauschild, D. W. Pennington and K. Chomkhamsri, 2013. Key issues
- 24 and options in accounting for carbon sequestration and temporary storage in life cycle
- 25 assessment and carbon footprinting. Int J Life Cycle Assess, 18:230–240
- 26
- 27 Corsten M., Andrea Ramírez, Li Shen, Joris Koornneef, André Faaij, 2013. Environmental
- 28 impact assessment of CCS chains – Lessons learned and limitations from LCA literature.
- 29 Int. J. Greenh. Gas Control. Volume 13, Pages 59-71.
- 30
- 31 Cooney G., J. Littlefield, J. Marriott and T. J. Skone, 2015. Evaluating the Climate Benefits
- 32 of CO₂ Enhanced Oil Recovery Using Life Cycle Analysis. Environ. Sci. Technol. 49,
- 33 7491–7500.
- 34
- 35 Cuellar-Franca R.M. and A. Azapagic, 2015. Carbon capture, storage and utilisation
- 36 technologies: A critical analysis and comparison of their life cycle environmental
- 37 impacts. J. CO₂ Util. 9, 82-102.
- 38
- 39 Dai, Z., Middleton, R., Viswanathan, H., Fessenden-Rahn, J., Bauman, J., Pawar, R., Lee,
- 40 S.-Y. and McPherson, B., 2014a. An integrated framework for optimizing CO₂
- 41 sequestration and enhanced oil recovery. Environ. Sci. Technol. Lett. 1 (1), 49–54.
- 42
- 43 Dai, Z., Viswanathan, H., Fessenden-Rahn, J., Middleton, R., Pan, F., Jia, W., Lee, S.-Y.,
- 44 McPherson, B., Ampomah, W. and Grigg, R. 2014b. Uncertainty quantification for CO₂
- 45 sequestration and enhanced oil recovery. Energy Procedia, 63 (0), 7685–7693.
- 46
- 47 Dávila M., O. Jiménez, R. Castro, V. Arévalo, J. Stanley and L.M. Cabrera, 2010. A
- 48 preliminary selection of regions in Mexico with potential for geological carbon storage.
- 49 Int. J. Phys. Sci. Vol. 5(5), pp. 408-414.
- 50
- 51 EPRI (Electric Power Research Institute), 2013. Update on Utilization or Storage of CO₂
- 52 through Chemical, Biological, or Mineral Conversion. Report No. 3002001006, Electric
- 53 Power Research Institute, Palo Alto, CA. Available at:
- 54 www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000003002001006
- 55 (accessed 05.17.15)
- 56
- 57 Faltison, J. and Gunter, B., 2011. Net CO₂ Stored in North American EOR Projects. Society
- 58 of Petroleum Engineers, Canadian Unconventional Resources and International
- 59 Petroleum Conference. Calgary: SPE.
- 60
- 61 Goedkoop M, Heijungs R, Huijbregts M, De Schryver A, Struijs J, VanZelm R, 2009.
- 62 ReCiPe 2008. VROM Ruimte en Milieu, Ministerie van Volkshuisvesting, Ruimtelijke
- 63 Ordening en Milieubeheer. Available at: www.lcia-recipe.net (accessed 12.11.15).
- 64
- 65

- 1
- 2
- 3
- 4 Global CCS Institute, 2015. The Global Status of CCS: 2015. Summary Report. Available
- 5 at: www.globalccsinstitute.com/publications/global-status-ccs-2015 (accessed
- 6 10.10.15).
- 7
- 8 Haas MJGde, van Dijk TA., 2010. Inventarisatie klimaatvriendelijke kunstmest.
- 9 Wageningen: Nutriënten Management Instituut NMI. Available at:
- 10 www.rvo.nl/sites/default/files/bijlagen/Inventarisatie%20klimaatvriendelijke%20kunstmest%20-%20Rapport%20-%20november%202010.pdf (accessed 08. 11.15)
- 11
- 12 Hertwich, E., Martin Aaberg, Bhawna Singh and Anders H. Strømman, 2008. Life-cycle
- 13 Assessment of Carbon Dioxide Capture for Enhanced Oil Recovery. Chinese J. Chem.
- 14 Eng., 16 (3) 343-353
- 15
- 16 Hussain D., David A. Dzombak, Paulina Jaramillo, Gregory V. Lowry, 2013. Comparative
- 17 lifecycle inventory (LCI) of greenhouse gas (GHG) emissions of enhanced oil recovery
- 18 (EOR) methods using different CO₂ sources. Int. J. Greenh. Gas Control. 16, 129–144.
- 19 IEA (International Energy Agency), 2015. Combining EOR with CO₂ storage (EOR+) for
- 20 profit. Available at:
- 21 www.iea.org/publications/insights/insightpublications/CO2EOR_3Nov2015.pdf
- 22 (accessed 05.11.15).
- 23
- 24 IEA and UNIDO (International Energy Agency- United Nations Industrial Development
- 25 Organization), 2011. Technology Roadmap Carbon Capture and Storage in Industrial
- 26 Applications. Available at:
- 27 www.iea.org/publications/freepublications/publication/ccs_industry.pdf (accessed
- 28 13.06.16).
- 29
- 30 International Organization for Standardization, 2006a. ISO-14040. Environmental
- 31 Management Standard- Life Cycle Assessment, Principles and Framework.
- 32 International Organization for Standardization. Switzerland.
- 33
- 34 International Organization for Standardization, ISO, 2006b. ISO 14044. Environmental
- 35 Management - Life Cycle Assessment - Requirements and Guidelines. International
- 36 Organization for Standardization. Switzerland.
- 37
- 38 IPCC (Intergovernmental Panel Climate Change), 2007. Climate Change 2007. The
- 39 Physical Science Basis; Intergovernmental Panel for Climate Change, Fourth
- 40 Assessment Report. Cambridge University Press, New York. Available at:
- 41 www.ipcc.ch/ipccreports/ar4-wg1.htm. (Accessed 20.11.15).
- 42
- 43 Jaramillo, P. W. Michael Griffin and S. Mc Coy, 2009. Life Cycle Inventory of CO₂ in an
- 44 Enhanced Oil Recovery System. Environ. Sci. Technol. 43, 8027–8032.
- 45
- 46 Lacy R., C. Serralde, M. Climent and M. Vaca, 2012. Initial assessment of the potential for
- 47 future CCUS with EOR projects in Mexico using CO₂ captured from fossil fuel
- 48 industrial plants. Int. J. Greenh. Gas Control. 19, 212–219.
- 49
- 50 Lacy R., M. Molina, M. Vaca, C. Serralde, G. Hernandez, G. Rios, E. Guzman, R.
- 51 Hernandez, R. Perez, 2015. Life-cycle GHG assessment of carbon capture, use and
- 52 geological storage (CCUS) for linked primary energy and electricity production. Int. J.
- 53 Greenh. Gas Control. 42, 165–174
- 54 León García A, F. Samaniego Verduzco, S. García Rodríguez, F. García Hernández, H.
- 55 Rodríguez García, 2015. Inyección de CO₂ en condiciones miscibles en el yacimiento
- 56 naturalmente fracturado Artesa [CO₂ injection in miscible condition in the Artesa
- 57 naturally fractured oil reservoir]. Ingeniería Petrolera. Vol. 55 No. 10, octubre · ISSN
- 58 0185-3899, México.
- 59
- 60
- 61
- 62
- 63
- 64
- 65

- Leach, A.; Mason, C. F.; Veld, K. v. t, 2011. Co-optimization of enhanced oil recovery and carbon sequestration. *Resour. Energy Econ.* 33 (4), 893-912.
- Leung, D. Y. C.; Caramanna, G.; Maroto-Valer, M. M. An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sustain. Energy Rev.* 2014, 39, 426–443.
- Levasseur A., 2015. Climate Change, in: *LCA Compendium – The Complete World of Life Cycle Assessment*. Michael Z. Hauschild and Mark A. J. Huijbregts (Eds.) Springer Science+Business Media Dordrecht, pp. 39–50.
- Luis, P. 2015. Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives. *Desalination*. Volume 380, Pages 93-99.
- Marx, J., Schreiber, A., Zapp, P., Haines, M., Hake, J. Fr. and Gale, 2011. Environmental evaluation of CCS using Life Cycle Assessment – a synthesis report. *Energy Procedia* 4, 2448 - 2456
- Mangmeechai, A., 2009. Life cycle greenhouse gas emissions, consumptive water use and levelised costs of unconventional oil in North America. Pittsburgh: Carnegie Mellon University.
- Makhlouf A, Tayeb Serradj, Hamza Cheniti, 2015. Life cycle impact assessment of ammonia production in Algeria: A comparison with previous studies. *Environ. Impact Assess. Rev.* 50, 35–41
- Manuilova, A., Koiwanit, J., Piewkhaow, L., Wilson, M., Chan, C.W. and Tontiwachwuthikul, P., 2014. Life Cycle Assessment of Post-Combustion CO₂ Capture and CO₂-Enhanced Oil Recovery based on the Boundary Dam Integrated Carbon Capture and Storage Demonstration Project in Saskatchewan. *Energy Procedia* 63, 7398 – 7407
- Morales-Mora M.A., Pretelín Vergara, C., Leiva, M.A., Martínez Delgadillo, S.A. and Rosa-Domínguez, E.R., 2016. Life cycle assessment of carbon capture and utilization from ammonia process in Mexico. *J. Environ. Manage.* 183, 998-1008.
- McCoy, S.T., Rubin, E.S., 2008. An engineering-economic model of pipeline transport of CO₂ with application to carbon capture and storage. *Int. J. Greenh. Gas Control.* 2, 219–229.
- National Institute of Ecology and Climate Change, 2014. Emission factors for the different types of fossil fuels and alternatives consumed in Mexico [Factores de emisión para los diferentes tipos de combustibles fósiles y alternativos que se consumen en México]. Available at: www.inecc.gob.mx/descargas/cclimatico/2014_inf_fin_tipos_comb_fosiles.pdf (accessed 12.10.15).
- National Hydrocarbons Commission, 2016. Statistics. Hydrocarbon Reserves. Available at: www.cnh.gob.mx/56000.aspx (Accessed 03.02.16).
- Nagashima, S.; Miyagawa, T.; Matsumoto, M.; Suzuki, S.; Komaki, H.; Takagi, M.; Murai, S., 2011. Life cycle assessment performed on a CCS model case in Japan and evaluation of improvement facilitated by heat integration. *Energy Procedia* 4, 2457–2464.
- NTEL (National Energy Technology Laboratory), 2010. An Assessment of Gate-to-Gate Environmental Life Cycle Performance of Water-Alternating- Gas CO₂-Enhanced Oil Recovery in the Permian Basin; DOE/NETL-2010/1433; National Energy Technology Laboratory: Pittsburgh, PA, 2010;

- http://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Coal/CO2_EOR_LCA_093010.pdf. (accessed 10.06.16)
- NETL, 2013a. Cradle-to-Gate Life Cycle Analysis Model for Alternative Sources of Carbon Dioxide. 50 p. Available at: www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Life%20Cycle%20Analysis/CtG-LCA-of-Alternative-CO2.pdf (accessed 21.02.16).
- NETL, 2013b. Gate-to-Grave Life Cycle Analysis Model of Saline Aquifer Sequestration of Carbon Dioxide. Available at: www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Life%20Cycle%20Analysis/GtG-LCA-of-Saline-Aquifer-Sequestration.pdf. (accessed 15.03.16).
- NETL, 2015. Commercial technologies. Available at: www.netl.doe.gov/research/Coal/energy-systems/gasification/gasifipedia/fertilizer-commercial-technologies (accessed 15.11.15).
- Overcash M., Yong Li, Evan Griffing and Gareth Rice, 2007. A life cycle inventory of carbon dioxide as a solvent and additive for industry and in products. *J. Chem. Technol. Biotechnol.* 82:1023–1038.
- Petrakopoulou F. and G. Tsatsaronis, 2014. Can Carbon Dioxide Capture and Storage from Power Plants Reduce the Environmental Impact of Electricity Generation?. *Energy Fuels*. 28 (8), 5327–5338.
- PEMEX (Petróleos Mexicanos), 2014. Sustainability Report 2014. Available at: www.pemex.com/en/responsibility/sustainable/reports/Paginas/default.aspx (accessed 02.09.15).
- PEMEX, 2015. Statistical. Institutional database. 2015 Available at: www.ebdi.pemex.com/bdi/bdiController.do?action=cuadro&cvecua=ECRURA (accessed 17.09.15).
- Rochelle G., E. Chen, S. Freeman, D. Van Wagener, Q. Xu, A., 2011. Voice, Aqueous piperazine as the new standard for CO₂ capture technology, *Chem. Eng. J.* 171, 725–733.
- SENER (Energy Secretariat), 2014. Mexico CCUS technological roadmap [Mapa de Ruta Tecnológica de CCUS en Mexico]. Mexico, DF. 31 p. Available at: www.gob.mx/sener/documentos/mapa-de-ruta-tecnologica-ccus (accessed 08.12.15).
- SEMARNAT-INECC ((Secretariat of Environment and Natural Resources-National Institute of Ecology and Climate Change), 2016. Mexico's Climate Change Mid-Century Strategy. Ministry of Environment and Natural Resources (SEMARNAT) and National Institute of Ecology and Climate Change (INECC), Mexico City, Mexico. Available at: unfccc.int/files/focus/longterm_strategies/application/pdf/mexico_mcs_final_cop22nov16_red.pdf (accessed 22.11.2016).
- Spath, P., Mann, M., 2004. Biomass Power and Conventional Fossil Systems with and Without CO₂ Sequestration—Comparing the Energy Balance, Greenhouse Gas Emissions and Economics. National Renewable Energy Laboratory, Colorado, United States of America.
- Stéphenne K., 2014. Start-Up of World's First Commercial Post-Combustion Coal Fired CCS Project: Contribution of Shell Cansolv to SaskPower Boundary Dam ICCS Project. *Energy Procedia* 63, 6106 – 6110

- 1
- 2
- 3
- 4 Stewart R Jamie and S. Haszeldine, 2014. Carbon Accounting for Carbon Dioxide
- 5 Enhanced Oil Recovery. Scottish Carbon Capture & Storage, UK. Available at:
- 6 www.sccs.org.uk. (Accessed 12.02.16).
- 7
- 8 Strazza C., Adriana Del Borghi and Michela Gallo, 2013. Development of Specific Rules
- 9 for the Application of Life Cycle Assessment to Carbon Capture and Storage. *Energies*,
- 10 6, 1250-1265.
- 11 USEPA (United States Environmental Protection Agency), 2015. Inventory of U.S.
- 12 Greenhouse Gas Emissions and Sinks: 1990-2013. EPA 430-R-15-004
- 13
- 14 Van der Zwaan, B. and K. Smekens, 2010. CO₂ Capture and Storage with Leakage in an
- 15 Energy-Climate Model. *Environ. Model. Assess.* 14 (2): p. 135-148.
- 16 Venkatesh, A.; Jaramillo, P.; Griffin, W. M.; Matthews, H. S., 2011. Uncertainty analysis
- 17 of life cycle greenhouse gas emissions from petroleum-based fuels and impacts on low
- 18 carbon fuel policies. *Environ. Sci. Technol.* 45, 125–131
- 19
- 20 Von der Assen N, P. Voll M. Petersb and A. Bardow, 2014. Life cycle assessment of
- 21 CO₂ capture and utilization: a tutorial review. *Chem. Soc. Rev.* 43, 7982-7994.
- 22
- 23 Volkart K, Ch. Bauer, C. Boulet, 2013. Life cycle assessment of carbon capture and storage
- 24 in power generation and industry in Europe. *Int. J. Greenh. Gas Control.* 16, 91–106
- 25 Wang, M., M. Wu, H. Huo, and J. Liu, 2008, “Well-to-Wheels Energy Use and Greenhouse
- 26 Gas Emissions of Brazilian Sugarcane Ethanol Production Simulated by Using the
- 27 GREET Model,” *Int. Sugar J.*, Vol. 110, No. 1317: 527-545.
- 28
- 29 Williams G. and Al-Ansari F., 2007. IFA Benchmarking of Global Energy Efficiency in
- 30 Ammonia Production. Workshop on Energy Efficiency and CO₂ Reduction Prospects in
- 31 Ammonia Production, In. Ho Chi Minh City, Vietnam: IFA Technical Committee
- 32 Meeting; [12-14 March].
- 33
- 34 Xiao L.S., R. Wang, P.-Ch. Chiang, S.Y. Pan, Q.-H. Guo, E.E Chang, 2014. Comparative
- 35 Life Cycle Assessment (LCA) of Accelerated Carbonation Processes Using
- 36 Steelmaking Slag for CO₂ Fixation. *Aerosol and Air Quality Research*, 14: 892–904.
- 37 Zapp, P., Schrieber, A., Marx, J., Haines, M., Hake, J., Gale, J., 2012. Overall
- 38 environmental impacts of CCS technologies- a life cycle approach. *Int. J. Greenhouse*
- 39 *Gas Contr.* 8, 12–21.
- 40
- 41
- 42
- 43
- 44
- 45
- 46
- 47
- 48
- 49
- 50
- 51
- 52
- 53
- 54
- 55
- 56
- 57
- 58
- 59
- 60
- 61
- 62
- 63
- 64
- 65

Table 1. Capacity of key facilities in Brillante oil field

Item	No	Nominal Bbl/d	Nominal MMSCF/d
Operation well	12		
Horizontal separator	1	55,000	16
Slag catcher	1	3.5	20
Storage tank	8	500	
Gas compressor	1		2
Pump	1	10,000	
Flare	1	-----	
Tanks	8	4000 bbl	

Table 2. Description of the CO₂-EOR subsystems
(Adapted from Makhlouf et al., 2015)

Subsystems		Operation units studied	Facility	Functions performed
I	Extraction NG	Extraction and pumping of associated natural gas to Atasta station boosting center (SBC) and then to Nuevo PEMEX Gas Processing Complex (NPGPC). Include separation of natural gas; gas compression; gas NG transport; recompression.	Offshore platform oil and gas and SBC	Natural gas extraction
II	NG processing	Cooling dehydration; separation of gas and liquid hydrocarbons; fractionation; recompression	NPGPC	Liquefaction-compressions
III	Ammonia production	Desulphurization; Primary reformer; Secondary reformer; Shift conversion; CO ₂ removal; Methanation; Compression; Ammonia synthesis	CPC	Ammonia production
IV	CO ₂ -EOR	Extraction and pumping of oil recovery to Minatitlan Refinery	Mature oil well	Oil recovery
V	Refining oil	Light, middle and heavy distillates	Minatitlan Refinery	Gasoline, diesel production
VI	Refinery product combustion	Gasoline combustion	Car	GHG emissions

Table 3. Sum up of key input parameters utilized in model of CO₂-EOR project model
(adapted from Hussain et al. 2013)

Input parameter/project emissions	Parameter value	Reference
Oil production ratio/EOR process efficiency (Barrels oil extracted per net metric ton CO ₂ injected)	7.07 bbl/tCO ₂	Arteaga-Cardona et al. (2015)
Geological sequestration of CO ₂ during EOR	0.20 tCO ₂ /bbl	Hussaint et al. (2015)
Refined oil product combustion emissions	0.44 t/bbl	INECC (2014)
CO ₂ capture efficiency	97.5 %	Ammonia plant in CPC
CO ₂ leakage rate	0.01%/year	(van der Zwaan and Smekens (2010)
Electricity use emissions (PEMEX)	460 kg CO _{2e} /MWh	Own estimate
Refinery operations (tCO ₂ /bbl oil refinery)	0.03	ARI & Melzer Consulting, 2010
CCS capture efficiency (Brillante field)	50 % or 0.263 tCO ₂ /bbl	Arteaga-Cardona et al. (2015)
CO ₂ transport Gg CO ₂ /km of pipeline per year	2.9602E-5	API,2011
Crude oil transport (gCO _{2eq} /bbl)	6.49E-5	Own estimate
EOR field operations (CO _{2e} /bbl)	0.06	Hussaint et al. (2013)
Ammonia plant Feedstock gas/combustion (tCO _{2e} /bbl)	0.260	Own estimate

Table 4. Method of allocation on the basis of the natural gas use as raw material

Function	Inputs	Used	Unit	Quantity	Allocation factor (%)	Output
Ammonia plant	NG	Process gas (NH ₃ +CO ₂)	NM ³	749	55.2	NH ₃ +CO ₂
	Gas dryers	Fuel	NM ³	606	44.7	Flue gas

Table 5. Comparisons of the estimating GHG emissions by subsystem and stages with US and API methods (tCO_{2e}/bbl)

Subsystem	Stage	Process	Tools GW (tCO _{2e} /bbl)					
			US			API		
			Emission	%	Emissions for subsystem	Emission	%	Emissions for subsystem
I	1	Oil and gas Marine NE (APC) Cantarell	0.019	2.2		0.034	3.8	
	2	Gas compression (APC)	0.006	0.7		0.002	0.2	
	3	Pipeline gas transport (APC to Atasta)	0.002	0.2	0.03	0.001	0.1	0.04
	4	Gas compression (Atasta)	0.005	0.5		0.003	0.3	
II	5	Pipeline gas transport (Atasta to Nuevo PEMEX)	0.004	0.4		0.002	0.2	
	6	NG sweetening plant (Nuevo PEMEX)	0.015	1.7		0.035	4.0	
	7	NG (Dry) compression	0.005	0.5	0.02	0.003	0.3	0.04
	8	Pipeline NG transport (Nuevo PEMEX to CPC)	0.004	0.5		0.002	0.3	
III	9	Ammonia plant (CPC)	0.259	30.5		0.270	30.7	
	10	CO2 compression (CPC to CP EOR Project)	0.001	0.2	0.26	0.001	0.2	0.27
	11	Pipeline CO2 transport (CPC to CP field)	3E-05	0.0		3E-05	0.0	
IV	12	Operation CO2-EOR (Brillante field)	0.060	7.1		0.060	6.8	
	13	Oil recovery pumping (CP field to Minatitlan Refinery)	2E-05	0.0	0.06	2E-05	0.0	0.06
	14	Oil recovery transport to Minatitlan Refinery	6E-05	0.0		6E-05	0.0	
V	15	Refining oil (Minatitlán Refinery)	0.032	3.8	0.03	0.030	3.4	0.03
VI	16	Refinery product combustion	0.44	51.6	0.44	0.44	49.7	0.44
Total emissions			0.85	100.0	0.85	0.88	100.0	0.88

Table 6. Comparison of energy uses with each barrel recovered (tCO_{2e}/MJ)

Subsystem	US	API
I	5.60	6.66
II	3.73	6.44
III	42.14	43.93
IV	9.71	9.71
V	5.16	4.85
Average ^a	66	72

a: Is not considered the Subsystem VI

Table 7. Lifecycle GHG emissions and inputs/outputs for EOR (metric tons of CO_{2e} per barrel of oil extracted) (adapted from Hussaint et al. 2013)

Process inputs/outputs	Ammonia plant- CO ₂ -EOR (US)	Ammonia plant- CO ₂ -EOR (API)
Feedstock used NG (t)	406	406
Ammonia product (t)	1	1
CO ₂ generated as byproduct (t)	1.4	1.4
Upstream emissions (Offshore)	0.019	0.034
Feedstock gas/combustion (Ammonia)	0.260	0.270
NG compression	0.015	0.007
Pipeline NG transport	0.009	0.005
NG Sweetening plant	0.015	0.035
CO ₂ compression	0.001	0.001
Pipeline CO ₂ transport	0.00003	0.00003
Oil field operations	0.060	0.060
Geological sequestration	-0.20	-0.20
CO ₂ leakage (100 years)	0.002	0.002
Crude oil transportation	0.0001	0.0001
Refinery operations	0.032	0.032
Oil product combustion	0.44	0.44
Ammonia/CH ₄ Displacement	-0.14	-0.14
Total (tCO_{2e}/bbl)	0.51	0.54
Energy to produce 1 bbl (MJ)	66	72

Table 8. LCIA results of ReCiPe for the production of 1 barrel of CO₂-EOR project

Midpoint impact category	Unit	Result/FU
Agricultural land occupation	m ² a	0.05
Climate change	t CO _{2e}	8.53E-01
Fossil depletion	t oil	4.11E+00
Freshwater ecotoxicity	t 1,4-DCB	4.60E-04
Freshwater eutrophication	P	1.46E-06
Human toxicity	t 1,4-DCB	4.45E-02
Ionising radiation	U235	4.41E-03
Marine ecotoxicity	t 1,4-DCB	1.19E-03
Marine eutrophication	t N	8.60E-04
Metal depletion	t Fe	1.80E-04
Natural land transformation	m ²	1.76E-04
Ozone depletion	t CFC-11	1.19E-07
Particulate matter formation	t PM10	7.70E-04
Photochemical oxidant formation	t NMVOC	7.16E-03
Terrestrial acidification	t SO ₂	1.56E-03
Terrestrial ecotoxicity	t 1,4-DCB	1.10E-04
Urban land occupation	m ² a	0.04
Water depletion	m ³	5.18

Table 9. Comparison effects amongst without and with Brillante CO₂-EOR project.

		Unit	Without project	With project
CO ₂ vented in the Ammonia plant (Four)	a	t/d	4632	
CO ₂ injected Brillante field	b	t/d	0	834 ^a
Duration of EOR operation	c	y		9 ^a
Total CO ₂ injected during EOR operation	d=b•365•c	t	0	2,739,690
CO ₂ storage	e	t/d	0	417 ^a
Annual CO ₂ storage	f=e•365	t/y	0	152,205
Total CO ₂ storage during EOR operation	g=f•c	t	0	1,369,845
Additional oil recovered by EOR	h	bbbl/d	0	5,900 ^a
Oil production ratio/EOR process efficiency	i=h/b	bbbl/tCO ₂	0	7.07
Net increase in oil production as a result of EOR operation	j ^a	bbbl	0	5,200,000
Storage factor CO ₂	k=g/j	tCO ₂ /bbbl	0	0.263
Emissions of oil field operations	l	tCO _{2e} /bbbl	0	0.060
Net storage factor	m=k-l	kgCO _{2e} /bbbl	0	203.4
Price one barrel	n	USD/bbl	0	25
Economic benefits by selling additional oil	o=j•n	MUSD	0	130
Energy of one barrel oil	p	MJ/bbl	0	6,382
Produce primary energy by EOR	p=j•p	TJ	0	33,186
Energy needed to capture one ton of CO ₂	r	MJ/tCO ₂	1350	----
Total loss energy by vented CO ₂ from ammonia plant	s=a-b•r•365•c	TJ	16751	----
Successful use of energy of CO ₂ from ammonia plant during EOR operation	t=b•r•365•c	TJ	0	3,699
Net energy generated by the EOR project	u=p-t	TJ	0	29,488
Energy generated/EOR process efficiency	v=i•p	TJ/tCO ₂	0	0.045

^a Arteaga-Cardona et al. (2015); ^b Own estimates for Brillante field

Table 10. Key findings

CO ₂ -EOR performance	Unit	Value
Gross sequestration benefit	tCO ₂ /bbbl oil produced	0.203
Energy consumption	MJ per MJ oil produced	0.010
Energy for CO ₂ capture from ammonia plant	MJ/kgCO ₂	1.35
Incremental oil produced	Mbbbl	5.2
Energy generated/EOR process efficiency	TJ/tCO ₂ injected	0.045

Figure

Figure 1. Sources of anthropogenic CO₂ (1: Cosoleacaque Petrochemical Complex (CPC); 2: Minatitlán Refinery; 3: Morelos PQC and Cangrejera PQC) and oil fields (A: Brillante; B: Rabasa and C: Los Soldados)

Figure 2. General process flow of typical synthesis ammonia, sources of CO₂ emissions and uses in the case of the CPC

Figure 3. Study area, trajectory and distance (500 km) from pipeline

Figure 4. System boundary for Brillante CO₂-EOR project using CO₂ derived from ammonia process for EOR

Figure 5. Contribution like cycle GHG emissions of main activities

a:Hussaint et al. (2013)

Figure 6. Comparison results amongst this study versus lifecycle GHG emissions per barrel of oil extracted using different EOR methods

Figure 7. Effects of GHG emissions results for oil field operation (S1), geological sequestration (S2) and CO₂ capture from flue gas ammonia plant (S3) using different perspectives