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Evaluating and improving environmental performance of HC's recovery system: A case study of distillation unit

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Abstract

Waste solvents/valuable products in the effluent stream are one of the major environmental problems in the chemical industry if not properly controlled. Separation processes are vital for the recovery of waste solvent/valuable product from the effluent stream to reduce the pollution along with improvement in economic performance. Among the various separation processes, distillation is most widely used. A number of environmental indicators, each satisfying researchers own need, and methodologies such as life cycle assessment (LCA), minimum environmental impact assessment (MEIM), waste reduction algorithm (WAR) and environmental fate and risk assessment (EFRAT) are available for evaluation of environmental performance of chemical processes. In this article, a systematic procedure, introducing an environmental performance index (EPI) based on potential environmental impact (computed from waste reduction algorithm (WAR)), energy consumption, resource conservation and fugitive emission, for evaluating environmental performance is presented. Analytical hierarchy process (AHP) is used at two levels for the determination of weighting of individual categories. The procedure is applied for the study of environmental performance of distillation column (steam stripping column) from a real chemical plant for the recovery of acetone and HC's from the off gases of the distillation fraction (DF) plant. Alternatives are compared using environmental performance index and best alternative is selected.
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Keywords: Environmental performance index; Analytical heirarchy process; Waste reduction algorithm; Distillation unit

1. Introduction

The chemical processing industry provides a variety of base and intermediate chemicals yielding about 30,000 consumer products [1]. Solvents are widely used in the chemical processing industry to make these processes economically feasible. However, waste solvents from these industries are one of the major environmental problems if not controlled properly [2]. Separation processes are vital for the recovery of waste solvent/valuable product from the effluent stream to reduce the pollution along with improvement in economic performance. Among the various separation processes, distillation accounts for over 95% of the applications in the chemical processing industry [3]. But distillation column unit itself contributes to process wastes by: (1) excessive energy used in separation which leads to direct release of criteria pollutants and global warming gases, (2) inadequate condensing of overhead products, (3) forming waste within the column unit itself (4) by allowing impurities to remain in the product. Reflux ratio, reboiler duty, feed position, feed and liquid distributions, preheating the column feed, etc. are ways to improve the separation efficiency and reduce environmental effects. Among them, optimizing the reflux ratio and reboiler duty are most common and important. Economic optimum conditions (e.g. optimum reflux ratio, steam rate) may be different from the environmental optimum conditions in distillation unit (see Fig. 1) due to soft composition (flexible) constraints.

Several attempts have been made to integrate environmental and health considerations in early design processes [4,5]. A variety of environmental indicators have been used in the environmental assessment of chemical processes from simple mass balance indices to more complicated methods based on multiple media, multiple exposure pathways and multiple categories of impacts. For example, Hoffman et al. [6] have used material intensity per service unit (MIPS) as an environmental proxy measure for the evaluation of alternatives. Heinzle et

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Nomenclature

CI	consistency index
CR	consistency ratio
E_C	energy consumption factor
E_f	fugitive emission factor
EPI	environment performance index
$\dot{M}$	mass flow rate
PEI	potential environmental impact
$\dot{Q}_r$	amount of heat energy supplied for separation
R	resource
RI	random index
W	weighting factors
x	mass fraction

Greek letters

ξ	average emission factor
ψ	normalized impact score

Subscripts

b	base stream
c	consumption
k	chemical
L	potential environmental impact category
p	product
RM	raw material
u	utility
vs	volatile substance or component

al. [7] have defined three indices i.e. mass loss indices, ecological indices for by-product formation and economic indices on the basis of simple mass balances for economic and ecological assessment during process design. Koller et al. [8] have given EHS methodology, a short cut method, combining safety, health and environmental aspects into single index for early assessment during process development. Bakshi [9] proposed a thermodynamic framework for ecology conscious process system engineering using emergy and energy analysis. A number of systematic methodologies are available for detail characterization of environmental impacts of chemicals, products and processes. However, the most commonly methods used are life cycle assessment (LCA) [10–12], methodology of environment impact minimization (MEIM) [13], waste reduction algorithm (WAR) [14–17] and environmental fate and risk assessment (EFRAT) [18]. Fig. 2 shows the scope of these methodologies.

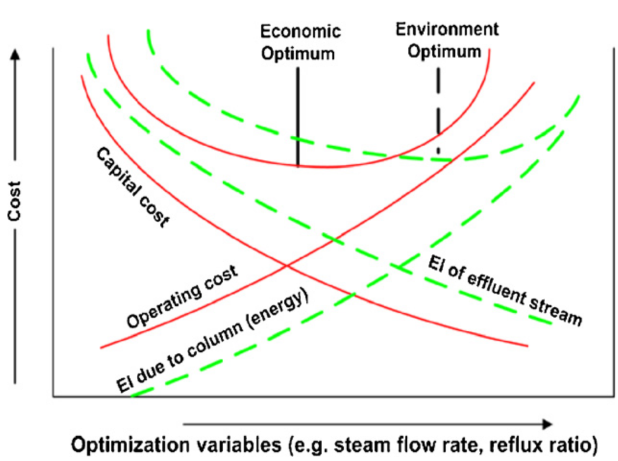

Fig. 1. Conceptual diagram of problem.

The common points in all these methodologies are the evaluation of local (human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation or dermal exposure (HTPE), aquatic toxicity potential (ATP), terrestrial toxicity potential (TTP)), regional (acidification potential (AP), photochemical oxidation potential (PCOP)) and global (global warming potential (GWP), ozone depletion potential (ODP)) environmental impacts or risks and tools used for environmental conscious design. LCA, by definition, tends to include a much broader scope of these impacts than is typically considered in process development, which emphasizes the manufacturing of the product, rather then its use. MEIM embeds LCA in optimization framework for design and operation of the process. EFRAT evaluate environmental performance of a flowsheet. WAR fits only to chemical manufacturing process (see Fig. 2). The WAR algorithm was established by Hilaly and Sikdar [14]. They introduced the concept of pollution balance that is the precursor to potential environment impact (PEI) balance, an amendment in the WAR, introduced by Cabezas et al. [15,16]. Later Young and Cabezas [17] have modified WAR further to account the PEI of energy consumed within that process. The WAR is simply a tool to be used by design engineers to aid in evaluating the environmental friendliness of a process and can be used in either design stage of the future process or in retrofitting of a current process. It does not represent the complete product life cycle but actually aids in the environmental evaluation of chemical manufacturing processes. The WAR algorithm does not include impact categories such as land use, resource depletion, noise, odor, etc. but does represent those categories that are considered as the most significant environmental concerns to the chemical manufacturing industry. These impact categories are human toxicity potential by ingestion, human toxicity potential by inhalation or dermal exposure, ozone depletion potential, global warming potential, acidification potential, photochemical oxidation potential, aquatic toxic potential and terrestrial toxicity potential, which are combined together using weighting factors. The detailed theoretical description and application to different chemical manufacturing processes of WAR can be found elsewhere [14–17,19].

However, in case of existing chemical processes, it is desirable to consider the environmental ramification of each unit operation in the process rather than the complete process. Several unit operation design heuristics for pollution prevention exists [20,21] but in case of existing plant degree of freedom for environmental ramification is often very low. A systematic procedure for the evaluation and improvement of environmental performance of existing unit operation based on WAR is presented. Along with WAR, the other factors such as resource depletion, energy consumption

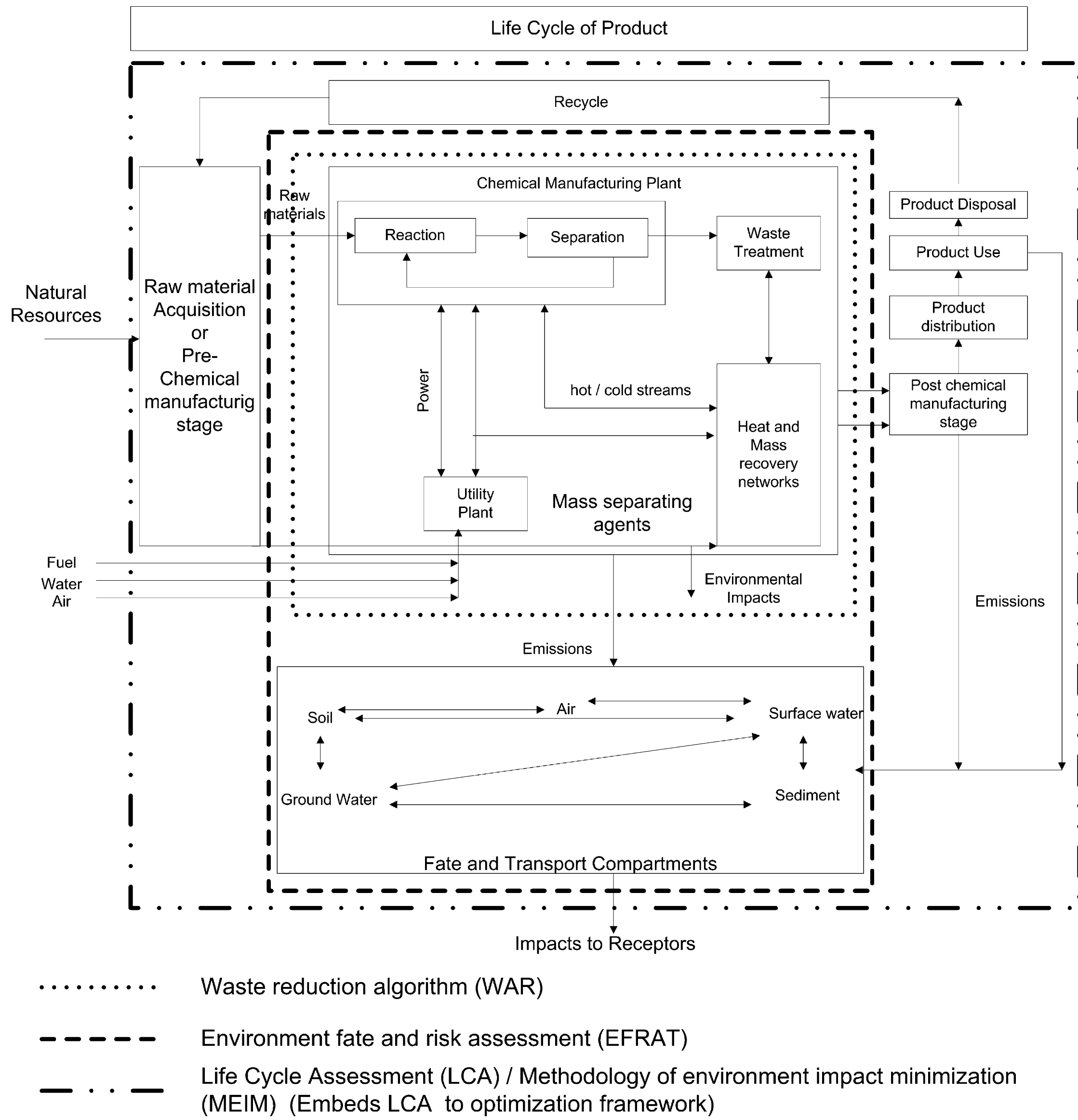

Fig. 2. Scope of environmental impact evaluation methodologies.

and fugitive emissions are also integrated. In this paper the evaluation and improvement of environmental performance of a distillation column unit (steam stripping column unit) is described. Section 2 describes the systematic procedure and this procedure is demonstrated with the help of case study of distillation column unit (steam stripping column) in Section 3. Finally in Section 4, the results obtained with recommendations are discussed.

2. Systematic procedure

The systematic procedure used consists of four steps. It is based on environmental performance index calculated by combining total PEI based on WAR, resource depletion, energy conservation and fugitive emission. The analytic hierarchy process (AHP) [22,23] is used as multicriteria decision analysis tool for combining these different impacts and determination of weighting factors of individual impact categories in total PEI and later on in environmental performance index (EPI) calculations. The steps are:

1. Problem definition and data gathering
2. Individual impact categories calculation
3. Determination of weighting factors (application of AHP)
4. Environmental performance index calculation (design evaluation stage)

Fig. 3 shows the simplified block diagram of environmental module and tasks to be performed.

2.1. Problem definition and data gathering

The primary task in step 1 is problem framing and scope definition. Information such as material and energy balance information, process conditions, process technology and nature of used materials/chemicals are gathered. Process flow diagram

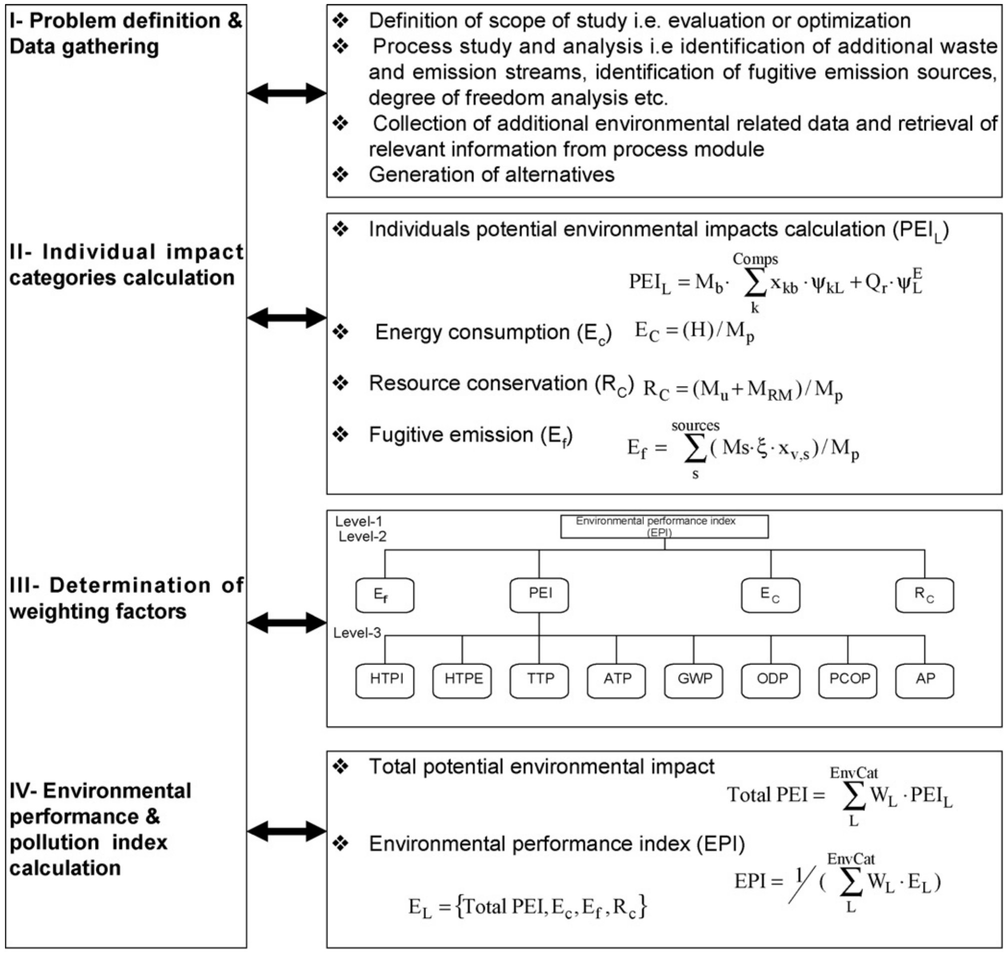

Fig. 3. Systematic procedures.

is examined for identification of waste and emission streams. Sources of emissions such as fugitive emission sources, venting of equipment, periodic equipment cleaning, incomplete separations, etc. are often missing in process flow diagram so process is analyzed carefully to identify these sources too.

2.2. Individual impact categories calculation

2.2.1. Potential environmental impact calculations based on WAR algorithm

The software WAR GUI (waste reduction algorithm graphical user interface) from the US Environmental Protection Agency is used to calculate individual potential environmental impacts. The generalized formula based on WAR algorithm for calculating individual PEI is given in Eq. (1).

$$\mathrm{PEI_L} = \frac{\dot{M}_\mathrm{b}\sum_k^{\mathrm{Comps}} x_{k\mathrm{b}}\psi_{k\mathrm{L}} + \dot{Q}_\mathrm{r}\psi_\mathrm{L}^\mathrm{E}}{\dot{M}_\mathrm{p}} \quad \text{(impact/kg product)} \quad (1)$$

where $\mathrm{PEI_L}$ is the potential environmental impact of category L, $\dot{M}_\mathrm{b}$ is mass flow rate of base (effluent) stream, $x_{k\mathrm{b}}$ is the mass fraction of component k in the base stream, $\psi_{k\mathrm{L}}$ the normalized impact score of chemical k for category L, $\dot{Q}_\mathrm{r}$ is amount of energy per unit time supplied for separation and $\psi_\mathrm{L}^\mathrm{E}$ is the normalized impact score of category L due to energy. The sensitivity analysis of individual potential environmental impact with respect to optimization variables should also be performed.

2.2.2. Energy consumption factor (E_C)

Energy consumption factor refers the total amount of energy consumed in the process per unit of product and is calculated as follow:

$$E_\mathrm{C} = \frac{\dot{H}}{\dot{M}_\mathrm{p}} \quad \text{(kJ/kg product)} \quad (2)$$

Here, $\dot{H} = \dot{M}_\mathrm{steam}\hat{h}_\mathrm{steam} + E_\mathrm{E}$ where $\dot{M}_\mathrm{steam}$ is the mass flow rate of steam (kg/h), $\hat{h}_\mathrm{steam}$ is the enthalpy of steam per kg (kJ/kg), E_E is electrical energy consumed per unit time (kJ/h) and $\dot{M}_\mathrm{p}$ is product rate (kg/h).

The sensitivity analysis of this factor with respect to optimization variables should also be performed.

2.2.3. Resource conservation factor (R_C)

The resource consumption refers all needed raw materials and utilities used and given by:

$$R_\mathrm{C} = \frac{\dot{M}_\mathrm{u} + \dot{M}_\mathrm{RM}}{\dot{M}_\mathrm{p}} \quad \text{(kg/kg product)} \quad (3)$$

where R_C is the resource conservation factor, $\dot{M}_u$ is utilities consumption rate, $\dot{M}_{RM}$ is raw material consumption rate.

2.2.4. Fugitive emission factor (E_f)

Fugitive emissions are unplanned or unmanaged, continuous or intermittent releases from unsealed sources such as storage tank vents, valves, pump seals, flanges, compressors, sampling connections, open ended lines, etc. and any other non point air emissions. These sources are large in number and difficult to identify. These emission rates depend on factors such as the age and quality of components, specific inspection and maintenance procedures, equipment design and standards of installation, specific process temperatures and pressures, number and type of sources and operational management commitment. However, four basic approaches for estimating emissions from equipment leaks in a specific processing unit, in order of increasing refinement, in use are:

- average emission factor approach,
- screening ranges approach,
- EPA correlation approach,
- unit-specific correlation approach.

All these approaches require some data collection, data analysis and/or statistical evaluation. On the other hand, using fundamental design/engineering calculations for accurate fugitive emission estimations for each source present in the process industry is difficult due to:

- large number and type of fugitive emission sources,
- dependence of emission rates on other factors along with design and operating conditions e.g. installation standards, inspection and maintenance procedure, etc.

Thus, to integrate fugitive emissions into environmental performance evaluation, average emission factor approach giving a bit over estimates are used. Average emission factors for estimating fugitive emissions from fugitive sources found in synthetic organic chemical manufacturing industries operations (SOCMI) obtained from the US Environmental Protection Agency L & E Databases are used. The relation used in this work for calculation of fugitive emissions is:

$$E_f = \frac{\sum_s^{\text{sources}} (\dot{M}_s \xi x_{v,s})}{\dot{M}_p} \quad (\text{kg/kg product}) \qquad (4)$$

Here E_f is fugitive emission factor per unit of product, $\dot{M}_s$ mass flow rate through the source ‘s’, ξ is average emission factor and $x_{v,s}$ is mass fraction of volatile component through source ‘s’. It is assumed $x_{v,s}$ for the process fluids through fugitive sources such as pump seals, valves, flanges and connection is equal to one i.e. fluids are composed entirely of volatile compounds.

2.3. Determination of weighting factors (application of AHP)

The integration of these individual impact categories into one index is a hierarchical multicriteria decision analysis problem. The analytic hierarchy process (AHP) is used for this purpose and a computer programme for it is developed in VB 6.0. This technique also finds applications in different fields such as planning, selecting a best alternative, resource allocations resolving conflict, optimization, etc. [23–25]. It is based on three principles, namely: construction of a hierarchy, priority setting and logical consistency [26]. Thus, the AHP methodology can be divided into following major stages:

1. Hierarchical structuring of the problem, which is structured hierarchically similar to a flow chart. The overall objective or focus is placed at the top, the criteria and sub-criteria below, and the alternatives at the bottom. For example, as shown in Fig. 4, the overall objective environmental performance index (EPI) is placed at the top (level 1), then below (level 2) are criteria as total PEI, E_f, E_C and R_C and after this (level 3) sub-criteria as HTPI, HTPE, TTP, ATP, GWP, ODP, PCOP and AP.
2. Assignment of relative importance weights: In this stage the decision maker determines the relative importance of a set of criteria and a set(s) of sub-criteria. An independent comparison among every combination of couple of elements from a certain level with respect to a relevant element from a higher level in the hierarchy is part of the procedure. This technique of comparisons of a couple of criteria or a couple of elements at a time is known as pairwise comparisons. A numerical rating scale from 1 to 9 (Table 1) is used for pairwise comparison. A reciprocal rating (i.e. 1/9, 1/8, etc.) is assigned when the second criteria is preferred to the first. The value 1 is always assigned when comparing an element with itself.
3. Overall priority weight determination: At this stage the priority weights of each of the criteria are calculated first by dividing each number in a column of the pairwise comparison matrix by its column sum and then averaging the row entries of the new matrix.
4. Inconsistency calculations: The level of inconsistency in decision making can be measured and calculated in comparison to random decision making by calculating consistency ratio. A consistency ratio of less than 0.1 is good and for

Table 1
Numerical comparison scale for construction of pair wise comparison matrix

Comparison scale suggested by AHP method	
1	Two criteria’s contribute equally
3	Experience and judgement slightly prefer one criteria over another
5	Experience and judgement strongly prefer one criteria over another
7	One criteria’s preferred very strongly over another, dominance demonstrated in practice
9	Affirmed evidence of preferring one criteria over another
2, 4, 6, 8	When compromise between values of 1, 3, 5, 7 and 9 is needed

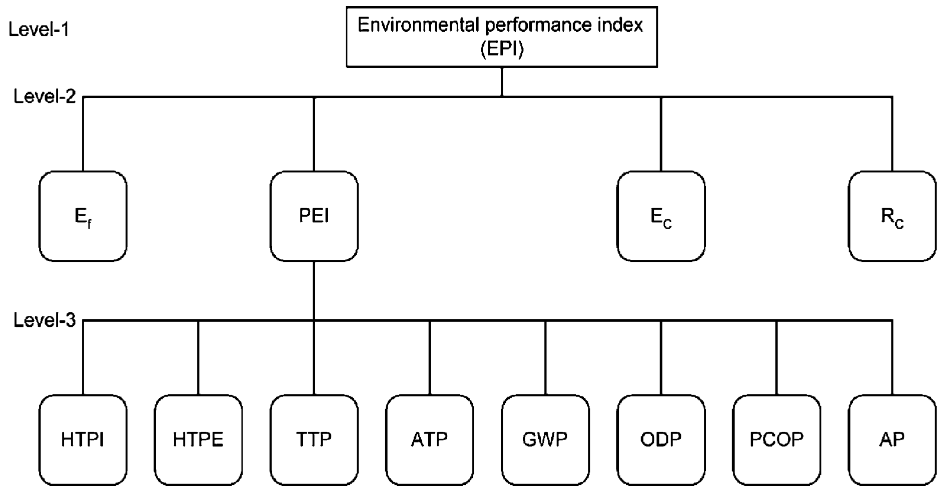

Fig. 4. Hierarchical structuring of multicriteria decision analysis problem for integrating individual environmental impacts.

ratios greater than 0.1, the input to pairwise matrix should be re-evaluated. Consistency ratio (CR) is calculated by:

$$CR = \frac{CI}{RI} \quad (5)$$

where CI = consistency index and is given by

$$CI = \frac{\lambda_{max} - m}{m - 1} \quad (6)$$

Here m is the total number of objectives, λ_{max} is calculated by averaging the values obtained by dividing the weighted sum (sum of the multiples of the entries of each row of pairwise comparison matrix by the priorities of its corresponding (column) criteria) by the priority of its corresponding (row) criteria and RI is random index depending upon the number of objectives. Its value is determined from Table 2.

The ability of AHP method to incorporate interaction among multiple attributes and to track consistency in judgment is leading factor that makes this method popular. A good description of AHP is available in the work of Traintaphyllou [22].

2.4. *Environmental performance index calculation (design evaluation stage)*

In the final step, first total PEI is determined by multiplying each impact category values with it relevant weighting factor W_L as given below:

$$\text{Total PEI} = \sum_{L}^{\text{EnvCat}} W_L \cdot \text{PEI}_L \quad (7)$$

After calculating total PEI, environmental performance index (EPI) is determined for each alternative by multiplying the values of total PEI, E_f, E_C and R_C with its relevant weighting factor W_L as given below:

$$\text{EPI} = \frac{1}{\sum_{L}^{\text{EnvCat}} W_L E_L} \quad (8)$$

where E_L = {total PEI, E_c E_f, R_c}

Table 2
Determination of random index (RI)

No. of objectives (m)	Random index (RI)
3	0.58
4	0.90
5	1.12
6	1.24
7	1.38
8	1.41
9	1.45
≥10	1.49

3. Case study

A distillation column (steam stripping column) unit from a real chemical plant, for the recovery of acetone and HC's from the off gases, is taken as case study.

3.1. *CSI—problem definition and data gathering*

Water, acetone, methanol and acetic acid are the main components of the feed stream. The product stream (acetone rich) is separated from the effluent by using live steam injection. The column has diameter of 0.728 m and consists of 35 trays. The live steam with flow rate of 603 kg/h is entered at stage 35 at temperature 141 °C and 375 kPa pressure. The feed, which is at its bubble point, is entered at stage 16 (the stages are numbered from top to bottom) with a column head pressure of 100 kPa and flow rate of 4000 kg/h. Reflux ratio is 0.7. The composition constraints (in mass%) on distillate and base (effluent stream) stream due to process and environment are:

Distillate: water <10% Base: acetone <2000 ppm ~0.22%; methanol <2%; acidity <2.5% where acidity is the sum of the mass fraction of the acids i.e. acetic acid, formic acid and propionic acid in the base stream. However, typical stream compositions are given in Table 3.

Fig. 5 shows the simplified process diagram of the distillation unit under study. This process seems to be simple and easy to

Table 3
Typical stream compositions (mass%)

Component	Feed	Head	Base
Methanol	1.65	4.62	0.55
Acetaldehyde	2.21	8.84	0
Methyl formate	3.77	15.03	0.01
Ethanol	1.06	4.13	0.03
Acetone	13.11	52.36	0.22
Methyl acetate	2.34	9.33	0.01
Methyl ethyl ketone	0.67	2.55	0
Ethyl acetate	0.25	0.98	0
Water	72.68	2.06	96.68
Acetic acid	1.75	0	1.94
Formic acid	0.37	0	0.41
Propionic acid	0.14	0	0.15

Table 4
Operating range of reflux ratio and steam flow rate

Reflux ratio	Steam flow rate (kg/h)	Distillate	Base		
		Water <10%	Acetone <0.22%	Methanol <2%	Acidity <2.5%
0.55	540	2.10	0.23	1.50	2.45
0.60	560	2.10	5.57×10^{-4}	1.48	2.46
0.65	580	2.12	1.34×10^{-8}	1.43	2.46
0.70	600	2.00	2.64×10^{-9}	1.36	2.45
0.75	620	1.90	8.85×10^{-10}	1.30	2.45
0.80	640	1.90	3.32×10^{-10}	1.20	2.45

operate. However, this has several challenging problems. One of them is the increase of concentration of middle boiling components at the intermediate trays at first and then accumulation of mass of middle boiling components or decrease of concentration may affect the performance of the column. Second, the flexible composition constraint on the distillate and base stream provides the opportunity to operate on wide range of manipulated variables such as reflux ratio and steam flow rate as shown in Table 4. This table also shows that, (a) there is no physical limit for steam flow rate, (b) more steam may results in less organic in effluent stream (base stream). Therefore, economic optimum conditions may be different from the environmental optimum conditions. Third, distillation columns itself contribute to process waste e.g. energy used for separation or recovery of HC's leads to direct release of criteria pollutants and global warming gases. So, column should be operated on conditions that the waste generated due to process itself is minimum along with adequate product quality.

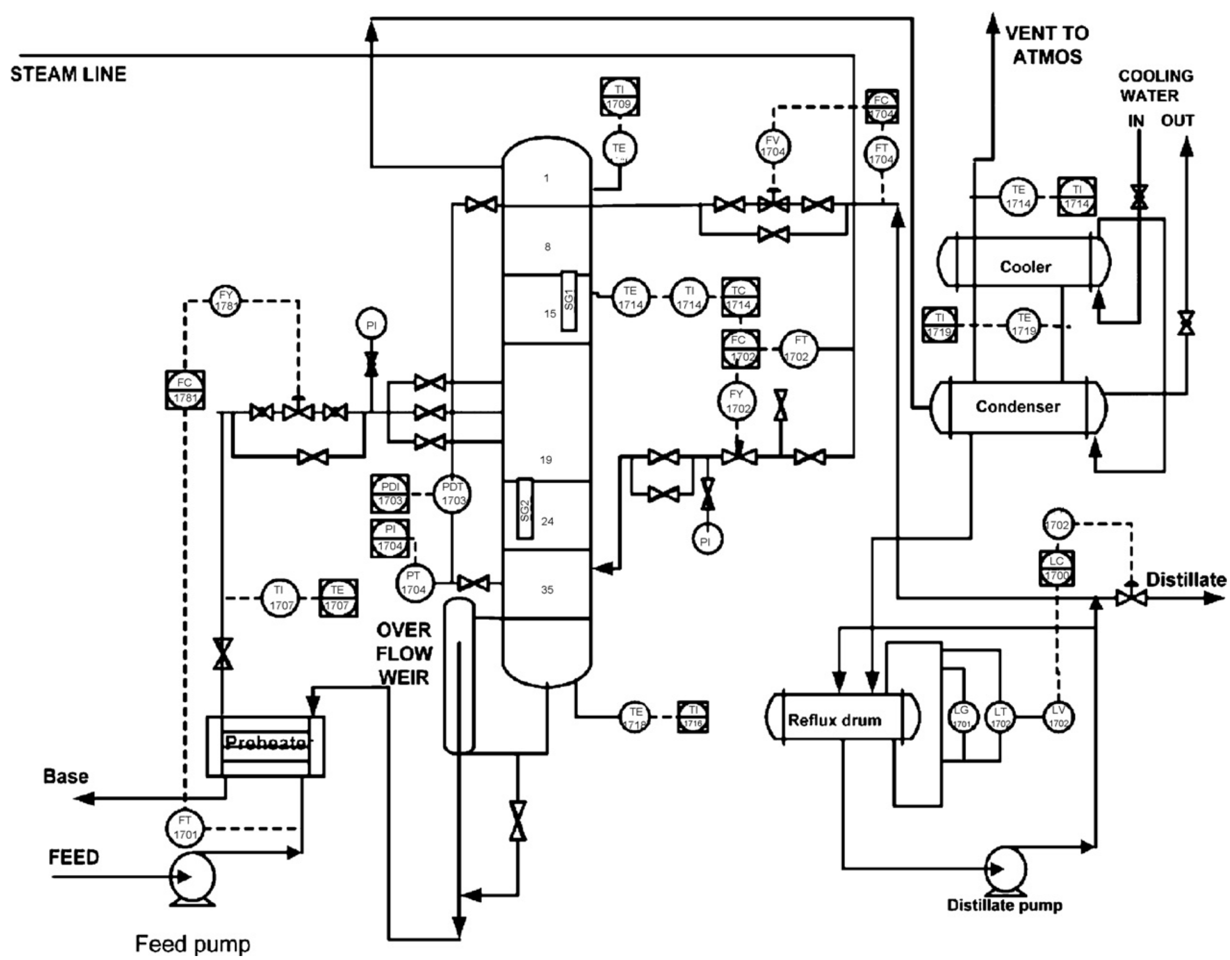

Fig. 5. Process flow diagram of distillation unit.

The scope of this study is to evaluate and improve the environmental performance of the process. At the first step, a steady state simulation model is configured in AspenPlus^{TM} for material and energy balance information. A detailed degree of freedom analysis is performed for the specification phase of the simulation and to select the variables to be optimized for improving the environmental performance along with meeting the top and bottom product compositions. Normally in case of distillation column, unit variables such as pressure at each stage, feed stream conditions, heat transfer rate for each stage, total number of stages, feed stage location, mole fraction of one component in distillate, mole fraction of one component in base and pressure at total condenser outlet or degree of cooling are always needed to be specified. So the reflux ratio and steam rate are selected as the two remaining degrees of freedom (optimization variables) to be optimized for improving environmental performance.

Two alternatives named base case and modified case (see Fig. 6) are generated for study in this case study. The base case (existing unit) is a simple multicomponent distillation unit. The primary source of inefficiency in multicomponent simple distillation is due to: (a) backmixing on intermediate trays, (b) maldistribution on trays and (c) concentration of middle boiling often reaches a maximum on intermediate trays which may result in flooding or oscillation. The use of complex column configurations can minimize these problems, as well as reduce energy consumption and decrease capital costs. Therefore, the main alternative proposed is to withdraw a side stream from the bottom section of the column. Fig. 6 shows the simplified diagram of alternatives generated.

The data related to toxicology and physical properties for the evaluation of impact scores is taken from the database based on the study of Heijungs et al. [27] incorporated in the WAR GUI developed by US Environmental protection agency. The objective is to optimize the reflux ratio and steam flow rate for improving environmental performance for each alternative and select the best alternative.

3.2. CSII—individual impact categories calculation

3.2.1. Potential environmental impact calculations based on WAR algorithm

Two different analyses can be performed using the WAR algorithm, product and non-product analysis, depending on product stream is included in the analysis or excluded from the analysis. Here non-product analysis is carried out i.e. the potential environment impact of product stream (distillate and side stream (in modified case)) is taken zero. Individual potential environmental impact categories such as human toxicity potential by ingestion (HTPI), human toxicity potential by inhalation or dermal exposure (HTPE), ozone depletion potential (ODP), global warming potential (GWP), acidification potential (AP), photo oxidation chemical potential (PCOP), aquatic toxicity potential (ATP) and terrestrial toxicity potential (TTP) are calculated using the Eq. (1). Each impact has two contributions. First contribution is due to the waste stream (base stream) after distillation and second due to energy consumption during distillation. The values of normalized impact scores of chemicals for different categories of environmental impact and normalized impact score of coal energy (assuming coal is being used as fuel for steam production in the plant) used in the calculation of PEI are given in Tables 5 and 6, respectively. The total mass flow rate of each stream is multiplied by the sum of normalized impact scores of the chemical in that stream for each category to calculate potential impact of that category due to first contribution and heat duty is multiplied with the normalized impact score of energy of each category to calculate the second contribution. Detailed sensitivity analysis of these individual environmental impacts with respect to selected optimization variables i.e. steam flow rate and reflux ratio for each alternative is also performed and shown in Fig. 7. Fig. 7(a–d) shows that ecological

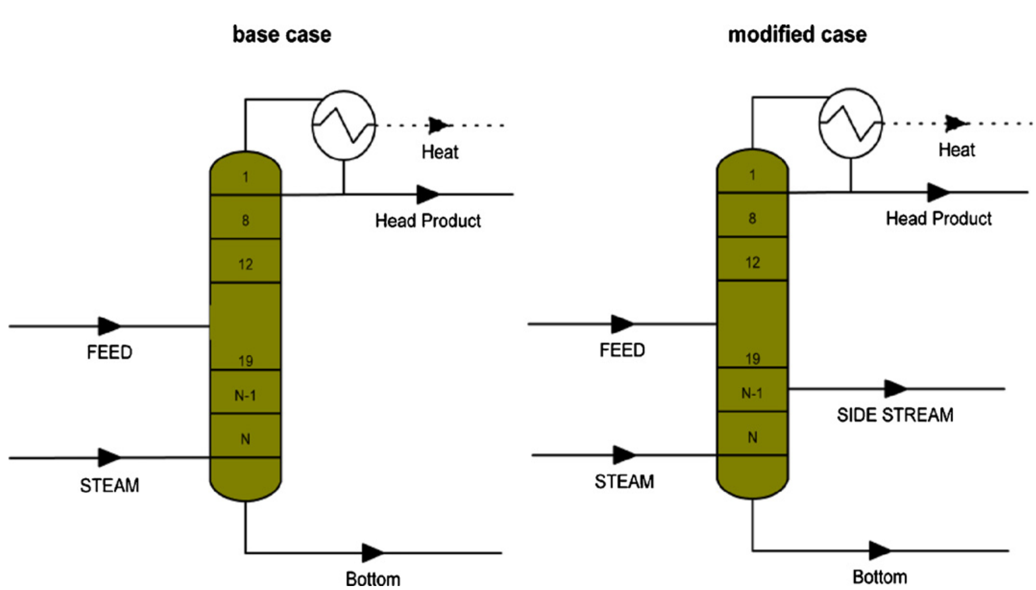

Fig. 6. Alternatives generated.

Table 5
Normalized impact scores for different categories of potential environmental impact of chemicals involved in the case study

Chemical	Normalized impact score (ψ_{kL})							
	HTPI	HTPE	TTP	ATP	GWP	ODP	PCOP	AP
Methanol	0.0626	0.0011	0.0626	0	0	0	0.2462	0
Acetaldehyde	0.5332	0.0008	0.5332	0.0265	0	0	1.0547	0
Methyl formate	0.1696	0.0012	0.1696	0.0061	0	0	0	0
Ethanol	0.0499	0.0002	0.0499	0.0001	0	0	0.5364	0
Acetone	0.0608	0.0001	0.0608	0.0001	0	0	0.3562	0
Methyl acetate	0.1375	0.0005	0.1375	0.0023	0	0	0.05	0
Methyl ethyl ketone	0.1288	0.0005	0.1288	0.0003	0	0	0.9466	0
Ethyl acetate	0.0627	0.0002	0.0627	0.0039	0	0	0.4363	0
Water	0	0	0	0	0	0	0	0
Acetic acid	0.1065	0.0117	0.1065	0.0107	0	0	0	0
Formic acid	0.3204	0.0326	0.3204	0.022	0	0	0	0
Propoinic acid	0.1007	0.0098	0.1007	0.0141	0	0	0	0

toxicity (health related impacts) (HTPI, HTPE) and local environmental impacts (TTP, ATP) reduces with the increase of steam flow rate. As normalized impact scores of the chemicals in the process (see Table 5) shows clearly that chemicals involved in the process have ecological toxicity impacts (HTPI, HTPE), local environmental impacts (TTP, ATP) while global impacts (GWP, ODP) are zero and regional impacts (PCOP, AP) are almost negligible. Thus increase in direct steam flow rate improves the separation and reduces the HC's in the base stream (effluent stream) hence results in reduction of ecological toxicity (health related impacts) (HTPI, HTPE) and local environmental impacts (TTP, ATP). But on the other hand, more direct steam flow increases the global and regional environmental impacts (GWP, ODP, PCOP and AP) due to contribution of energy consumption term as shown in Fig. 7(e–h). This also shows the conflicting nature of these individual impact categories i.e. the improvement of environmental performance in one group of impact categories (such as HTPI, HTPE, TTP and ATP) results in reduction of environmental performance in other group of impact categories (such as GWP, ODP, PCOP and AP). As the objective of distillation unit under study is recovering HC's from waste stream which otherwise results in pollution to the environment and loss of economic performance of the process. Thus during the optimization of the process, variables should be selected such as the combined total potential environmental impact (i.e. potential environmental impact of the residual waste stream (base stream) and potential environmental impact due to the energy consumption in the process) is less than the impact without distillation column unit (3.047×10^3 PEI/h) along with satisfaction of process constraints.

3.2.2. *Energy consumption E_C*

Distillation column units are responsible for significant energy consumption in the process industry. In the process under study, heat energy is supplied by direct steam input. Electrical energy needed to run the feed pump and reflux pump is constant for all alternatives and small as compared to heat energy provided for separation so neglected in the energy consumption calculation. Eq. (2) is used for factor E_C calculation. Fig. 8(a) shows the sensitivity analysis of this factor with respect to optimization variables of distillation column unit under study.

3.2.3. *Resource conservation R_C*

The resource conservation factor is calculated using Eq. (3). The distillation column unit under study is a non-reactive distillation process so this factor considers only water resource, which is used as heating utility (steam) and cooling utility (water). Fig. 8(b) gives the sensitivity analysis results of this factor with respect to optimization variables (reflux ratio and steam flow rate). It is clearly evident that increase in reflux flow rate increases the steam flow rate, which in terms increases the cooling water requirement and decreases the head product so resource consumption per kg of product increases.

3.2.4. *Fugitive emission (E_f)*

Fugitive emissions are releases which include fugitive equipment leaks from valves, pump seals, flanges, compressors, sampling connections, open ended lines, etc. and any other non point air emissions. These emissions occur from process sources that are large in number and difficult to identify. P & ID of the process under study is examined carefully and sources for fugitive emissions are identified. Average emission factors

Table 6
Normalized impact score of coal energy for different categories of potential environmental impact

Normalized impact score of energy ($\Psi_L^E \sim \Psi_L^{ep-g}$)							
HTPI	HTPE	TTP	ATP	GWP	ODP	PCOP	AP
7.83×10^{-5}	1.22×10^{-6}	7.83×10^{-5}	2.65×10^{-4}	2.03×10^{-9}	1.93×10^{-4}	7.07×10^{-8}	5.98×10^{-3}

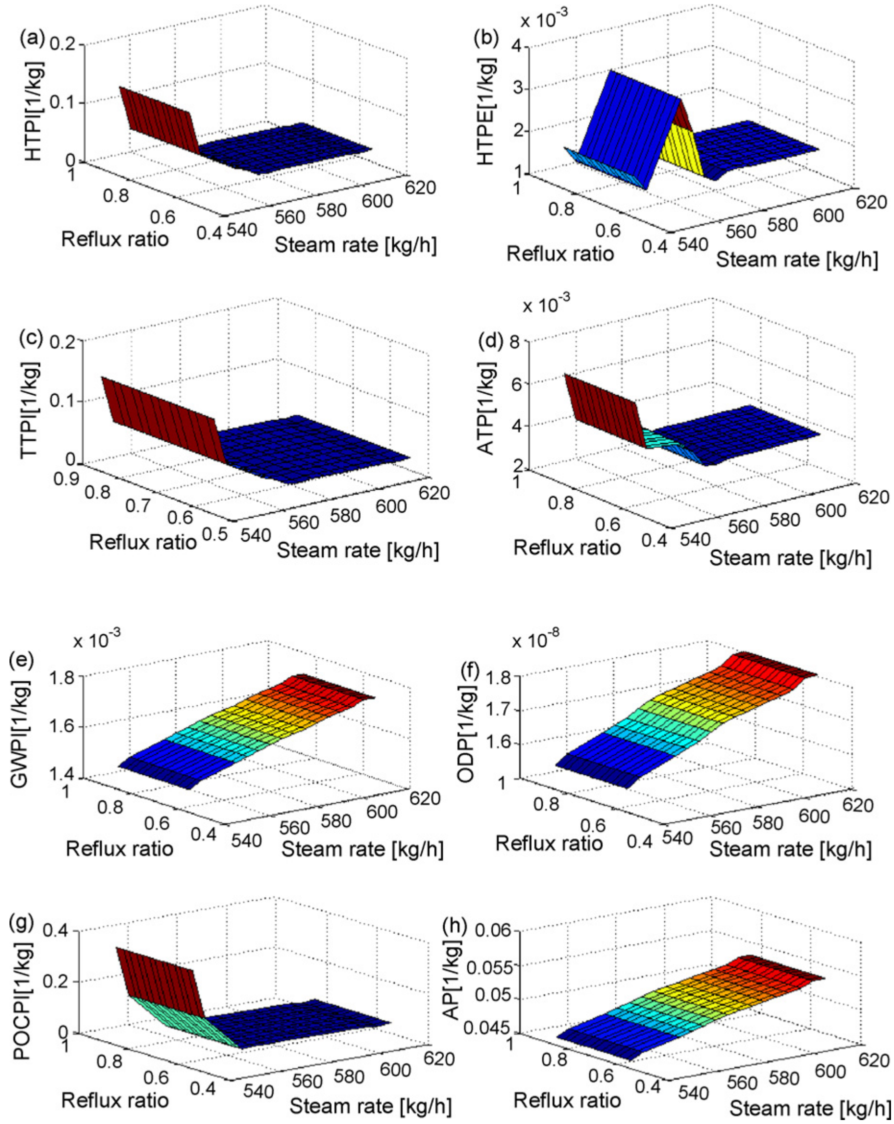

Fig. 7. Sensitivity analysis of individual environmental impacts for base case.

for estimating fugitive emissions from fugitive sources found in synthetic organic chemical manufacturing industries operations (SOCMI) obtained from the US Environmental Protection Agency L & E Databases listed in Table 7 are used in Eq. (4) for calculation of fugitive emissions E_f. For the base case, the fugitive emissions sources identified includes 53 valves, 4 pump seals, 17 sampling valves, 17 open ended lines and 211 flanges and other connections. The E_f calculated for this alternative per kg of product is 1.26×10^{-3}. While for modified case, the fugitive emissions sources identified include 58 valves, 4 pump seals, 18 sampling valves, 18 open ended lines and 238 flanges and other connections. So E_f calculated for this alternative per kg of product is 9.27×10^{-4}. The interesting point to be noted is that for modified case the total fugitive emission is greater as compared to base case but the factor E_f i.e. fugitive emission per kg of product is less as compared to base case alternative because of considering the side stream also as product stream. However, Table 8 gives results of the individual environmental impact categories calculation for environmental optimum conditions.

3.3. CSIII—determination of weighting factors (application of AHP)

In order to integrate individual environment impact categories into one index, weighting factors among these individual environment impact categories are determined using a multiattribute decision analysis method, analytic hierarchy process (AHP) as explained in Section 2. A pairwise comparison matrix (Table 9) is constructed for determination of weights for aggregation of individual potential impact categories into total potential environmental impact. Numerical comparison scale 1–9 (see Table 1) is used for pairwise comparison. The numerical comparison scale is chosen using the guidelines of US EPA science advisory board (SAB-EC-90-021). The ecological toxicity (health related impacts) (HTPI, HTPE) is slightly preferred over local environ-

Table 7
Average emission factors for estimating fugitive emissions from sources found in synthetic organic chemical manufacturing operations from US-EPA

Sources	Service	Emission factors (kg/h/source)
Distillation column vents	–	0.70 (kg emitted/1000 kg throughput)
Valves	Hydrocarbon gas Light liquid Heavy liquid	0.00597 0.00403 0.00023
Pump seals	Light liquid Heavy liquid	0.0199 0.00862
Compressor seals	Hydrocarbon gas	0.104
Pressure relief valves	Hydrocarbon gas Liquid	0.104 0.007
Flanges and other connections	All	0.00183
Open ended lines	All	0.0017
Sampling connections	All	0.015

Table 8
Individual potential environmental impacts for each alternative

	Optimum base case	Optimum modified case
HTPI	2.21×10^{-2}	1.05×10^{-2}
HTPE	1.58×10^{-3}	9.19×10^{-4}
TTP	2.21×10^{-2}	1.05×10^{-2}
ATP	3.47×10^{-3}	2.16×10^{-3}
GWP	1.59×10^{-3}	1.05×10^{-3}
ODP	1.67×10^{-8}	1.11×10^{-8}
PCOP	4.35×10^{-2}	8.76×10^{-3}
AP	4.93×10^{-2}	3.19×10^{-3}
E_f	1.26×10^{-3}	9.27×10^{-4}
E_c	8.23	5.67
R_C	15.49	10.35

Each impact has units of 1/kg product, E_f has units of kg/kg product, E_C has units MJ/kg product and RC has units of kg/kg of product. Reflux ratio and steam rate for base case is 0.7 and 580 kg/h. Reflux ratio and steam rate for modified case is 0.7 and 569 kg/h.

Table 9
Pairwise comparison matrix for individual impact categories

	Pairwise comparison matrix							
	HTPI	HTPE	TTP	ATP	GWP	ODP	PCOP	AP
HTPI	1	1	3	3	1	1	3	3
HTPE	1	1	3	3	1	1	3	3
TTP	0.333	0.333	1	1	1	1	1	1
ATP	0.333	0.333	1	1	1	1	1	1
GWP	1	1	1	1	1	1	3	3
ODP	1	1	1	1	1	1	3	3
PCOP	0.333	0.333	1	1	0.333	0.333	1	1
AP	0.333	0.333	1	1	0.333	0.333	1	1
W_L	0.194	0.194	0.090	0.090	0.152	0.152	0.065	0.065

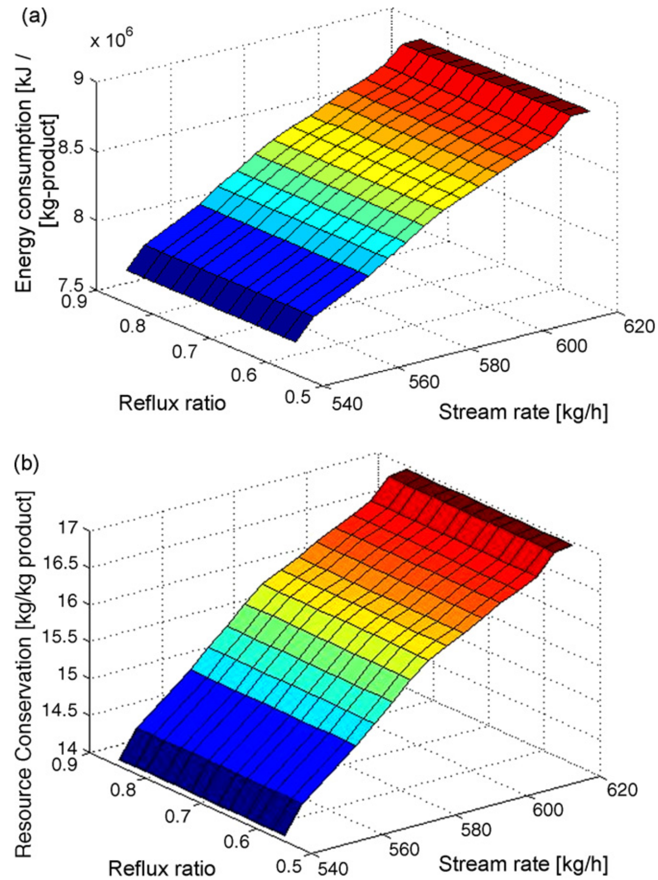

Fig. 8. Sensitivity analysis of energy consumption and resource conservation for base case.

mental impacts (TTP, ATP) and regional impacts (PCOP, AP) so a score of three is given in pairwise comparison. The global environment impacts (GWP, ODP) are slightly preferred (score given three) over regional impacts (PCOP, AP). Once a pairwise comparison matrix is constructed, then priority weights of each individual impact category is determined by dividing each number in a column of the pairwise comparison matrix by its column sum and then averaging the row entries of the new matrix. Priority weights obtained are also given in Table 9. The consistency ratio of this pairwise comparison matrix is 0.031, which is less than 0.1, showing the good level of consistency in decision maker's preferences. Similarly a pair wise comparison matrix (Table 10) is constructed to determine the weighting factors for aggregation of individual categories total PEI, R_C, E_C and E_f according to decision maker's preferences using AHP

Table 10
Pairwise comparison matrix for individual impact categories at level 2

	Pairwise comparison matrix			
	PEI	R_C	E_C	E_f
PEI	1	1	1	1
R_C	1	1	1	1
E_C	1	1	1	1
E_f	1	1	1	1
W_L	0.25	0.25	0.25	0.25

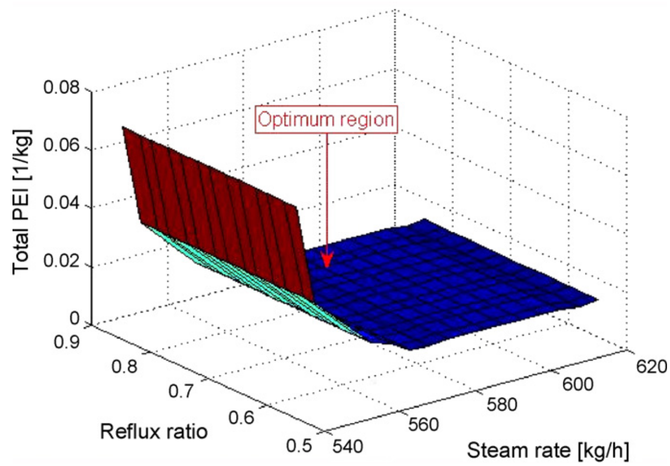

Fig. 9. Sensitivity analysis of total potential environmental impact for base case alternative.

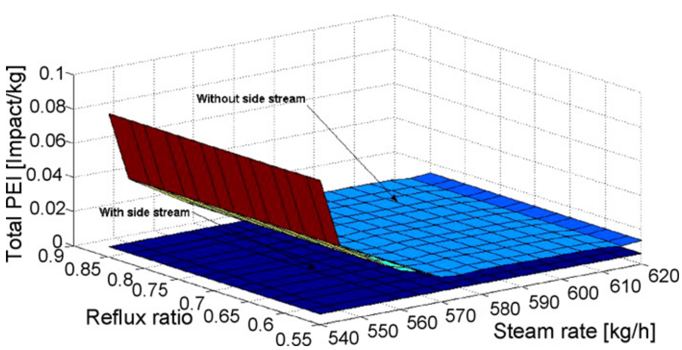

Fig. 10. Effect of side stream on total potential environmental impact.

method into environmental performance index. In this study, equal preference is given to all factors for determination of overall environmental performance index.

3.4. CSIV—environmental performance index calculation

In final step, the total potential environmental impact is obtained by multiplying each impact category value with its relevant weighting factor using Eq. (7). The total potential environmental impact (total PEI) for base case and modified case under environmental optimum conditions is 1.32×10^{-2} 1/kg and 4.29×10^{-3} 1/kg, respectively. Fig. 9 shows the sensitivity analysis of total potential environmental impact with respect to optimization variables (reflux ratio, steam flow rate) for base case alternative. However, difference in total potential environmental impact between the base case and modified is shown in Fig. 10. After calculating total PEI, environmental performance index (EPI) is determined using Eq. (8). The value of environmental performance index for base case and modified case is 5.93 and 3.98, respectively. This shows withdrawal of side stream improves the environmental performance of the process.

4. Summary

Environmental performance evaluation is needed for incorporation of pollution prevention in each stage of a chemical process. This paper illustrates a systematic methodology, which integrates not only local (HTPI, HTPE, ATP, TTP), regional (AP, PCOP) and global (GWP, PCOP) environmental impacts (which are integrated within WAR) but also incorporates other factors such as resource depletion, energy consumption and fugitive emissions. Instead of using the typical range between 0 and 10 for value of weighting factors (*W*), multiobjective decision analysis technique-analytic hierarchy process (AHP) is used for determination of weighting between different impact categories. Data used for impact categories are based on the study by Heijungs et al. (1992). The hydrocarbon recovery process (distillation unit) from an industrial plant is used to explain the different steps of the methodology. The following conclusions are drawn from case study:

Table 11
Economic and environmental optimum conditions for base case alternative

	Economic optimum	Environmental optimum
Steam flow rate (kg/h)	560	580
Reflux ratio	0.61	0.7

- For distillation column units designed to separate waste solvent or valuable products from effluent stream, the economic optimum conditions may be different from the environmental optimum conditions due to soft composition constraints of product streams. For example, Table 11 gives the economic and environmental optimum conditions for base case alternative in above case study.
- In designing or modifying distillation column units or processes, the care should be taken that the total environmental impact after the separation process or modification is less than before separation process or modification.
- Detailed degree of freedom analysis is or should be performed to select the optimization variables to optimize the base case and modified alternative before comparison to select the best alternative. In the above case study, reflux ratio and steam flow rate are selected as optimization variables.
- The simulation model should, if possible, be validated against plant conditions before using the results.
- The sensitivity analysis of objective function is or should be performed with respect to optimization variables to see the effect of optimization variables on the objective function.
- The modification to withdrawal of side stream proves to have considerable affect on the improvement of environmental performance and also carries economic potential if alcohols are separated from it and used as fuel.

Although this method is illustrated with a distillation column, it can be used for any unit operation.

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