Designing sustainable processes with simulation: the waste reduction (WAR) algorithm

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Abstract

The WAR algorithm, a methodology for determining the potential environmental impact (PEI) of a chemical process, is presented with modifications that account for the PEI of the energy consumed within that process. From this theory, four PEI indexes are used to evaluate the environmental friendliness of a process design. These indexes are used in a comparative manner in the process design stage to help minimize the environmental impact of that process. Eight PEI categories (four global and four toxicological) are used in the evaluation of the PEI indexes. Details for relating these categories to known or measured quantities are also presented. An illustrative case study is presented which provide an example for the intended use of the WAR algorithm within the scope of process design and simulation. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The concept of implementing pollution prevention techniques into process design is not new; although, it has received more attention in recent years. The premise of which is to attack the environmental concerns of a process in the design stage instead of relying on end-of-pipe treatment or remediation. This concept was first introduced in the 1970s by way of heat exchange networks (HENs). They were employed to minimize energy consumption of manufacturing processes. A great deal of research has been spawned from this innovation as discussed by Shenoy (1995) and Gunderson and Naess (1988) in their reviews of the subject matter.

Heat exchange networks led to the creation of mass exchange networks (MENs) which were introduced by El-Halwagi and Manousiouthakis (1989). The idea behind MENs is to concentrate pollutants in desired waste streams while removing them from other streams. This technique minimizes the volume of waste generated within a manufacturing process. Within both HENs and MENs, a number of optimization routines have been employed to maximize the efficiency of these pollution prevention techniques (El-Halwagi, 1997).

Both of these techniques help reduce the quantity of pollution or waste generated during the operation of a manufacturing process. However, neither technique addresses the impact of the pollution generated within a process. For example, process design option A may produce 100 kg/h of pollutants while process design option B may produce 200 kg/h. However, the pollutants generated during option A may be much more environmentally unfriendly than those generated during option B. This difference in impact may be such that it may be more desirable to produce 200 kg/h of pollutants in option B than producing 100 kg/h of pollutants in option A.

To address this idea of including environmental impact considerations into process design, Cabezas, Bare and Mallick (1997) introduced a potential environmental impact (PEI) balance as an amendment of the Waste Reduction (WAR) algorithm. The WAR algorithm was first introduced by Hilaly and Sikdar (1994). They introduced the concept of a pollution balance which was the precursor to the PEI balance. The pollution balance, basically, was a methodology that allowed the
user to track the pollutants throughout a process. The PEI balance quantifies the impact of those pollutants in a process. Ultimately, the PEI balance is a quantitative indicator of the environmental friendliness or unfriendliness of a manufacturing process.

Cano-Ruiz and McRae (1998) provide a comprehensive review of the different techniques used to incorporate environmental considerations into process design. Most commonly, environmental concerns are treated as constraints in an economic optimization problem where the constraints are designated by regulations. Minimizing the amount of waste or pollutants generated within a process is another common method to incorporate environmental considerations into process design (Cano-Ruiz & McRae, 1998). A number of index type methods have been implemented to evaluate the environmental impact of the emissions of chemical processes: Houghton, Fihlo, Callander, Harris, Kattenberg and Maskell (1996) proposed an index for global warming defined as the emissions rate multiplied by the global warming potential of that chemical relative to CO₂. Grossman, Drabbant and Jain (1982) proposed a toxicity index by multiplying the effluent flow rate of a chemical by the inverse of its LD₅₀ value, Fathi-Afshar and Yang (1985) proposed an index for gaseous emissions by dividing the effluent flow rates of the chemicals by their threshold limit values as defined by the ACGIH and then multiplied by their specific vapor pressures, and Heinzle et al. (1998) and Koller et al. (1998) proposed ecological indices based on a classification approach to assess the environmental impact of a process. Pistikopoulos, Stefanis and Livingston (1994) proposed relative environmental impact indices for multiple categories, i.e. air pollution, water pollution, global warming, ozone depletion, photochemical oxidation, and solid wastes, and optimized the process for each impact category. The PEC/PNEC (predicted environmental concentration/predicted no effect concentration) ratio has also been used to evaluate the environmental impact of a process design (Cano-Ruiz & McRae, 1998). King, Banares-Alcantara and Manan (1999) used case base reasoning to evaluate the environmental impact of a process design which relies on past experience.

This paper presents an illustrative case study that exemplifies the intended use of the WAR algorithm, which is to aid in the environmental evaluation of a process design. It also presents modifications to the WAR algorithm and the PEI balance, such as the inclusion of energy into the balance, from their previous descriptions (Cabezas et al., 1997). Also, the database containing the potential environmental impacts of the chemicals is detailed. ChemCad 4.0 (Chemstations, 1997) was used as the chemical process simulator in this case study. (Use of ChemCad 4.0 as the chemical process simulator does not imply United States Environmental Protection Agency, USEPA, endorsement of that product.)

The function of the WAR algorithm is best depicted in Fig. 1. This figure displays a schematic of the steps of a product's life. These steps include the acquisition of the raw materials, the manufacturing of these raw materials into desirable products, the distribution and use of these products, and the product disposal or

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**Product Life Cycle**

- Manufacturing Process
- Product Distribution
- Product Use
- Raw Material Acquisition
- Recycle
- Product Disposal

**Environment**

Fig. 1. The waste reduction (WAR) algorithm is a methodology that aids in the environmental evaluation of chemical manufacturing processes. This is where the WAR algorithm fits into the overall life cycle of a product.
Fig. 2. The overall mass and energy balance around a chemical process facility including the energy generation facility. The system boundary is designated with a dashed line.

2. Potential environmental impact theory

The potential environmental impact of a given quantity of material and energy can be generally defined as the effect that this material and energy would have on the environment if they were to be emitted into the environment. Since the definition implies that the impact is an unrealized quantity, i.e. something that has yet to happen, potential environmental impact is, therefore, probabilistic in nature. That is, the potential environmental impact of a particular emission of material and energy into the environment is an estimate of the effect that this emission is likely to have on average. Consequently, one should realize and expect that deviations from this average expected impact would manifest themselves for particular situations. Further, potential environmental impact is a conceptual quantity that can not be directly measured. One can, however, construct a theory to relate potential environmental impact to measurable quantities as will be discussed below.

2.1. Impact balance: products, non-products, and energy

As has already been discussed in a previous publication (Mallick, Cabezas, Bare and Skidar, 1996), traditional chemical process design relies on the application of mass and energy balances along with thermodynamics, chemical reaction engineering, and engineering economics. Cabezas, Bare and Mallick (1997) and Cabezas, Bare and Mallick (1999) have previously proposed that to properly incorporate environmental effects into process design, a balance equation describing the potential environmental impact of the process must be considered. Since one of the purposes of this paper is to extend this analysis to include the environmental consequences of the energy consumed by chemical processes, the PEI balance equation is extended to include the energy generation process. The energy generation process can be considered to be simply an electric power generation facility. This is shown schematically in Fig. 2. The PEI balance is derived by drawing a boundary around the chemical process (denoted by superscript cp) and the energy generation process (denoted by superscript ep) and then writing a general balance expression. The PEI balance simply states that potential environmental impact can enter the system, exit the system, be generated within the system, and accumulate within the system. The actual expression is:

\[
\frac{dI_{\text{syst}}}{dt} = I_{\text{in}}^{\text{cp}} + I_{\text{in}}^{\text{ep}} - I_{\text{out}}^{\text{cp}} - I_{\text{out}}^{\text{ep}} - I_{\text{we}}^{\text{cp}} - I_{\text{we}}^{\text{ep}} + I_{\text{gen}}^{\text{syst}} \tag{1}
\]

where \( I_{\text{syst}} \) is the amount of potential environmental impact inside the system (chemical process plus energy generation process).
generation process), \( \dot{I}_{\text{in}}^{(ep)} \) and \( \dot{I}_{\text{out}}^{(ep)} \) are the input and output rates of potential environmental impact to the chemical process, \( \dot{I}_{\text{in}}^{(ep)} \) and \( \dot{I}_{\text{out}}^{(ep)} \) are the input and output rates of potential environmental impact to the energy generation process, \( \dot{I}_{\text{we}}^{(ep)} \) and \( \dot{I}_{\text{out}}^{(ep)} \) are the outputs of potential environmental impact associated with waste energy (denoted by the subscript we) lost from the chemical process and the energy generation process, and where \( \dot{I}_{\text{gen}}^{(syst)} \) is the rate of generation of potential environmental impact inside the system. For chemical processes, \( \dot{I}_{\text{gen}} \) represents the creation and consumption of potential environmental impact by chemical reactions inside the process. For steady state processes, the balance expression reduces to:

\[
0 = \dot{I}_{\text{in}}^{(ep)} + \dot{I}_{\text{out}}^{(ep)} - \dot{I}_{\text{we}}^{(ep)} - \dot{I}_{\text{gen}}^{(syst)} \tag{2}
\]

which simply states that at steady state the amount of potential environmental impact inside the system does not change with time. This expression can be used to generate a series of indexes characterizing the internal and external environmental efficiency of the system as will be further discussed later. Eq. (2) represents a more accurate depiction of the potential environmental impact of a chemical process than previous versions of the WAR algorithm (Cabezas et al., 1997, 1999) that neglected the consumption of energy by the process. The case study discussed in this paper will be assumed to be processes operating at steady state, and, therefore, all further analysis will be based on Eq. (2) above. The very interesting case of non-steady state processes will be the subject of a future paper.

2.2. Chemical processes: products, non-products, and energy

In order to make use of Eq. (2) in chemical process design, it is necessary to relate the conceptual potential environmental impact to measurable quantities. A generalized linear theory has been constructed (Mallick et al., 1996; Cabezas et al., 1997, 1999) which relates potential environmental impact to measurable quantities such as stream flow rates and compositions and chemical specific overall environmental impacts (\( \psi_k \)). This theory is extended here to include the energy generation process.

The expressions for the chemical process are:

\[
\dot{I}_{\text{in}}^{(ep)} = \sum_j \dot{I}_{\text{in}}^{(ep)} = \sum_j M_j^{(\text{in})} x_j \psi_k + \ldots \tag{3}
\]

\[
\dot{I}_{\text{out}}^{(ep)} = \sum_j \dot{I}_{\text{out}}^{(ep)} = \sum_j M_j^{(\text{out})} x_j \psi_k + \ldots \tag{4}
\]

\[
\dot{I}_{\text{we}}^{(ep)} = \sum_j \dot{E}_j^{(ep)} \psi_{\text{we}} \approx 0 \tag{5}
\]

where \( \dot{I}_{\text{in}}^{(ep)} \) is the rate of potential environmental impact in (\( i = \text{in} \)) or out (\( i = \text{out} \)) of the chemical process, \( \dot{I}_{\text{out}}^{(ep)} \) is the potential environmental impact flow rate with stream \( j \) which may be an input or an output stream, \( M_j^{(in)} \) is the mass flow rate of stream \( j \) which again may be an input or an output stream, \( x_j \) is the mass fraction of component \( k \) of stream \( j \), \( \psi_k \) is the potential environmental impact for chemical \( k \), \( \dot{I}_{\text{we}}^{(ep)} \) is the rate of potential environmental impact output due to the emission of waste energy from the chemical process, \( \dot{E}_j^{(ep)} \) is the rate of waste energy emission from the chemical process, and \( \psi_{\text{we}} \) is the potential environmental impact for energy emission. Eqs. (3) and (4) contain only the potential environmental impacts associated with the pure chemicals. For now, they ignore the combinatorial impacts that could be associated with mixtures of chemicals which accounts for the additional terms not included into those equations. Although the emission of energy directly into the environment is likely to have some impact, for purposes of this article, the impacts due to the emission of waste energy directly into the environment will be neglected, and, therefore, \( \psi_{\text{we}} \) assumed to be zero. This is consistent with the fact that:

(i) chemical process plants do not generally emit large amounts of waste energy into the environment; and that (ii), at least for chemical process plants, the potential environmental impact associated with the emission of mass is usually much greater than that associated with the emission of energy. The sums for subscripts \( j \) and \( k \) are, respectively, taken over all input or all output streams and all components \( k \) including all products and non-products associated with the chemical process. The expressions for the energy generation process are:

\[
\dot{I}_{\text{in}}^{(ep)} = \sum_j \dot{I}_{\text{in}}^{(ep)} = \sum_j M_j^{(\text{in})} x_j \psi_k + \ldots \approx 0 \tag{6}
\]

\[
\dot{I}_{\text{out}}^{(ep)} = \sum_j \dot{I}_{\text{out}}^{(ep)} = \sum_j M_j^{(\text{out})} x_j \psi_k + \ldots \approx 0 \tag{7}
\]

\[
\dot{I}_{\text{we}}^{(ep)} = \sum_j \dot{E}_j^{(ep)} \psi_{\text{we}} \approx 0 \tag{8}
\]
and another sum over solid output streams, \( \psi_{\text{out}} \). The potential environmental impact of the solid output streams can be assumed to be negligible compared to that of the gaseous output streams. Again, the extra terms in Eqs. (6) and (7), which represent the potential environmental impacts associated with mixtures of chemicals, have been omitted. This will be discussed in detail below. Also the potential environmental impact associated with the emission of mass is usually much greater than that associated with the emission of waste energy and, therefore, it is assumed that \( \psi_{\text{we}} \) is approximately zero similar to the chemical process analysis.

The potential environmental impact of the mass inputs, \( \tilde{I}_{\text{in}}^{(cp)} \), to the energy generation process is also assumed to be approximately zero for reasons that will now be discussed. The energy generation process is assumed to be a coal-fired electrical power plant, and the mass inputs to this process consist mainly of coal and air along with water. Of these input streams, the only one that has a significant potential environmental impact is the coal feed stream. Coal ought to have a significant potential environmental impact because it consists of a very complex solid mixture that includes metals, sulfur, and a wide range of organic compounds. Many of these metals and compounds are known to be hazards to human health and the environment. Fortunately, all of these otherwise hazardous components are locked in a solid matrix which makes them unavailable to cause environmental impacts in the way that liquids and gases could, and, thus, the \( \psi_{\text{air}} \) for the components in coal is approximately set to zero. The air and the water have no potential environmental impact so \( \psi_{\text{air}} \) and \( \psi_{\text{water}} \) are set to zero and \( \tilde{I}_{\text{in}}^{(\text{air})} \) and \( \tilde{I}_{\text{in}}^{(\text{water})} \), are, consequently, zero. In summary, all of the terms under the summation in Eq. (6) can be approximately set to zero so that the entire term \( \tilde{I}_{\text{in}}^{(cp)} \) is zero or at least very small compared to the output term, \( \tilde{I}_{\text{out}}^{(cp)} \).

The potential environmental impact of the mass outputs, \( \tilde{I}_{\text{out}}^{(cp)} \), from the energy generation process are divided into gaseous and solid streams as already mentioned. The gaseous streams mainly consist of air pollutants, e.g. NO\textsubscript{x}, CO\textsubscript{2}, SO\textsubscript{2}, etc., which are known to have impacts on human health and the environment, and these are included in the analysis. The solid streams consist of coal slag, i.e. non-combustible ashes and residue, and coal impurities such as metals removed in coal pre-treatment. All of these are in solid form which makes them relatively unavailable for causing environmental impacts as compared to gases. In addition, present practice dictates that these residues be carefully sequestered and rendered environmentally harmless. One additional complication is that data for estimating these environmental impacts is highly uncertain, and these would render any analysis fraught with difficulty. For these reasons, it is assumed here that the potential environmental impact of the components in the solid output streams is negligibly small, i.e. \( \psi_{\text{out}} \approx 0 \), it is further assumed that the potential environmental impact of the mass outputs, \( \tilde{I}_{\text{out}}^{(cp)} \), can be approximated by that of the gaseous component as shown in Eq. (7).

Eqs. (3)–(8) include all products and non-products because they all have potential environmental impacts, and there is in general no reason for presuming that one class of components, say products, should be excluded from the analysis except as previously discussed. In addition, there is significant benefit to conducting a more complete analysis that includes all potential environmental impacts associated with a process. For example, if one is interested in comparing two alternative products, e.g. two detergents, and their associated manufacturing processes, then it becomes quite important to include both products and non-products in the analysis. This is particularly important when the products of a process are likely to eventually be emitted into the environment, e.g. consumer products. The objective here is to have processes that emit and generate as little potential environmental impact as possible consistent with the need to have processes that manufacture products that fulfill human needs. It is important to keep in mind is that once new potential environmental impact is generated and embodied in a product or a non-product, it will very likely require money and other resources to keep the potential environmental impact from being realized. It is, thus, prudent to have processes and products that emit, generate, and embody as little potential environmental impact as possible consistent with societal needs.

2.3. Environmental impact indexes: products, non-products and energy

Eqs. (2)–(8) can be used to generate indexes that characterize the relative environmental efficiency of a process. There are two different classes of indexes; those associated with potential environmental impact output and those associated with potential environmental impact generation. Of the output indexes, the two most important ones are the total rate of impact output, \( \tilde{I}_{\text{out}}^{(\text{out})} \), and the total impact output per mass of products, \( \tilde{I}_{\text{out}}^{(\text{cp})} \):
where $\dot{P}_p$ is the mass flow rate of product $p$ and the sum is taken over all product streams $p$. Of the generation indexes, the two most important ones indexes are, similarly, the total rate of impact generation, $I_{\text{gen}}^{(t)}$ and the total impact generated per mass of product, $I_{\text{gen}}^{(t)}$ defined by:

$$I_{\text{gen}}^{(t)} = I_{\text{in}}^{(cp)} + I_{\text{we}}^{(cp)} + \frac{\sum \dot{M}_j^{(out)} \sum x_{kj} \psi_k}{\sum \dot{M}_j^{(in)} \sum x_{kj} \psi_k}$$

(11)

$$I_{\text{gen}}^{(t)} = \frac{I_{\text{in}}^{(cp)} - I_{\text{in}}^{(cp)} - I_{\text{we}}^{(cp)} + I_{\text{we}}^{(cp)} + \sum \dot{P}_p}{\sum \dot{M}_j^{(in)} \sum x_{kj} \psi_k}$$

(12)

In general, the lower the value of these indexes the higher the environmental efficiency of a process, i.e. the less potential impact the process is likely to have on the environment. However, it should be noted that the effort to design processes with lower environmental indexes needs to be constrained by considerations of engineering economics and societal needs. After all, one could conceivably simply shut down the process which would bring all the mass flow rates to zero and all the indexes to zero. This is not the objective here because it ignores the fact that there may be a human need for the products that the process manufactures.

The total rate of potential environmental impact output, $I_{\text{out}}^{(t)}$ and the potential environmental impact output per mass of product, $I_{\text{out}}^{(t)}$, define the external environmental efficiency of the process. They allow us to compare alternative processes in terms of their potential impact on the environment external to the process. $I_{\text{out}}^{(t)}$ is most useful in assessing whether a particular site is or is not able to accommodate a given process plant. For example, if a process has a low rate of impact output, $I_{\text{out}}^{(t)}$, then the surrounding environment is more likely to be able to dissipate the impact being emitted than would be the case for a process with a high impact output rate. Consequently, a process with a low rate of impact output could be located in a more ecologically sensitive area than would be the case for process with a high rate of impact output. The total potential environmental impact output per mass of products, $I_{\text{out}}^{(t)}$, can decrease either because the rate of potential environmental impact emitted has decreased or because the mass flow rates of products have increased or both. This means that any measures that improve the material utilization efficiency of the process will also tend to lower the potential environmental impact output per mass of products. $I_{\text{out}}^{(t)}$ allows us to compare different process alternatives on the basis of the potential environmental impact emitted by the process per unit mass of products. This means that comparisons can be made regardless of manufacturing plant size. For example, one can compare the environmental consequences of having one large plant versus several small ones.

The rate of potential environmental impact generation, $I_{\text{gen}}^{(t)}$, and the potential environmental impact generated per mass of products, $I_{\text{gen}}^{(t)}$ define the internal environmental efficiency of the process. They allow us to compare different process in terms of their generation of new potential environmental impact within the process. As has already been discussed, the generation of potential environmental impact is quite important because once it is created, it will likely take resources to keep the potential environmental impact from becoming actual impacts on the environment. Therefore, the prudent course of action is to generate as little potential environmental impact as possible consistent with engineering economic constraints and societal needs. Because at least some of the potential environmental impact in the output from a process is likely to have come into the process with the input, the generation of new potential environmental impact within a process is the one item that the process designer can most directly control, i.e. one can manipulate the operating conditions to increase or decrease $I_{\text{gen}}^{(t)}$ and $I_{\text{gen}}^{(t)}$. The quantity $I_{\text{gen}}^{(t)}$ is useful in comparing processes based on how fast they generate impact, and $I_{\text{gen}}^{(t)}$ is useful in comparing processes and products based on the amount of new potential environmental impact generated in producing products. Obviously, the lower the rate of potential environmental impact generated, the better the process will be assuming all other factors are equal.

2.4. Impact balance and indexes: non-products and energy

There are cases where inclusion of the products in the potential environmental impact balance and indexes of Eqs. (3)–(12) may be deemed inappropriate. Three illustrative examples where it could be decided that products would not be included in the analysis are: (i) where the product is an intermediate which is directly fed into another process producing, a different product; (ii) where the social need for the product is deemed so high that its potential environmental impact would not be a consideration, e.g. chemotherapeutic agents used to treat neoplasms are all highly toxic and yet no one would consider stopping their production, and (iii) where the objective of the analysis is simply one of waste reduction given a certain product and process that for economic or other reasons can not be altered.
Exclusion of the products can be done by either simply not including the products in the sums over components \( k \), or by assuming that the potential environmental impact index of all products \( k \) is zero \( \psi_k \approx 0 \). One would, therefore, use the same Eqs. (3)–(12) as deemed appropriate but not include the products. Excluding the products has the benefit of focusing the analysis on the reduction of waste by-products and their potential environmental impacts, but this can come at the price of missing the opportunity to consider the true total potential environmental impact of the process which by necessity must include the products.

### 3. Chemical environmental impacts

Implementation of the WAR algorithm requires the definition of impact categories for which the specific chemical environmental impacts can be relatively quantified. These specific chemical environmental impacts will be used to determine the potential environmental impact indexes of a process.

#### 3.1. Chemical impact expression

The overall potential environmental impact of chemical \( k \), \( \psi_k \), can be determined by summing the specific potential environmental impact of chemical \( k \), \( \psi_{k,l} \), over all of the possible impact categories (Mallick et al., 1996):

\[
\Psi_k = \sum_l a \psi_{k,l}
\]

where \( a \) represents the relative weighting factor of impact category \( l \). The units for Eq. (1) have been corrected from previous versions of the WAR algorithm (Cabezas et al., 1997, 1999). The units for both the overall and specific environmental impacts of the individual compounds should be potential environmental impact of chemical \( k \)/mass of chemical \( k \). The weighting factor should be, of course, dimensionless.

The relative weighting factors, \( a \), are used to express the relative importance of the impact categories. Typically, the weighting factors should range between 0 and 10; however, this is not a steadfast rule. The user should assign the weighting factors according to their specific process conditions. The weighting factors should emphasize or de-emphasize specific concerns that are relevant or irrelevant to their process conditions and locality. Since the primary objective of this algorithm is to determine the relative environmental impact indexes of a process design which ultimately will be compared to alternative designs, the actual values of the weighting factors are not as important as their relative values. The weighting factors are essential to this methodology in that they permit the combining of the impact categories.

#### 3.2. Classification of impacts

The classification of impact categories was initially based on a study by Heijungs, Guinee, Huppes, Lankreijer, Udo de Hayes and Wegener (1992). The categories were then refined to promote the most useful quantities with respect to process design. The result was a list of eight environmental impact categories. These categories fall into two general areas of concern with four categories in each area: global atmospheric and local toxicological. The four global atmospheric impact categories are global warming potential (GWP), ozone depletion potential (ODP), acidification or acid-rain potential (AP), and photochemical oxidation or smog formation potential (PCOP). The four local toxicological impact categories are human toxicity potential by ingestion (HTPI), human toxicity potential by either inhalation or dermal exposure (HTPE), aquatic toxicity potential (ATP), and terrestrial toxicity potential (TTP). Again, this represents a modification to previous presentations of this material (Cabezas et al., 1997, 1999). In their presentation, they included separate categories for both inhalation and dermal exposure in the area of human toxicity.

The weighting factors in Eq. (13) should be used to emphasize the particular areas of concern for individual process designers. For instance, if a process were to be constructed in a rural, wetland area, the process designer would likely de-emphasize the photochemical oxidation potential of the process and emphasize the aquatic toxicity potential of the process.

#### 3.3. Chemical impact database

To implement the WAR algorithm, the specific potential environmental impacts of each chemical in the database, \( \psi_{k,l} \), needed to be determined. The initial chemical database mimics the ChemCad 4.0 (Chemstations, 1997) chemical database which is comprised of \( \approx 1600 \) chemicals. The \( \psi_{k,l} \) values are normalized within each impact category. There are two reasons for this. First, normalization will ensure that values of different categories contain the same units to allow for their combination as in Eq. (13). Second, a proper normalization will ensure that values from different categories will have on average equivalent scores. Without the second condition, implicit weighting factors could be present in the chemical database causing unintentional bias in the calculation of the PEI indexes.

The scores used in the WAR algorithm will be calculated using the following normalization scheme:

\[
\psi_{k,l} = \frac{(\text{Score})_{k,l}}{\langle (\text{Score})_k \rangle_l}
\]

where \( (\text{Score})_{k,l} \) represents the value of chemical \( k \) on some arbitrary scale for category \( l \) and \( \langle (\text{Score})_k \rangle_l \)
represents the average value of all chemicals in category \( l \). Normalizing each category by the average value of non-zero entries in that category insures that the average value in that category will be unity. This normalization eliminates unnecessary bias within the database. Previous versions of the WAR algorithm (Cabezas et al., 1997, 1999) had indicated that a Chebyshev normalization would be used. However, this type of normalization would have resulted in biases in the database.

The next issue is determining the appropriate mechanisms by which scores can be assessed for each of the 1600 chemicals in each of the impact categories. Data for the four global atmospheric impact categories were taken from values published by Heijungs et al. (1992). A brief summary of their methodology for determining these parameters would be informative and, thus, will be presented here.

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 CO\(_2\) absorbs infrared radiation over its respective lifetimes. The half-lives of each of these chemicals was factored into the calculation for determining the GWP. Since, chemicals have different atmospheric half-lives the length of time over which the comparison is made will change the GWP of a chemical. For this database, 100 years was chosen as the base time frame.

The ODP is determined by comparing the rate at which a unit mass of chemical reacts with 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, also, must contain a chlorine or bromine atom.

The PCOP or smog formation potential is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical (OH\(^+\)) to the rate at which a unit mass of ethylene reacts with OH\(^+\).

The AP or acid rain potential is determined by comparing the rate of release of \( H^+ \) in the atmosphere as promoted by a chemical to the rate of release of \( H^+ \) in the atmosphere as promoted by SO\(_2\).

The values reported by Heijungs et al. (1992) were inserted directly into Eq. (14) to determine the chemical potential environmental impacts of these four categories. Note, only a portion of the 1600 chemical database had values for these four global atmospheric impact categories.

Two categories were used to estimate the potential for human toxicity: ingestion and inhalation/dermal exposure. These two categories were used to estimate toxicity potential because they considered all of the primary routes of exposure of a chemical. As a general rule, HTPI were calculated for a chemical if it existed as a liquid or solid at a temperature of 0°C and atmospheric pressure, and an exposure potential, HTPE, was determined for that chemical if it existed as a gas at those conditions. Some chemicals, however, were assigned values for both categories if it was warranted.

As a first approximation, the lethal-dose that produced death in 50% of rats by oral ingestion (LD\(_{50}\)) was used as an estimate for the HTPI. The value was chosen because of its prevalence in the literature and acceptance as a standard toxicity indicator. For those chemicals for which a rat-oral LD\(_{50}\) value was not available, a value was estimated by molecular methods (Young, in progress). LD\(_{50}\) are typically reported in units of mg of chemical/kg rat. By inspection of this scale, it is quite apparent that a chemical with a higher LD\(_{50}\) represents a chemical with lower toxicity. This scale is inverted from the manner in which the WAR algorithm is presented where a higher score represents a greater potential environmental impact. Thus, the score for chemical \( k \) in the HTPI category was calculated by:

\[
\text{(Score)}_{k,\text{HTPI}} = \frac{1}{(\text{LD}_{50})_k}
\]

This inversion assigns scores to chemicals in the database so that the more toxic chemicals have higher scores which follows with the concepts of the WAR algorithm. This inversion also maintains a proportional relationship between chemicals. For example, a chemical with an LD\(_{50}\) of 200 mg/kg, producing a (Score)\(_{\text{HTPI}}\) = 0.005, is considered to be twice as harmful as a chemical with an LD\(_{50}\) of 400 mg/kg, producing a (Score)\(_{\text{HTPI}}\) = 0.0025. The TTP was also estimated using this same rat-oral LD\(_{50}\) data in exactly the same manner.

To estimate the HTPE, time-weighted averages (TWA) of the threshold limit values (TLV) were used. These values were obtained from OSHA, ACGIH, NIOSH and represent occupational safety exposure limits. This was considered to be an adequate measuring stick for comparison of chemicals that would pose a threat to human health through inhalation and dermal exposure routes. Recall, only a relative comparison within categories is needed for this methodology. Again, these values were inverted as in Eq. (15) to maintain the proper relationships within the database.

These estimations of human toxicity potential should be considered to be a first-order approximation only. Research is currently being undertaken to obtain a more thorough and relevant human toxicity value. Once completed, those values will supplant the human toxicity values that are currently stored in the database. However, for the time being the LD\(_{50}\) values will be used to provide a relative toxicity comparison for both human and terrestrial entities.

The ATP was estimated by using toxicological data for a single, representative species of fish, Pimephales promelas (fathead minnows). This species was chosen...
again because of its acceptance as a universal aquatic indicator and its prevalence of data. The data for this assay comes in the form of a LC$_{50}$, a lethal concentration which causes death in 50% of the test specimens. Similar to Eq. (15) the scores for this category were calculated by the following:

$$\text{(Score)}_{k,\text{ATP}} = \frac{1}{(LC_{50})_k} \quad (16)$$

The data used in this database specifically comes from 96 h, LC$_{50}$ experiments. For those chemicals which an LC$_{50}$ value was not found in the literature, a value was estimated using molecular estimation techniques (Young, in progress).

### 3.4. Including energy into the WAR algorithm

To provide a more accurate representation of the potential environmental impact of a process, energy has been included into the WAR algorithm by considering the emissions of a typical power plant. These emissions are then evaluated according to the impact criteria mentioned above. The result is a value of PEI/MWh of power plant production. This value is then multiplied by the rate of energy input required for the operation of a specific process. For the case study discussed in this work, the predominat emissions from a typical coal-fired power plant were used (SO$_2$, NO$_2$, NO, HCl, HF, CO$_2$, and CO) (USEPA, 1997) to perform PEI calculations.

The energy required to operate a process was calculated by summing all of the energy requirements of the system. Included into the calculation were the energy used by the compressors, the pumps, the reboilers of the distillation columns, and the energy used in heat exchangers to heat streams. Also included into this calculation was the energy required to pump cooling water through the condensers and the coolers (heat exchangers). The energy required to operate refrigeration units was also taken into consideration. The energy produced by a turbine was considered to be directly available to the process and represented a reduction in energy consumption of the process. No effort was made in this case study to minimize energy consumption by the use of HEN. However, in principle this technique could be integrated into the WAR analysis.

### 4. An illustrative case study: acrylic acid production

The case study will be an acrylic acid production process, as shown in Fig. 3 (Turton, Bailie, Whiting & Shaeiwitz, 1998). The process is designed for the production of 50,000 tonnes of acrylic acid/year. The process begins with the catalytic oxidation of propylene with air to form acrylic acid (Eq. (17)), and by-products (acetic acid, hydrogen, water, and carbon dioxide) which are formed through parallel reactions, Eqs. (18) and (19).

\[
\begin{align*}
\text{C}_3\text{H}_6 + \frac{3}{2} \text{O}_2 \rightarrow & \text{C}_3\text{H}_4\text{O}_2 + \text{H}_2\text{O} \quad (17) \\
\text{C}_3\text{H}_6 + \frac{5}{2} \text{O}_2 \rightarrow & \text{C}_2\text{H}_4\text{O}_2 + \text{H}_2\text{O} + \text{CO}_2 \quad (18) \\
\text{C}_3\text{H}_6 + \frac{9}{2} \text{O}_2 \rightarrow & 3\text{H}_2\text{O} + 3\text{CO}_2 \quad (19)
\end{align*}
\]

The reactor is assumed to operate isothermally at 310°C. The effluent from the reactor is quenched in an adiabatic flash drum with a substantial recycle stream. The vapor effluent of the flash drum is then stripped with a deionized water stream to recover the small fraction of acrylic acid that escaped in the vapor stream.

![Fig. 3. The process flow diagram for acrylic acid production case study.](image-url)
Table 1
The specifications of the feed streams used in the acrylic acid case study

<table>
<thead>
<tr>
<th>Feed streams</th>
<th>Propylene</th>
<th>Steam</th>
<th>Air</th>
<th>DI water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>159</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>11.5</td>
<td>6</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Flow rate (kg/h)</td>
<td>5344</td>
<td>17 876</td>
<td>39 047</td>
<td>2540</td>
</tr>
<tr>
<td>PEI (impact/h)</td>
<td>11 000</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Stream composition in mass fractions

- Propylene: 1
- Water: 0.0173
- Oxygen: 0.0671
- Nitrogen: 0.8275
- Carbon dioxide: 0.9992
- Acrylic acid: 0.0003
- Acetic acid: 0.0003

The number of significant figures associated with environmental impact calculations should be restricted to one, however, for the purpose of this illustration two significant figures will be used.

The potential environmental impacts were calculated using uniform weighting factors, \( z_1 = 1 \) for all \( l \) categories, the potential environmental impacts for each chemical used in this case study were calculated and presented in Table 2. Note, DIPE does not appear in Table 2 because it is not seen in any of the input or output streams. Using these weighting factors, the potential environmental impact of the energy consumed by this process was calculated as 24 PEI/MWh.

Table 2 provides a quick reference for determining the relative impact ranking of the chemicals. From this table, it can be seen that the desired product, acrylic acid, is, coincidentally, the most environmentally unfriendly chemical used in this process. Note, the values in this table will vary when different weighting factor schemes are used.

The potential environmental impacts of the effluent streams from this process are shown in Table 3 with the other stream specifications for Unit 300. The acrylic acid stream is considered the only product stream in this case study. The other three, effluent streams are viewed as non-product streams.

The case studies used in previous papers published on the WAR algorithm focused on process modification primarily through the addition of recycle streams. The three design scenarios were considered in this case study: a base case (Unit 300) and two, alternative designs (Units 301 and 302). The four input streams were consistent in all three designs; their specifications are given in Table 1 including the PEI of each. Note, from the flash drum. The vapor effluent of the stripper is delivered to an incinerator and is considered a waste stream. The liquid effluent of the flash drum is mixed with the liquid effluent of the stripper to form a stream of which 98% is recycled back to the flash drum for the quenching process. The non-recycled, liquid effluent is sent to a liquid-liquid extraction tower and extracted with a solvent mixture of diisopropyl ether (DIPE, 87% mol) and water. The aqueous effluent contains small amounts of acetic acid, acrylic acid, and DIPE. This stream is distilled to recover a pure water stream that is also considered to be a waste stream. The acids and the DIPE are recycled back to the extraction column. The organic effluent of the extraction tower is sent to solvent recovery column and then to an acrylic acid column. The acrylic acid product is 99.9% (mol) pure. There is no consumption of DIPE in this process design. There is simply an initial charge which is completely recovered within the process, mostly within the solvent recovery column.

Three design scenarios were considered in this case study: a base case (Unit 300) and two, alternative designs (Units 301 and 302). The four input streams were consistent in all three designs; their specifications are given in Table 1 including the PEI of each. Note,
case study discussed here will focus on using the WAR algorithm as a decision tool for other types of process modifications.

With the goal in mind of limiting the PEI while maximizing production of the acrylic acid stream, the base case results were examined to identify possible improvement areas. Obviously, from inspection of Table 3, to reduce the PEI of this process the off-gas and acetic acid non-product streams need to be addressed. The off-gas waste stream contains unreacted propylene and a primary by-product, carbon dioxide. To address this issue, the operation of the reactor was examined. The kinetics of the reaction scheme is such that lower temperatures favor the selectivity to acrylic acid.

The second process improvement involves lowering the PEI of the acetic acid stream. From Tables 2 and 3, it can be seen that the primary contributor to PEI is the excess acrylic acid that has been lost in this stream. An obvious process modification is one that improves the separation efficiency of the acrylic and acetic acids while maintaining a product purity of 99.9%. This separation is performed in the acrylic acid column, see Fig. 3. An improvement in the separation is achieved by increasing the reflux ratio of that column which results in a purer acetic acid non-product stream and a greater recovery of acrylic acid in the product stream. The cost of this improvement is increased usage of energy.

Both alternative designs employ both of these process modifications; lowered reactor temperatures and increased reflux ratio in the acrylic acid column. The first alternative design, Unit 301, incorporated a 30°C reduction in reactor temperature to an operating temperature of 280°C. It also incorporated a 54% increase in the reflux ratio of the acrylic acid column. Interestingly, decreasing the temperature in the reactor resulted in an equivalent conversion of propylene. However, there was a greater selectivity towards acrylic acid.

The second alternative design (Unit 302) consists of lowering the reactor temperature another 20°C to 260°C and doubling the reactor volume. Increasing reactor volume is required to maintain an equivalent level of propylene conversion. The reflux ratio in the acrylic acid column was also increased; however, only a 9% increase was required to achieve the same separation as observed in Unit 301.

The performance specifications of the three process designs are summarized in Table 4. The selectivity was determined by comparing the amount acrylic acid (desired product) that was made to the amount of acetic acid and carbon dioxide (undesired by-products) that was produced.

For this research, PEI indexes are presented in two different analyses. The first one includes the PEI of the product stream into the calculations of the indexes. The second one excludes the PEI of the product stream from the calculations of the indexes. The graphical interpretation of the four, basic potential environmental impact indexes ($I_{\text{gen}}$, $I_{\text{out}}$, $I_{\text{out}}$, and $I_{\text{out}}$) are presented in Figs. 4 and 5. These indexes are presented for both situations where the product stream was included in the analysis (product analysis, Fig. 4) and where the product stream was excluded from the analysis (non-product analysis, Fig. 5).

A comparison of the potential environmental impact indexes of all three process designs are shown in Figs. 4 and 5. The indexes are plotted in units of impact/h and impact/kg of product. They both can provide valuable insight which will be discussed later. From the non-product analysis, both the generation and the output of PEI was found to decrease in each case with Unit 302 presenting the most environmentally friendly design. Further discussions including the all components (product and non-products) will be given later. It is quite apparent that Unit 302 provides the best process design option of the three since it has the lowest PEI and the highest rate of production of acrylic acid. Note, economic considerations have not been included into this analysis.

5. Discussion

The most significant modification to the WAR algorithm is the inclusion of energy consumption into the potential environmental impact calculations. The energy consumed by a process has been assumed to come directly from a power generating facility. The energy generating by this facility has been directly related to the emissions of the facility. These emissions are the basis for quantifying the PEI of the energy consumed.
Fig. 4. The potential environmental impact (PEI) output and generation indexes for acrylic acid production. Calculations include the PEI of the product stream (product analysis). The units of $I_{out}^{(t)}$ and $I_{gen}^{(t)}$ are PEI/h; the units of $I_{out}^{(t)}$ and $I_{gen}^{(t)}$ are PEI/kg product stream.

Fig. 5. The potential environmental impact (PEI) output and generation indexes for acrylic acid production. Calculations do not include the PEI of the product stream (non-product analysis). The units of $I_{out}^{(t)}$ and $I_{gen}^{(t)}$ are PEI/h; the units of $I_{out}^{(t)}$ and $I_{gen}^{(t)}$ are PEI/kg product stream.

by a process. The inclusion of energy into the WAR algorithm’s calculations provides a more realistic view of the PEI generated by a chemical processing plant.

5.1. An illustrative case study: acrylic acid production

In the case study, the PEI of the energy consumed in the process is approximately equal to PEI of the acetic acid, 1700 PEI/h, and off-gas, 1300 PEI/h, non-product streams the base design case, 1700 PEI/h. Obviously, including the PEI of energy consumption is vital in this case study because of the significant contribution of energy generation to the creation of PEI. Each of the alternative designs increased the energy consumption of the process, from Table 4, which translates into a greater generation of PEI. Thus, any design modification must reduce the amount of PEI generated within the process by an amount that would offset the increase in PEI due to energy consumption. This represents a minimum reduction in PEI for a process modification.
From Fig. 5 (non-product analysis), it can be seen that the process modifications accomplish this.

Fig. 4 (product analysis) indicate that the process modifications did not achieve the goal of reducing the PEI of the original design. This contradiction presents a good opportunity to discuss the advantages of using both types of analysis to extract useful information.

The PEI calculations which incorporate the PEI of the product into the analysis (product analysis) show that the acrylic acid product stream is, by far, the most significant contributor to PEI in this process. From the viewpoint of this analysis, neither of the process modifications resulted in an improved design. However, both designs resulted in a greater acrylic acid production rate (Table 4). From the view of a process designer, this would be a favorable improvement. The increase in acrylic acid production accounts for the increase in the PEI indexes in Fig. 4.

To separate these seemingly competing factors, a second analysis is introduced which calculates the PEI without including the product stream into the calculations, non-product analysis. The non-product analysis, Fig. 5, shows that the modifications have reduced the PEI of the process. Since the process designer is usually concerned about the potential environmental impact of the only waste streams, the PEI indexes from the non-product analysis will be the indexes that will most often be used in evaluating process modifications. Indeed, these were the indexes used to evaluate the alternative process designs in this research. However, there is very useful information to be obtained from the product analysis as well. For instance, in this case study the process designer would observe that acrylic acid is the most environmentally unfriendly chemical. This may promote research to find an alternative chemical that would satisfy their end needs and be more environmentally friendly.

In these discussions of PEI indexes, note that the comparisons have been made on a quantitative basis, e.g. one design option had a PEI index that was greater or less than the PEI index of another design option. Due to the uncertainties in the parameters and to the approximations made in the methodology, comparisons of indexes should be restricted to a quantitative nature.

6. Conclusions

The WAR algorithm, a methodology for determining the PEI of a chemical process, has been modified to include the PEI of the energy consumed by that chemical process. This is accomplished by relating the emissions of a typical power plant to the production of energy by that power plant. These emissions, in turn, have an PEI associated with them. The categories over which the PEI are measured have been re-configured to include eight environmental concerns (human toxicity, both by ingestion and inhalation/dermal exposure, aquatic toxicity, terrestrial toxicity, global warming, ozone depletion, acid rain formation, and smog formation). This paper details the method for converting measured values of individual chemicals into PEI values for those chemicals in each category. These chemical PEI values are used to determine four, primary PEI indexes ($I_{\text{out}}^p$, $I_{\text{out}}^e$, $I_{\text{gen}}^p$, and $I_{\text{gen}}^e$) These four indexes are used to determine the environmental friendliness of a process design. Two types of analysis are used to calculate the PEI indexes: product and non-product. The product analysis includes the PEI of the product streams into the calculations; whereas, the non-product analysis omits the PEI of the product streams from the calculations. Both analyses are useful which was shown in the case study that was presented in this paper. The product analysis provides global information about the process, such as the PEI impact of the product streams. This raises issues about the environmental friendliness of the products and questions whether more suitable chemicals can replace the current products. The non-product analysis provides more focused information which can be used to optimize the environmental friendliness of a chemical process. The WAR algorithm is intended to be used in tandem with process simulation.

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Appendix A. Nomenclature

- $E_j^{(cp)}$: the rate of waste energy emission from a chemical process (units of energy/time)
- $E_j^{(ep)}$: the rate of waste energy emission from an energy generation process (units of energy/time)
- $I_{\text{gen}}^{(sys)}$: the rate of PEI generated within a system including the energy generation process (units of PEI/time)
\( I_{\text{gen}}^{(i)} \) the total rate of PEI generated within a system (units of PEI/time)

\( \dot{I}_{\text{gen}}^{(i)} \) the total PEI generated within a system per mass of product stream leaving the system (units of PEI/mass of product streams)

\( \dot{I}_{\text{in}}^{(c)} \) the rate of PEI entering a chemical process (units of PEI/time)

\( \dot{I}_{\text{in}}^{(e)} \) the rate of PEI entering an energy generation process (units of PEI/time)

\( \dot{I}_{\text{in}}^{(m)} \) the rate of PEI entering a process in stream \( j \) (units of PEI/time)

\( \dot{I}_{\text{j}}^{(o)} \) the rate of PEI leaving a process in stream \( j \) (units of PEI/time)

\( \dot{I}_{\text{j}}^{(c)} \) the rate of PEI leaving into a chemical process (units of PEI/time)

\( \dot{I}_{\text{j}}^{(e)} \) the rate of PEI leaving an energy generation process (units of PEI/time)

\( \dot{I}_{\text{j}}^{(w)} \) the total rate of PEI leaving a system per mass of product streams leaving the system (PEI/mass of products)

\( I_{\text{syst}} \) the PEI of a chemical process system including the energy generation process (units of PEI)

\( \dot{I}_{\text{we}}^{(c)} \) the rate of PEI waste energy lost from a chemical process (units of PEI/time)

\( \dot{I}_{\text{we}}^{(e)} \) the rate of PEI waste energy lost from an energy generation process (units of PEI/time)

\( M_{\text{j}}^{(\text{in})} \) the mass flow rate of stream \( j \) into a process (units of mass/time)

\( M_{\text{j}}^{(\text{out})} \) the mass flow rate of stream \( j \) leaving a process (units of mass/time)

\( \dot{P}_{\text{p}} \) the mass flow rate of product stream \( p \) (units of mass/time)

PEI potential environmental impact

\( \text{(Score)}_{kl} \) a characteristic quantity of chemical \( k \) used to determine a PEI value of that chemical for impact category \( l \) (units vary for each category)

\( \langle \text{(Score)}_{k} \rangle_{l} \) the average value of all \( k \) chemicals in category \( l \) (units vary for each category)

\( T \) Time

\( x_{kj} \) the mass fraction of chemical \( k \) in stream \( j \) (units of mass of chemical \( k \)/mass of stream \( j \))

Greek symbols

\( \alpha_{i} \) the weighting factor for impact category \( i \) (dimensionless)

\( \psi_{k} \) the overall PEI of chemical \( k \) (units of PEI/mass of chemical \( k \))

\( \psi_{k,l} \) the specific PEI of chemical \( k \) for impact category \( l \) (units of PEI/mass of chemical \( k \))

\( \psi_{we} \) the overall PEI of the waste energy lost from a process (units of PEI/energy)

Appendix B. List of acronyms

ACGIH American Conference of Governmental Industrial Hygienists
AP acidification potential
ATP aquatic toxicity potential
GWP global warming potential
HEN heat exchange network
HTPE human toxicity potential by exposure
HTPI human toxicity potential by ingestion
MEN mass exchange network
NIOSH National Institute for Occupational Safety and Health
ODP ozone depletion potential
OSHA occupational safety and health administration
PCOP photochemical oxidation potential
PEI potential environmental impact
TTP terrestrial toxicity potential
USEPA United States Environmental Protection Agency
WAR waste reduction

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