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Environmental Evaluation of the Potential Impacts Generated by a Refinery Unit for Hydrogen Production from Natural Gas

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Hydrogen production process is one of the most coveted today, thanks to its multiple uses in the industry. It can be obtained through various methods, such as: electrolysis, reforming, biological methods and gasification. The production of hydrogen by this generations method begins with a natural gas feed stream, which requires a series of treatments where process equipment with associated an energy consumption is usually implemented. In addition, effluents, such as combustion waste gases, unreacted compounds, among others, are emitted into the environment. In the order to carry out the global analysis the hydrogen generation process, a simulation software was implemented, which allowed us to obtain operation process data. These processes usually tend to have certain impacts on the environment; In order to analyze this, an environmental assessment was executed in the WARGUI software that uses the waste reduction algorithm to quantify the total environmental impacts generated and outputted in the Hydrogen unit in two different topologies, the first is based on the actual configuration of a unit in a Latin American refinery where an external energy source is not needed because the residual combustion gases of the reformer are used in steam generation and heating other streams, for this the environmental analysis was carried out with two case studies. The second on is a hypothetical configuration in which 4 case studies were made, including a variation in the energy source. For both topologies 8 impact categories were evaluated.

1. Introduction

Hydrogen is currently one of the most desired products, since it is a clean fuel that is used in hydrogen cells. Hydrogen is also used in petroleum refineries for the desulfurization of crude oil and for the hydrocracking process (Wu et al., 2017). The facilities of NASA use liquid hydrogen as fuel in their rockets accompanied by fluorine or oxygen, as it is one of the flammable substances known until now. The process for obtaining hydrogen can be carried out by electrolysis, reforming, gasification, thermochemical cycles, geothermal energy (Karapekmez et al., 2018), solar hydrogen (Goto et al., 2017) or biological production, such as microalgae (Khelkop et al., 2017), through the fermentation of lactose (Tanzi et al., 2017), among others; in the case of the refinery, hydrogen is produced with a purity of 99.9% from steam reforming. The need to implement increasingly efficient and environmentally friendly processes forces the human being to look for ways to optimize and improve many of the processes to obtain hydrogen (Elsherif et al., 2015). For this reason, the environmental evaluation of the production of hydrogen from the steam reforming was developed, quantifying the environmental impact generated by the hydrogen production unit of a Latin American refinery and a topological modification; comparing the results generated and demonstrating which of these two options is the most favorable for the environment.

2. Methods

Simulation process and environmental evaluation of two topologies of a process for obtaining hydrogen with steam reforming was carried out, the first topology (Figure 1 (a)) is based on the real configuration of a Latin

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American oil refinery where the waste gases of the PSA, Pressure Swing Adsorption unit, (CEPSA, 2007) are used as fuel in the burners of the reformer, in the second topology (*Figure 1 (b)*), this stream is wasted at the same time that the sources of energy are varied to supply the energy duty.

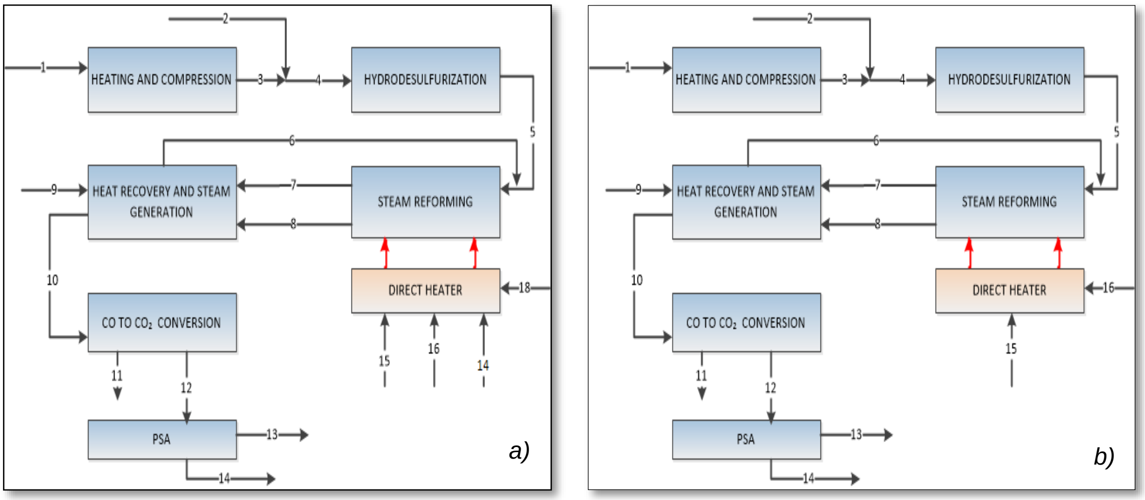

Figure 1: Block diagram for topologies of hydrogen production in refinery evaluated.

2.1 Simulation of topologies

In the steam reformer a simplified conversion model was taken into account for both the production of synthesis gas and for the combustion of a fuel heater that provides the heat necessary for the conversion of natural gas and steam into hydrogen. The Peng-Robinson model was used because the results obtained with this model are accurate when a process include hydrocarbons and gases (Marcelo, 2007), and have shown good results in modeling specifically hydrogen processes (Ersoz, 2018). The simulation of the process for obtaining hydrogen was carried out taking into account two topologies, one using a refinery located in Latin America as a reference (figure 1) which consists of a natural gas inlet (stream 1) to a pretreatment where it is compressed and preheated, then imported hydrogen is added (stream 2) to reduce the mercaptan content, converting them into hydrogen sulfide (H_2S), passing to a desulphurisation where the H_2S is eliminated and directed to a steam reforming (stream 5), where synthesis gas is produced. To increase production, the synthesis gas stream enters the reactor where the CO_2 obtained is converted to CO and hydrogen, the resulting gas is cooled to condense most of the steam. Finally, the synthesis gas enters a PSA unit (pressure swing adsorption) in (stream 12), separating most of the hydrogen (88 %), a residual current (stream 14) can be recirculated to a combustion system in the reformer. On the other hand, a model established by us of the same refinery, where the recirculation of the gases was eliminated (figure 2) does not present the recirculation (stream 14) but the evaluation of a power source (coal, gas, oil) in (stream 15).

Table 1: Main reactions involved in the process

Section	Equation	Base compound	Conversion (%)
Reformer	$C_nH_{2n+2} + nH_2O + heat \leftrightarrow nCO + (2n+1)H_2$	C_nH_{2n+2}	100
Hydrotreatment	$RSH(g) + H_2(g) \rightarrow H_2S + RH\ (g) + heat$	RSH	100
Desulfurization	$ZnO(g) + H_2(g) \rightarrow ZnS(s) + H_2O$	H_2S	96.8
Direct heater	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + heat$	CH_4	100
	$2H_2 + O_2 \rightarrow 2H_2O + heat$	H_2	100
	$CO + \frac{1}{2}O_2 \rightarrow 2H_2O + heat$	CO	100
CO to CO_2 conversion	$CO + H_2O(g) \leftrightarrow CO_2 + H_2 + heat$	CO	66.4

2.2 Environmental evaluation using WAR algorithm

WARGUI software was created by the United States Environmental Protection Agency (EPA) and uses the WAR (waste reduction algorithm) algorithm (D. Young et al., 1999) which is a method where potential environmental impacts (PEI) are evaluated, this is defined as the effect that a chemical would have in the environment if it were issued to the environment (EPA, 2011). The PEI is evaluated by WAR in eight categories of environmental impacts; collected in two groups: toxicological impacts, Potential human intoxication by ingestion (HTPI); Potential human intoxication due to dermal exposure or inhalation (HTPE); Potential terrestrial toxicity (TTP); Potential aquatic toxicity (ATP); and atmospheric impacts Potential global warming (GWP); Potential destruction of ozone (ODP); Potential formation of photochemical smog (PCOP); Acidification potential (AP). Unlike the life cycle, the WAR algorithm represents the results per unit of time, which represents a benefit for environmental assessment (Herrera et al., 2017).

The implementation of the WAR algorithm is based on two different topologies; the first topology (based on the real data plan of a Latin American oil refinery), in the first case study (case 1) the evaluation is carried out without considering the products (hydrogen and steam); in the second case (case 2), the evaluation is made considering the products of this topology. In the second topology, which is based on a reform to the conventional process, 4 case studies were carried out, the base case (case 1) where the impacts of the products or of the energy were not considered; the second case of this topology (case 2), in which only the impacts of the products were taken into account; the third case of this topology (case 3), in which energy impacts are evaluated, the fourth case of this typology (case 4) includes the impacts of both products and energy.

3. Results and discussion

3.1 Simulation results

Only main products of the process (outlet streams) are shown in table 2. Molar flow of inlet streams from data plant were introduced to the process simulation software. It can be observed that a simple conversion model predicts accurately behavior of the hydrogen unit.

Table 2: Simulation results

Stream	Molar flow (kmol/h)	
	Plant	Simulation
Hydrogen product	2,508.86	2,508.16
Steam	1,598.03	1,823.72

3.2 Topology 1

3.2.1 Total Potential Environmental Impacts

In Figure 2, the PEI generated was negative for both cases of study, in both results by units (mass and time) that manages the WAR algorithm, which indicates that the process internally has a good environmental performance. When can also see that possible environmental impacts of this unit are not influenced by the products, since they are steam (water) and hydrogen and the most of PEI are caused by combustion gases in the reformer.

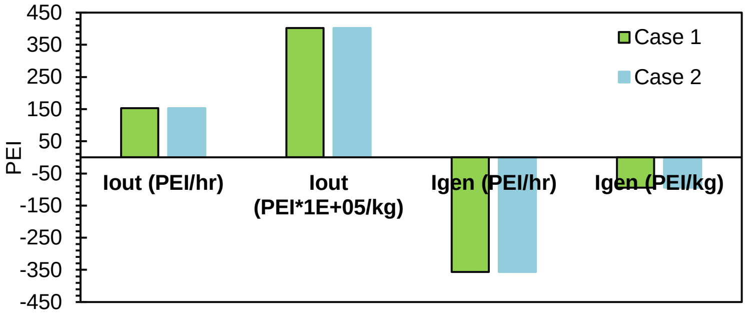

Figure 2: Total Potential Environmental Impact (PEI), topology 1

3.2.2 Local toxicological and atmospheric impacts

The present analysis shows the local toxicological impacts generated and the result of the process, Figure 3, includes human impacts (HTPI and HTPE) and ecological impacts (ATP and TTP). It is identified that the highest possible impacts generated from the Hydrogen unit are those of the ecosystem category, with Potential Aquatic Toxicity (ATP) being the highest within the process and with the output of the product (24.5 PEI / h , 39.3PEI/ h, respectively), in addition to the terrestrial and human ingestion toxicological impacts are the same when the products are released and inside the process (5.58 x 10^-5 PEI/h, 21.1 PEI/h respectively), negligible HTPE impacts are considered.

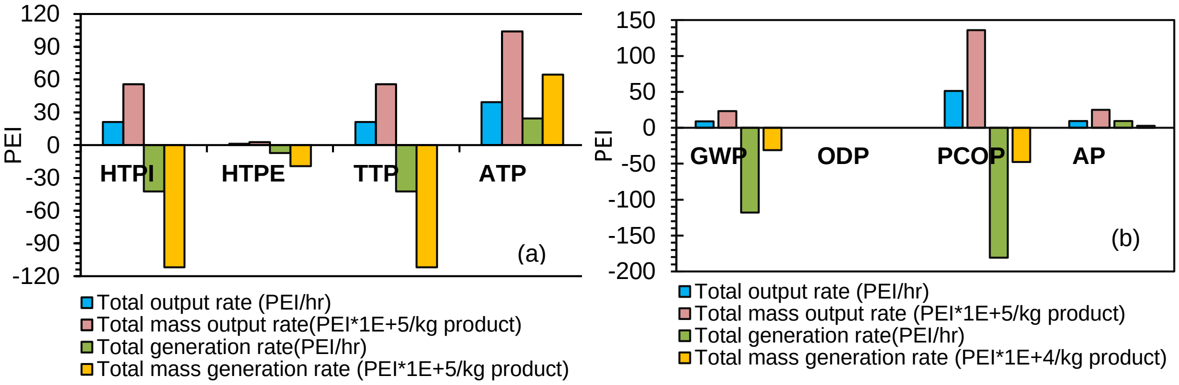

Figure 3: (a) Toxicological and (b) atmospheric impacts of hydrogen unit in refinery under topology 1

Figure 3 (b) identifies the possible atmospheric impacts generated by the hydrogen unit and is evaluating global (GWP and ODP) and regional impacts (AP and PCOP), in this graph it can be seen that the impacts of the AP and GWP categories they are minimal, when talking about product outputs and generated, in addition that the ODP impacts are zero for this case study, in the case of the PCOP category, if a higher value is found for the output impacts per unit of mass, this is due to the amount of residual gases that leave the PSA to the burners, here what is known as smog occurs causing the increase in the category. In Figure 4, it is possible to stand out at the time of performing the environmental assessment, taking into account the energy used in the process, a high increase is seen in each of the PEIs within the systems, as well as in the output of this system. impacts generated inside the system when case 1 and 3 are taken into account, are negative or do not generate impacts, and in the PEI of output it is identified that when case 1 or 3 is being worked there will be no significant change in the possible impacts generated.

3.3 Topology 2

3.3.1 Total Potential Environmental Impacts

In Figure 4, it is possible to stand out at the time of performing the environmental assessment, taking into account the energy used in the process, a high increase is seen in each of the PEIs within the systems, as well as in the output of this system. impacts generated inside the system when case 1 and 3 are taken into account, are negative or do not generate impacts, and in the PEI of output it is identified that when case 1 or 3 is being worked there will be no significant change in the possible impacts generated.

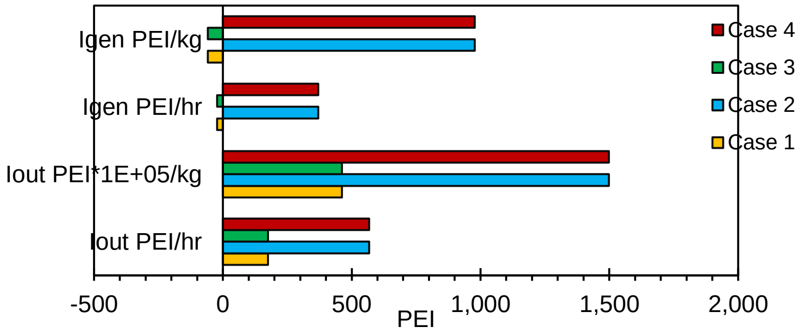

*Figure 4**:** Total Potential Environmental Impacts (PEI), topology 2*

3.2.3 Local toxicological and atmospheric impacts

In figure 5 (a) it is possible to highlight that the impacts HTPI and TTP are zero for the total of possible impacts of output and negative for the generation of the process which means that they reduce the impact of these categories, for the categories ATP and HTPE is achieved identify a significant increase in the possible impacts generated for the total output, this being the highest with (1.07 x 10^-4 PEI/kg and 5.73 x 10^-5 PEI/kg, respectively).

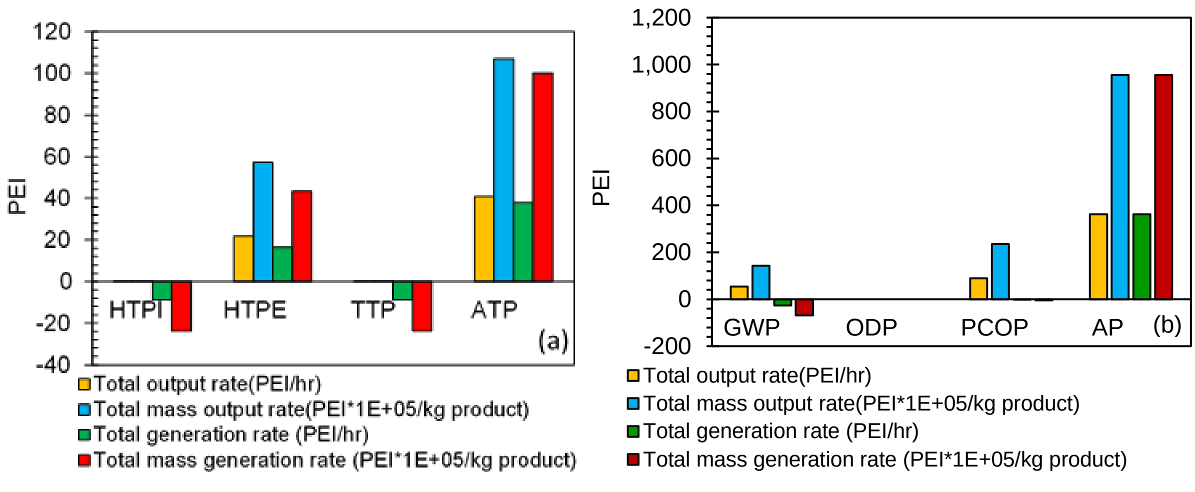

Figure 5: (a) Local toxicological and (b) atmospheric impacts of the process

In Figure 5 (b), the possible atmospheric impacts generated by the Hydrogen unit are identified global (GWP and ODP) and regional impacts (AP and PCOP) are being evaluated, it is highlighted that there are no impacts by the ODP category, and that the GWP and PCOP categories are minimal compared to PA, the drastic increase in the AP category is due to the fact that the residual gases of the PSA are no longer being used causing acid rain.

3.2.4 Effect of energy source

Three types of fuel (gas, coal and oil) were evaluated for each impact category, including energy and excluding the flow of products. Figure 6 shows the change in the production of PEI according to the type of fuel used in the production unit, it is observed that by using irregular behaviors in the three different types of fuels, in addition to the oil fuel increases the category TTP and HTPE, although it is lower in other categories with respect to gas and coal such as PCOP.

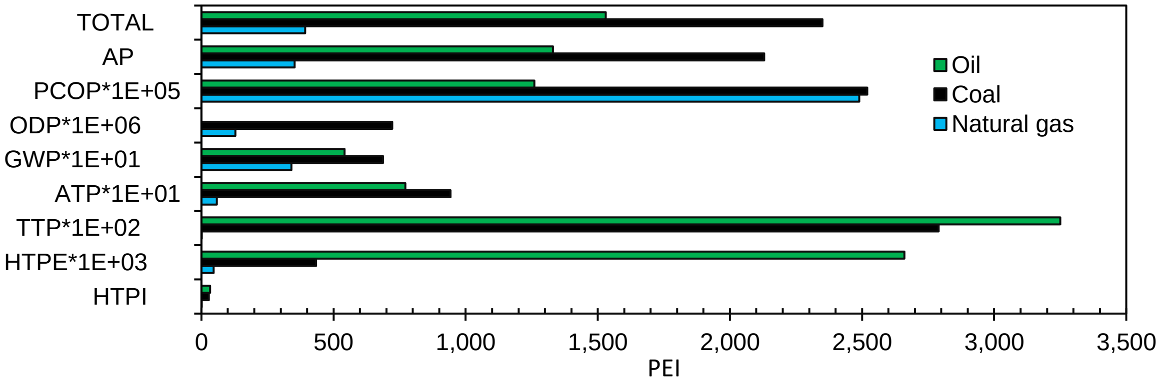

Figure 6: Effect of energy source

4. Conclusions

The waste reduction algorithm has been used for the environmental analysis of the hydrogen production unit in the refinery, both in normal operation and with the incorporation of an energy system. From the results obtained, a series of comparisons were made. In the total of impacts generated within the Hydrogen unit it is possible to observe a notable increase when the residual steam of the PSA is not recirculated. It is recommended that operators maintain the recirculation of the PSA output to the burners in the hydrogen unit studied, because it generates less environmental impacts. It is found that the category of toxicological impacts by ingestion in humans (HTPI) disappears at the time of eliminating waste gas recycling of PSA, but it seems that it is generating toxicological impacts by dermal exposure (HTPE) the results remain (5.58 x 10 ^ -5 PEI/kg and 5.73 x 10 ^ -5 PEI / kg, respectively), this is due to the fact that the gases would not go directly to the environment, since the impacts generated atmospherically by eliminating the use of energy in the burners generate greater impact in category (AP) indicating the formation of acid rain (362 PEI/h), in both studies with changes and in the normal operation of the unit the potential aquatic toxicology category can be seen elevated this is due to contamination by the acid rain and outside due to the formation of smog that prevents sunlight from entering the water sources, finally, in the study of the type of fuel when it is omitted recirculation it is noted that petroleum fuel increases the TTP and HTPE category (32.5 PEI/h and 2.66 PEI/h, respectively), although it is lower in other categories with respect to gas and coal.

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