FLOWCHART MONITORING FOR THE DEVELOPMENT OF SUSTAINABLE PROCESSES USING THE WASTE REDUCTION ALGORITHM IN A NATURAL GAS PRODUCTION PLANT

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ABSTRACT
This paper presents a flowchart monitoring study to be used on investigating conditions that can promote environmental impact. The study relies on a computational simulation of the natural gas separation process, using COCO modeling software and communication of the WAR algorithm. The WAR algorithm is a methodology used to analyze the potential environmental impact (PEI) of a chemical process, and to study the environmental compatibility of this process. The WAR algorithm proved efficient and effective when accessing the CCO currents to obtain pressure and temperature parameters of each equipment used in the modeling and simulation of the plant. The results indicate the need for optimization requiring further research on ways to reduce the impact generated by the terrestrial toxicity potential, the toxicity potential for man, and the photochemical oxidation potential, which presented higher PEI generated in the process.

KEYWORDS
COCO simulator; Potential Environmental Impact; modeling; natural gas separation, WAR algorithm

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1. INTRODUCTION

Natural gas is a petroleum-derived compound that is considered a strong world power and is used extensively in petrochemical (as a combustion gas or a raw material in the production of hydrogen gas) and automotive industries (as a fuel). Its sustainability and price have justified a considerable increase in its consumption. Burning natural gas is significantly less aggressive to the environment, when compared to other fossil fuels, such as gasoline and diesel (Luyben, 2013).

To extract crude oil, first, it is necessary to remove the natural gas of the wells both offshore and onshore. After extraction, the fuel undergoes a primary treatment process to separate oil, gas, and water. This gas, called natural gas, is composed of light hydrocarbons (methane, ethane, propane, and butane), which are sent directly to the petrochemical industries for secondary treatment, for removing impurities such as CO₂ and H₂S (Wang & Betley, 2020).

The increased interest in environmental protection has motivated the development of a growing number of researches that target promoting the use of fuels that are less aggressive to the environment. In recent years, natural gas has been used widely for being considered less polluting than other alternatives available. However, as renewable energy source, it does not yet have a sufficient level of maturity and technology to make communities independent of fossil fuels (Aregbe, 2017; Wood et al., 2012).

Process control is of fundamental importance for any organization that wants to increase its profitability and reduce the final cost of its products. Process simulation has great relevance in this aspect. It is a field of engineering that has gained the attention of large companies for having this differential of measuring a productive process without needing a pilot model for such analysis (Mourtzis et al., 2014). Researchers have proposed the use of Computer Aided Process Engineering (CAPE) software to evaluate process design alternatives, but they have reported difficulty in obtaining accurate information about the process (Pons, 2003).

An alternative to the use of simulators, the CAPE-OPEN (COCO simulator) is a software that offers tools for modeling, simulating, and optimizing chemical processes. This software allows users to explore several options throughout the process. Thermodynamic packages and unitary operation models can be used in different process modeling environments directly, while the current CAPE-OPEN standards are focused primarily on the interoperability between process modeling (Barret Jr et al., 2011).

Currently, the COCO simulator, developed by EPA (Environmental Protection Agency), has an application called WAR (Reduction Algorithm) that allows the calculation of the PEI (Potential Environmental Impact) of each equipment and the whole process. This WAR algorithm adds access to the chemical flows and unit operations directly from the PME and calculates the WAR (PEI) for the process modeled using the process data obtained directly from the flowchart. Users have the option to select the entire flowchart or a subgraph of the individual unit operations for the WAR evaluation (Cardona et al., 2004).

The present work highlights a novel aspect of the WAR utilization in a natural gas separation process, including the COCO approach. The objective of the present work is to make, with the aid of the WAR algorithm and the COCO software, the environmental impact study in the process of the natural gas production.

1.1 Energy balance

Figure 1 shows the primary energy production by source between 2007 and 2016. Note that the production figures in a tonne of equivalent oil (TEP) of renewable and non-renewable sources.

The data show that natural gas is the second most non-renewable source of energy produced in Brazil. The period from 2007 to 2016 shows the growth of the continuous production of nonrenewable primary energy, see Figure 1. About 99 percent of the world’s primary energy comes from fuels such as oil, coal, and natural gas. The rest of the primary energy comes from a renewable source, such as hydroelectric power, wind energy, and solar energy, the latter representing only a small fraction. According to the data released by the Brazilian government (Brasil, 2015), natural gas is produced generally in conjunction with petroleum, and it accounts for 11.3% of Brazil’s energy consumption. It is used mostly in the production of liquified petroleum gas- LPG (cooking gas), in industries and thermoelectric plants, and in the production of motor fuels.
2. MATERIALS AND METHODS

This work used a software for modeling and simulating the process of natural gas purification. It also used an algorithm called "WAR algorithm" for analyzing the environmental impact of the process. However, to model the entire process, we used the thermodynamic model for one of the main phases of the flowcharting process because it allowed us to select components that would react according to distinct boiling points since, under different temperatures and pressures, components react according to the particular volatility of each one of them.

The potential of environmental impact in a process involves observing the effects of both energy and material used. In the present study, we used, in parallel with the COCO simulator, the WAR algorithm. Currently, CHEMCAD has an integrated WAR application. The implementation made available is the one developed and included in the COCO.

The COCO version makes use of an early version of the Flowsheet monitoring interfaces. Flowsheet monitoring interfaces are expected to be finalized and adopted more widely. Thus, tools such as WAR can be used in any simulator to measure the environmental impact potential generated by the analyzed plant, the equations that describe the calculation of the environmental impact potential, and the categories analyzed by the WAR algorithm, as shown in equations 1 and 2.

\[
\frac{dl_{\text{system}}}{dt} = I_{in} - I_{out} + I_{gen} 
\]

\[
I_{out} = \sum_{i=1}^{\text{flows}} \sum_{j=1}^{\text{streams}} \sum_{k=1}^{\text{component}} \alpha \left( M_j^{(\text{in})} x_k \psi_k j \right) 
\]

The input and output equations above show the fluid material - points "M" - and compositions/molar fractions "x" - values for k component in the flow of "j" - and are part of the equilibrium equation. The specific PEI factor for "k" component in category "i" is the value of "k" of sub psi commas "i". "X" is the composition; "H" point is the mass flow of a feed stream or product. The superscripts for PEI values indicate that these values are specific; resulting from the value of a particular chemical, normalized by the average value of many chemicals.

2.1 Peng Robinson's Equation of State

To achieve excellent reliability with simulations, the equipment must be operated at high pressures.
(greater than 5 bar) and use ideal thermodynamic models. These models will be able to predict temperatures and pressures in and out of the equipment, as well as volume, density, and energy, among other variables.

One of the most used equations to calculate the compressibility factor \( Z \) is the Equation of the State in cubic form. 

\[ Z = \frac{P.V}{RT} \]  

\[ Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - AB + B^2 + B^3 = 0 \]  

\[ m = 0.480 + 1.574w - 0.17w^2 \]  

\[ a(T) = \left[ 1 + m(1 - \sqrt{T_c}) \right]^2 \]  

\[ a = \frac{0.45724R^2T_c^2 \propto (T)}{P_c} \]  

\[ a = \frac{0.07780RT_c}{P_c} \]  

Thus, with all these constants, values of \( A \) and \( B \) are calculated and replaced in the cubic equation of Peng Robinson. This equation will have three roots. The nearest of 1 will be considered the \( Z \) value in the gaseous state, the nearest of zero will be the \( Z \) value for the liquid state, and the root value in the medium will have no physical significance.

### 2.2 Introduction WAR algorithm

The use of the WAR algorithm “Waste Reduction,” presents a method for the study of environmental impact in chemical processes. It is not a tool for life-cycle analysis. The WAR algorithm takes into account the production aspects of the product life cycle, so it does not consider other stages of the life cycle, such as product distribution, acquisition of raw material, elimination of the product, recycling of the product, and use of products.

The flowchart in Figure 2 illustrates an example of how the WAR algorithm acts in the complete life cycle of a product. This method can be used at any stage of a process or even in an improvement that already exists.

- **Process of Transformation**
- **Product Distribution**
- **Product Use**
- **Recycling**
- **Product Abandonment**
- **Ambient**

Figure 2. WAR Algorithm performance.
Material and energy can be characterized based on the potential of environmental impact that they may have on the environment. Therefore, this affirmation implies that the impact is something that has not occurred yet or that is about to occur. However, this is probabilistic. Since the environmental impact is something conceptual that cannot be measured directly, we have developed a theory to measure the environmental impact using a quantitative model, as we will show in the course of this work.

2.3 Environmental impact assessment

In general, the environmental impact balance (PEI) represents the potential of (PEI) entering the system and leaving the system, which is being generated by the system as well as what is also accumulated by the system (PEI). The dotted line refers to the boundary of the system represented in Equation 2. This approach was based on the work of Cabezas et al. (1999). The expression related to the energy consumption in the chemical process is described in Equation 11.

\[
\frac{dI_{\text{system}}}{dt} = I_{\text{in}}^{(cp)} + I_{\text{in}}^{(ep)} - I_{\text{out}}^{(cp)} - I_{\text{out}}^{(ep)} - I_{\text{we}}^{(cp)} - I_{\text{we}}^{(ep)} + I_{\text{gen}}^{(ep)}
\]

\( I_{\text{system}} \) represents the PEI within the system “chemical process plus energy.” \( I_{\text{in}}^{(cp)} \) and \( I_{\text{out}}^{(cp)} \) refer to the PEI rates of entry and exit of the chemical process, in the same way \( I_{\text{in}}^{(ep)} \) and \( I_{\text{out}}^{(ep)} \) are the PEI input and output rates of the power generation process, respectively. \( I_{\text{we}}^{(cp)} \) and \( I_{\text{we}}^{(ep)} \) are the outputs of the PEI linked to the energy waste that is lost in the chemical and the energy generation processes. Lastly, \( I_{\text{gen}}^{(ep)} \) represents the rate of PEI generation within the system, for the chemical process \( I_{\text{gen}} \) corresponds to the production and consumption of the PEI by the reactions in the process. For the steady-state process, Equation 11 is reduced to Equation 12. It is necessary to describe the concept of PEI in measurable quantities, a method has been developed to understand the PEI in a quantity that is measurable such as mass flow, compositions, and the total PEI of a given chemical component (\( \Psi_k \)), which method has been extended to take into account the process energy generation. The equations that correspond to the chemical components are showed below (Equations 13-15).

\[
i_{\text{in}}^{(cp)} = \sum_j^{cp} i_j^{in} = \sum_j^{cp} M_j^{in} \sum_k x_{kj} \Psi_k + \ldots
\]

\[
i_{\text{out}}^{(cp)} = \sum_j^{cp} i_j^{out} = \sum_j^{cp} M_j^{out} \sum_k x_{kj} \Psi_k + \ldots
\]

\[
i_{\text{we}}^{(cp)} = \sum_j^{cp} i_j^{we} \Psi_{we} x_{kj} \approx 0
\]

Where \( i_{\text{in}}^{(cp)} \) represents the rate of PEI entering (\( i = \text{in} \)) or leaving (\( i = \text{out} \)) the process. \( i_j^{(i)} \) is the PEI rate of current \( j \) that is found or output; \( M_j^{(i)} \) is the mass current rate \( j \), which can be input or output; \( x_{kj} \) corresponds to the mass fraction of the component \( k \) of the current \( j \); \( \Psi_k \) is the PEI of the chemical component \( k \); \( \Psi_{we} \) is the rate of PEI correlated to the energy residue allowed by the chemical process, and \( \Psi_{we} \) is the PEI for energy waste.

The energy residue index, that is acceptable in the chemical process concerning the environment, produces an inevitable impact. However, this impact can be neglected since \( \Psi_k \) is assumed to be zero because (a) chemical process plants do not emit a large amount of energy into the environment and (b) chemical process plants’ PEI correlated with mass emission has a value far higher than that of energy.

The expressions that associate the generation of energy in the process are presented in Equations 16-18.

\[
i_{\text{in}}^{(cp)} = \sum_j^{cp} i_j^{in} = \sum_j^{cp} M_j^{in} \sum_k x_{kj} \Psi_k + \ldots
\]


\[ i_{\text{out}}^{(cp)} = \sum_{j}^{cp} i_{\text{out}}^{j} = \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \]

\[ + \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \ldots \approx 0 \approx \]

\[ = \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} \]

\[ i_{\text{we}}^{(cp)} = \sum_{j}^{cp} \dot{E}_{j}^{\text{cp}} \Psi_{\text{we}} \approx 0 \]

\[ i_{\text{in}}^{(cp)} \] represents the rate of PEI that is entering or leaving the power generation process, \( i_{\text{we}}^{(cp)} \) corresponds to the PEI correlated to the energy residues that is being lost in the process in which there is the generation of energy, \( \dot{E}_{j}^{\text{cp}} \) refers to the rate of energy waste lost in the power generation process, and \( \Psi_{\text{we}} \) is the PEI of energy waste.

Very similar to the analysis of chemical processes, the environmental impact potential related to mass emission is much higher (higher) if compared to the emission of energy residues, \( \Psi_{\text{we}} \) is very close to zero.

### 2.4 Environmental impact indexes (product and non-product)

Equations 3 - 10 can be used to measure the environmental impact efficiency indexes in a given process. There are currently two different index classes:

- Correlated the environmental impact of exit;
- Correlated with the environmental impact of generation.

The two exit indexes are considered the most important. They are the total environmental impact rates of exit \( i_{\text{gen}}^{(t)} \), described by Equations 19-20 (Petrescu & Cormos, 2015).

\[ i_{\text{out}}^{(t)} = i_{\text{out}}^{(cp)} + i_{\text{we}}^{(cp)} + i_{\text{out}}^{(cp)} + i_{\text{out}}^{(ep)} = \]

\[ = \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \]

\[ + \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} \]

\[ = \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \]

\[ = \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \]

\[ = \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \]

Where \( P_{p} \) is mass flow rate of product p and the sum taken over all product streams p of the generation indexes, the two most important ones indexes are, similarly, the total rate of impact generation \( f_{\text{gen}}^{(t)} \) and the total impact generated per mass of product, \( f_{\text{gen}}^{(t)} \), defined by Equations 21 and 22.

\[ f_{\text{gen}}^{(t)} = i_{\text{out}}^{(cp)} - i_{\text{in}}^{(cp)} + i_{\text{we}}^{(cp)} + i_{\text{out}}^{(cp)} + i_{\text{out}}^{(cp)} = \]

\[ = \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \]

\[ + \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} \]

\[ f_{\text{gen}}^{(t)} = \frac{i_{\text{out}}^{(cp)} - i_{\text{in}}^{(cp)} + i_{\text{we}}^{(cp)} + i_{\text{out}}^{(cp)} + i_{\text{out}}^{(cp)}}{\Sigma_{p} P_{p}} = \]

\[ = \frac{\sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k} + \sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k}}{\Sigma_{p} P_{p}} = \]

\[ + \frac{\sum_{j}^{cp} \frac{M_{j}^{\text{out}}}{\Sigma_{p} P_{p}} \sum_{k} x_{jk} \Psi_{k}}{\Sigma_{p} P_{p}} \]

In general, the lower the value of these indexes are, the higher the environmental efficiency of a process will be, that is, the less potential impact that the process will probably have on the environment. However, the effort to design processes with lower impact indexes needs to be constrained by considerations of engineering economics and social needs. After all, one could conceivably turn off the process that would bring all mass flow rates to zero and the whole indexes to zero. This is not the goal here because it ignores the fact that there may be a human need for the products that the processes manufacture (Moreno-Sader et al., 2020).

### 2.5 Impact balances and indexes: non-products and energy

There are cases where the inclusion of products in the potential environmental impact balance and Equations 16-22 indexes may be considered
inappropriate:

- When an intermediate product is fed directly into another production process;
- When the environmental impact of a product is disregarded due to its social need, for example, chemotherapeutic agents used to treat neoplasm are all highly toxic, and, still, no one would consider stopping their production;
- When the purpose of the analysis is just targeting the reduction of waste given a particular product and process that, for economic or other relevant reason, cannot be changed.

The exclusion of products comes from the fact that these products are not included in the sums on components k, or the potential environmental impact index of all products k is assumed to be zero ($\Psi = 0$). In these cases, we would use the same Equations (3) - (12) for considering them as appropriate, but we would not include the products. Withdrawing the products has the benefit of giving a greater focus to the analysis of waste reduction and its potential environmental impacts. Nevertheless, excluding products may come at the expense of losing the opportunity to consider the real potential full environmental impact of the process which, by necessity, must include the products (Moreno-Sader et al., 2020).

2.6 Environmental impacts on chemical processes

Communication of the WAR algorithm requires a definition of the categories of environmental impacts, so that chemical impacts emitted may be quantified relatively. Impact indexes are used to quantify the environmental impacts generated by chemical processes.

2.7 Chemical impact expression: Component k

The potential global environmental impact of chemicals k and $\Psi_k$, can be measured by summing the potential environmental impact of chemical substance k and $\psi_{kl}$ on all possible impact categories. Based on these observations, we have the following Equation 23.

$$\Psi_k = \sum_i \alpha_{i\psi_{kl}}$$

The expression $\alpha_i$ corresponds to the weighting factor relative to impact category 1. For the units specified therein, the environmental impact index has to be the potential of the individual PEI of substances k/mass in substance K. The weighting factor should be, of course, dimensionless.

Therefore, the relative weighting factors, $\alpha_i$, are used to express the importance of the categories of environmental impacts. Typically, the weighting factors should vary between 0 and 10. However, this may change. The user must assign weighting factors according to specific process conditions. The weighting factors should emphasize or not specific concerns that are relevant or irrelevant to their process and local conditions.

As the primary goal of this algorithm is to determine the relative environment impact indexes of a process project that is ultimately compared to alternative designs, the actual values of the weighting factors are not critical relative values. Weighting factors are essential for this methodology in that they allow the combination of impact categories.

2.8 Environmental impact data bank

To communicate the WAR algorithm, the specific potential of the environmental impacts of each chemical in the database, $\psi_{kl}$, had to be determined. The ChemCad 4.0 chemical process database needed to be triggered. There are about 1,600 chemical substances in this database, values $\psi_{kl}$ are normalized within each impact category. There are two reasons for this. First, standardization will ensure that values from different categories contain the same units to allow for their combination (Barret Jr. et al., 2011). Second, adequate normalization will ensure that the values of different categories will have similar average scores. Without the second condition, the implicit weighting factors present in the chemical database would cause unintended bias in the calculation of the PEI indexes. The scores used in the WAR algorithm will be calculated using the normalization scheme described in Equation 24.
The Score $k_l$ corresponds to the value of substances $k$ on a random scale in category $l$. The $\langle \text{Score} \rangle_k$ represents the mean value of all chemical substances that make up category $l$.

### 2.9 Process description

The most expensive massive hydrocarbon recovery of natural gas is carried out in a series of five distillation columns. The first and second columns are high-pressure cryogenic columns in which methane and ethane are sequentially absorbed. The third column produces a propane distillate. The fourth column removes isobutane and standard butane overhead for separation in the fifth column. The bottom product of the fourth column is a mixture of hydrocarbons that are heavier than the C4 components.

The first and last columns require composition controllers to effectively deal with disturbances in the composition of the feed. Operational details of the column process can be found in Figure 3. The present plant studies the dynamic control of this train of distillation columns and useful control structures because they are developed and tested in all the columns using Controllers.

The painful separation in the large reflux ratio and high butane splitter is well controlled by an unusual control structure that regulates the reflux level. The composition of the natural gas varies from source to source. Usually, it uses a series of distillation columns made mainly by methane (85 mol% C1) with small amounts of ethane (C2), propane (C3), isobutane and normal butane and nC4) and heavier hydrocarbons up to the C7. The C2 and heavier components are called liquid natural gas (NGL). They are more valuable than methane, so their recovery is desired (Luyben, 2013).

First, methane is separated at high pressure (25 atm) in the cryogenic distillation column using expansion to generate low temperatures (180 K). A complex configuration of the conventional and intermediate reboilers are used to provide steam and cooling in the feed. Two exchangers, one expander, two flash drums, and the valves are used to produce four different column feed flows. They are designed to achieve two objectives: to recover a desired percentage of ethane in the feed and maintain a low concentration of methane in its bottom product (Luyben, 2013).

The third column has the function of producing a propane distillate. So that the cooling water can be used in the condenser, it operates at 17 atm with a reflux temperature of 322 K. It is designed to achieve set concentrations of isobutane impurity in the distillate and propane impurity at the bottoms.

The fourth column has the objective of bringing isobutane to usual butane overload with higher separation in the column. This separation $iC4 / nC4$ is the most difficult one (relative lower volatility) out of all distillations, so it is more economical to remove the other, more light and heavy, components first and, then, run it. This column operates at 7.1 atm at the reflux temperature of 322 K so that the cooling water can be used in the condenser. It is designed to achieve concentrations of isopentane impurity in the distillate and standard butane impurity in the back.

Figure 3 shows the complete modeling of the natural gas purification process using the COCO process simulator. The final column has the function of producing a distillate product of isobutane and a normal butane lower part. For cooling water to be used in the condenser, the column operates at 6.6 atm with a reflux temperature of 322 K. The process is designed to achieve specified concentrations of standard butane impurity in the distillate and isobutane impurity in the back.

### 3. RESULTS AND DISCUSSIONS

The COCO Simulator uses an algorithm to calculate the analysis of the potential environmental impact generated in the natural gas separation process. To this end, the use of the flowchart monitoring interface implemented in the COFE process simulation environment allows easy access to unit operations and material flows through the CAPE-OPEN interfaces.

The complement of the WAR algorithm demonstrated in this document uses the flow chart monitoring interfaces to perform an environmental analysis of the process modeling. It provides the flexibility of being able to not only consider the
flowchart as a whole but also conduct the evaluation in a subset of the flowchart. Table 1 shows the total rate of PEI generation in the system by hour and by product mass.

While the HTPI has the potential for toxicity to humans upon ingestion; the HTPE has the potential for human exposure toxicity (contact with skin or inhalation); the TTP is the terrestrial toxicity potential; ATP is the aquatic toxicity potential; GWP is the global warming potential; ODP is the ozone depletion potential; PCOP is the photochemical oxidation potential and AP is the acidification potential. When accessing the flows of the flowchart, the WAR algorithm presents the total PEI/h within the system. Note that the data associated with the PCOP category corresponds to a negative value, so the total PEI generated by the system corresponds to $-6 \times 10^4$ calculated according to Equation 12.

In this example, we considered the flowchart as a whole, so we included all unitary operations. The resulting feed flows are immediately visible; we have the product flows. Some of these are considered waste, and some of them are considered products, we have to specify which of these are products.

![Flowchart of COCO natural gas separation plant.](image)

**Figure 3.** Flowchart of COCO natural gas separation plant.

| Environmental Impact | Total PEI/h | Total PEI/product mass |
|----------------------|-------------|------------------------|
| HTPI                 | $-3.50 \times 10^4$ | $-3.43 \times 10^{-2}$ |
| HTPE                 | $-9.21 \times 10^2$ | $-9.04 \times 10^{-3}$ |
| TTP                  | $-3.50 \times 10^3$ | $-3.43 \times 10^{-2}$ |
| ATP                  | $-4.99 \times 10^3$ | $-4.90 \times 10^{-2}$ |
| GWP                  | $-4.10 \times 10^3$ | $-4.02 \times 10^{-3}$ |
| ODP                  | 0            | 0                      |
| PCOP                 | $-3.69 \times 10^4$ | $-4.60 \times 10^{-1}$ |
| AP                   | 0            | 0                      |
| Total                | $-6.02 \times 10^4$ | $-5.91 \times 10^{-1}$ |

HTPI: potential for toxicity to humans upon ingestion; HTPE: potential for human exposure toxicity (contact with skin or inhalation); TTP: terrestrial toxicity potential; ATP: aquatic toxicity potential; GWP: global warming potential; ODP: ozone depletion potential; PCOP: photochemical oxidation potential; AP: acidification potential.
A potential environmental impact is also associated with energy, but this depends on which energy source we use. A selection of parameters with the potential for environmental impact is available for various types of energy. The factors for the relative weights $\alpha_i$ were taking into consideration the units. Since $\alpha_i = 1$ was used in all $i$ categories, we also calculated how much each chemical component would be polluting in the studied plant. Figure 4 illustrates the PEI potential for each chemical component.

As we can see, methane, ethane, and propane emit a more considerable amount of pollution in the atmosphere than the other components used in the analyzed plant. This is because the flows of the respective streams with these components are high as shown in Figure 3 where the flowchart presents all plant specifications.

The WAR algorithm, after accessing the flows of the flowchart, imitates a final report with all data referenced in the PEI. Generated by the process, the equations representing this environmental impact balance, represented in Topic 3.8 of this work, form the equation (Equation 24) as the final result. We can observe the normalized impact score based on each score in Figure 5.

In the calculation of the environmental impact potential, we can observe that the potential for terrestrial toxicity, the toxicity potential for man, and the photochemical oxidation potential are more evidence concerning the "Fima" or "environmental impact" analysis.

The appropriate mechanisms will determine the assessment of the scores for each of the 1600 chemicals in each of the impact categories. Data for the four global categories of atmospheric impact were taken from the values published by Heijungs et al. (1992). A summary of his methodology for determining these parameters would be informative and, thus, it is presented below.
The GWP is determined by comparing the extent to which a unit mass of a chemical absorbs infrared radiation over its atmospheric lifetime to the extent that CO₂ absorbs infrared radiation over its respective lifetimes. The half-life of each of these chemicals has been factored into the calculation to determine the GWP, since the chemicals have different atmospheric half-lives. The period during which the comparison is made will change the GWP of a chemical to this database. 100 years was chosen as the base period. The ODP is defined by the comparison between the rate at which a unit mass of chemical reacts with the ozone to form molecular oxygen at the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen. For a chemical to have ODP, it must exist in the atmosphere long enough to reach the stratosphere. It must also contain a chlorine or bromine atom.

PCOP or smog formation potential is defined when comparing the rate at which a unit mass of chemistry reacts with a hydroxyl radical (OH) at the rate at which one unit of ethylene mass reacts with OH. The AP or acid rain potential is determined by comparing the rate of H₂⁺ release in the atmosphere promoted by a chemical to the rate of release of H₂⁺ into the atmosphere promoted by SO₂.

Two categories were determined for the estimation of human toxicity potency: ingestion and inhalation, because they judged all the primary routes of exposure of a chemical. HTPI were calculated for a chemical if it existed as a liquid or solid state at a temperature of 0°C, atmospheric pressure, and potential for exposure. The HTPE was defined for that chemical if it existed as a gas under these conditions. Some chemicals, however, were assigned values for both categories if they were guaranteed.

As a first approximation, the lethal dose killed 50% of rats by oral ingestion (LD₅₀) was used as an estimate for HTPI. For the chemicals for which a rat LD₅₀ value was not available, a value estimated by molecular methods LD₅₀, typically reported in units of mg of chemical: kg rat. Analyzing this balance, it becomes quite apparent that a chemical with a higher LD₅₀ represents a chemical with lower toxicity. To estimate the HTPE, we used the time-weighted averages of the limit values. These values obtained from OSHA, ACGIH, and NIOSH represent the occupational safety limits. That was considered a suitable rod measurement for comparison of chemicals that would pose a threat to human health through inhalation and exposure routes. Only a relative comparison within the categories is required for this methodology.

The ATP was estimated using toxicological data for a single and representative specie of fish; this specie was chosen because of its acceptance as a universal aquatic indicator and prevalence data. Data for these assays come in the form of an LC₅₀, a lethal concentration that causes death in 50% of the test specimens.

4. CONCLUSIONS

The simulations obtained in the COCO presented satisfactory results for each equipment. The simulations promoted the purification of the natural gas, as well as the change of the input parameters. The WAR algorithm proved efficient and effective in accessing the COCO currents to obtain pressure-temperature parameters of each equipment used in the modeling and simulation of the plant. The results indicate the need for a plant optimization study to reduce the impact generated by the terrestrial toxicity potential, the toxicity potential for man, and the photochemical oxidation potential presented higher PEI generated in the process. Based on the results obtained in the present work, the computer assisted simulations can optimize time in a manufacturing environment as well as contribute significantly to the environmental issues cited here.

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