AIChE

Implementation of Sustainability Drivers in the Design of Industrial Chemical Processes

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DOI 10.1002/aic.12497
Published online February 3, 2011 in Wiley Online Library (wileyonlinelibrary.com).

A methodology based on key performance indicators was developed and applied to the design of sustainable industrial processes. The methodology provides a procedure for the definition of a dynamic set of quantitative key performance indicators suitable to capture the environmental, economic and societal impacts of process options, thus, tracing the sustainability footprint of alternatives. The preliminary design of a production plant for cyclohexanone is presented as the leading case in the discussion. The influence of design choices on environmental impact profiles, economic efficiency and inherent safety performance was pointed out. The application evidenced that the definition of appropriate indicators may have an important added value in supporting design activities, both for the correct assessment of alternative options and for the proactive identification of design improvements. *AIChE J*, 57: 3063–3084, 2011
Keywords: inherent safety assessment, sustainability assessment, cyclohexanone, process key performance indicators, process design

Introduction

Over several years the society has been asking to the chemical and process industry for a growing commitment toward the development of sustainable and safe production processes. As a matter of fact, beside conventional economic and technical drivers, the development of innovative production processes is increasingly conditioned by their environmental and safety performances, that influenced the social acceptability of new technologies.[1,2] The adoption of a sustainability perspective is proposed to address by a structured and comprehensive strategy, the economic, societal and environmental aspects of industrial activities.[1,3] Following this approach, the optimization efforts focused on specific aspects of the system performance may more easily overcome conflicting strategies or risk-shift phenomena (e.g., process intensification vs. safety[4]).

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The development of specific guidelines and tools is required to effectively implement sustainability at the different scales of industrial activity. Guidelines as the principles of "green chemistry"[5] and of "green engineering"[6] cast a preliminary conceptual base. However, these principles are not adequate for a sound support of design activities,[1,7] and quantitative assessment tools are required to check the effectiveness of design choices and to allow tradeoffs.

The first conceptual step in the definition of a sustainable process is the selection of the reaction scheme. Quantitative indices for the analysis of reaction schemes have been proposed and reviewed in several studies.[8–14] These metrics mostly rely on the data that may be directly obtained from reaction stoichiometry and yields, and may give only partial results, since energy consumption, process hazards, material recovery and recycle may not be fully accounted.

More complete quantitative approaches were proposed in the literature to assess the sustainability of a process,[15] requiring a higher level of information. However, existing methods are not fully suitable for application as design support tools. Several metrics are focused on the assessment of

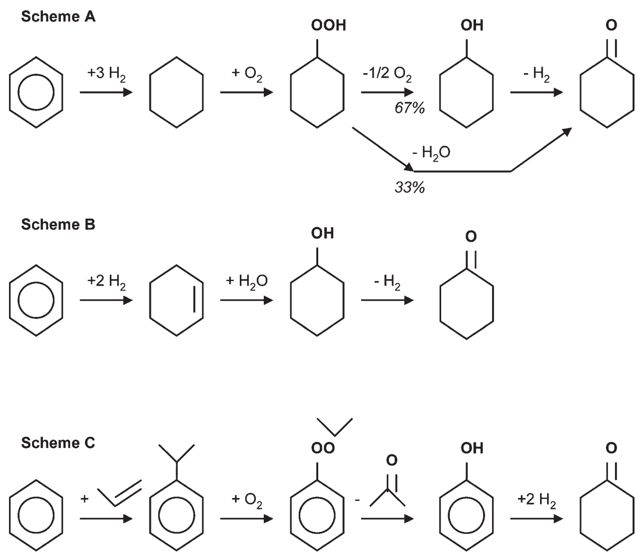

Figure 1. Reference reaction schemes considered for the leading case in this study.

single impacts (e.g., material and energy flow analysis,[1] exergy balances,[16–17] specific midpoint environmental indicators,[2,18–21] endpoint environmental indicators,[22–23] etc.), requiring aggregation for a complete and comprehensive assessment. The numerical aggregation usually proposed for process performance analysis (e.g., BASF,[24–26] SCENE,[21,27,28] WAR,[29,30] LCA techniques,[22,23] analytic hierarchy process,[31] multi-attribute utility theory,[32] etc.) introduces critical issues, still not thoroughly investigated, concerning the different nature of indicators, the completeness of the selected indicator set, the definition of reference values and the use of subjective parameters.[1] The approaches resorting to a single common unit of measurement (e.g., economic measures, exergy, emergy, etc.[16,17,33–35]) avoid only formally the problems and may not be suitable to assess all the domains concerning sustainability (e.g., usually do not account for societal and economic impacts). Although being a promising and powerful tool, conventional environmental life cycle assessment (LCA)[22] presents some open issues in the specific application to the preliminary assessment of process flow diagrams (PFDs), although valuable proposals were recently advanced.[36] Critical points concern the large amount of data required over the entire lifecycle (thus, well apart from the process section to be designed), the identification of a specific but yet complete set of indicators for assessment of chemical process diagrams and the inclusion of site-specific factors. A standardized approach to account for multiple impacts (environmental, safety, costs, etc.), to define tailored indicators applicable in preliminary design and to include the nonlinear correlations that may be present among some design actions and their impacts still needs to be consolidated.

This study focused on the application to the preliminary design of an industrial plant of a methodology specifically developed for the sustainability assessment of alternative process flow diagrams, and based on the definition of a dynamic set of design key performance indicators (KPIs). The preliminary design of a plant for the production of cyclohexanone, a widely used chemical intermediate, is presented as a leading sample case to demonstrate the potentiality of the approach. Three reference process flow diagrams were compared, representing possible industrial processes that may be implemented. The sustainability fingerprint of each option was assessed. A specific normalization approach was applied to rank the impacts of each option according to their relevance in the specific site considered for process implementation. The relative performance of the three process alternatives was compared, aiming at the identification of the critical process sections and at the support of further design improvements.

The application of a method specifically designed for the assessment of preliminary process flow diagrams overcomes the limitations of nonspecific assessment tools and the oversimplifications of methods based, e.g., on the sole reaction stoichiometry. The KPIs, selected and aggregated according to a customized tree of impacts, provide a quantitative assessment which limits built-in assumptions in evaluation, promotes completeness of the analysis and allows the introduction of site-specific factors.

Leading Case: Cyclohexanone Alternative Production Processes

The leading case selected to analyze the potentialities of the methodology is related to the assessment of the more sustainable strategy for cyclohexanone production. Three alternative process options were compared and the critical issues to be addressed in further design and optimization steps were identified. Cyclohexanone is an important intermediate in chemical industry, used in the production of nylon 6,6, of adipic acid, and of other fine chemicals.[37] Several process options were proposed and applied for cyclohexanone production in the last 70 years. In this study, three alternative reaction strategies (Figure 1) applied in industrial processes[38] were selected to represent alternative routes for cyclohexanone production:

- Scheme A: synthesis via oxidation of cyclohexane;
- Scheme B: synthesis via hydration of cyclohexene;
- Scheme C: synthesis via hydrogenation of phenol.

The simple definition of reaction schemes conveys only information on the stoichiometry of the reactions. This allows the calculation of a preliminary green chemistry index, the atom economy (AE) index[14] (Table 1). Although schemes B and C are identified as very promising (no wastes generated from elimination reactions), such analysis ignores elements as the yields of reactions and the separation and recycle structure of the process that deeply influence the material efficiency performance. Table 1 also reports the reaction mass efficiency (RME) index, calculated considering

Table 1. Green Chemistry Indices Used in the Preliminary Analysis of Reaction Schemes (AE, Atom Economy; RME, Reaction Mass Efficiency[14])

	Option A	Option B	Option C
AE	0.86	1.00	1.00 (0.63)
RME No recycle	0.017	0.161	0.048 (0.046)
RME	0.553	0.832	0.763 (0.510)

AE = (mass of product according to stoichiometry)/(mass of all reagents according to stoichiometry).
RME = (mass of product)/(total mass fed to the process).
Values in brackets refer to the case of acetone considered as waste.

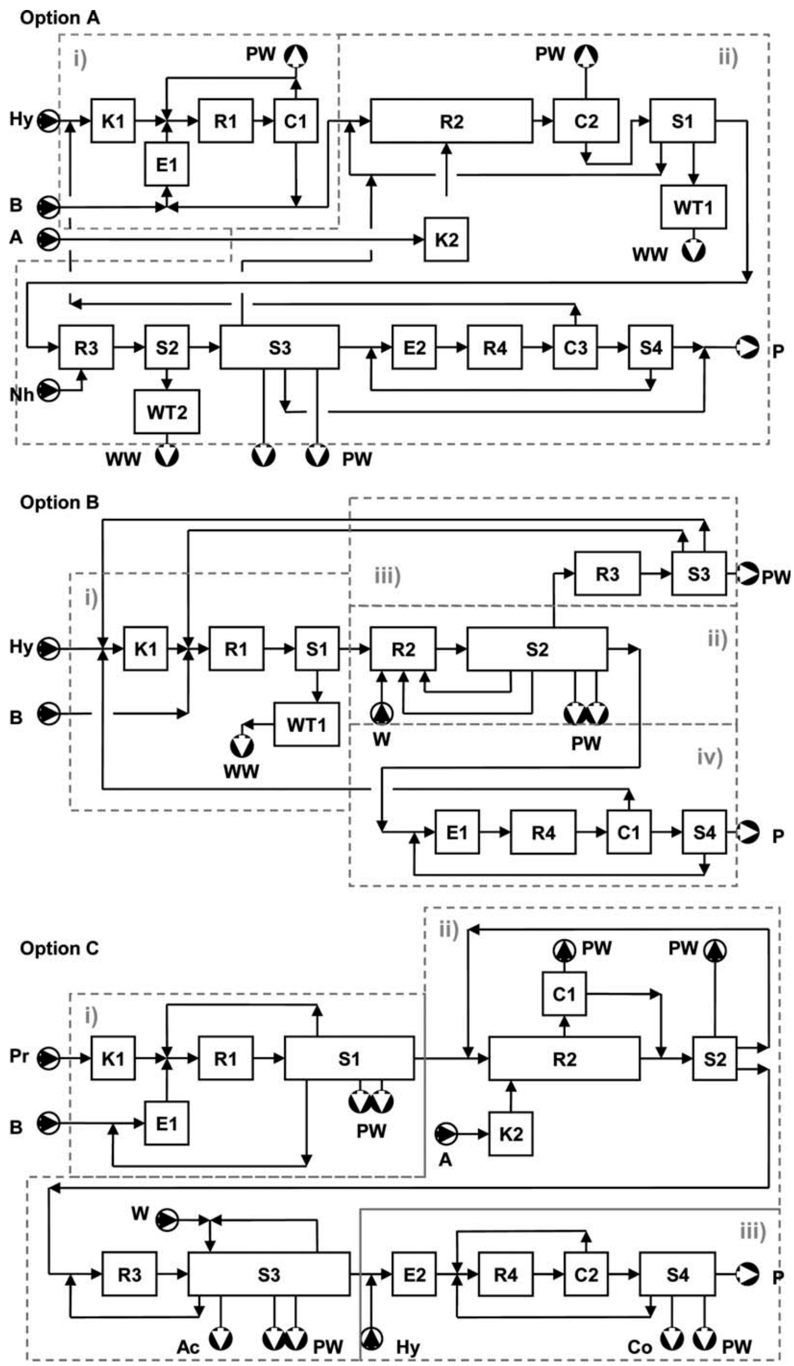

Figure 2. Block diagram of the three reference processes considered for the leading case.

Materials: B, benzene; A, air; Ac, acetone; Co, cyclohexanol; Hy, hydrogen; Nh, sodium hydroxide; P, product (cyclohexanone); Pr, propene; PW, purge/exhaust/waste/minor co-product; SS, salt solution; W, water; WW, waste water.

Blocks: C, condensation; E, vaporization; K, compression; R, reaction; S, separation; WT, water treatment.

separation efficiencies and recycles. The values clearly show the dramatic effect on the performance of options A and C, since low conversion is required in the oxidation stages to enhance selectivity.

Going beyond the preliminary reaction indices derived from green chemistry requires the application of a more comprehensive approach aimed at sustainability assessment, as that considered herein. The application of the approach was based on the definition of reference PFDs for each of the three reaction schemes in order to quantify the effect of separation and recovery performance. Figure 2 summarizes in a simplified block diagram the three process options defined for the analysis. The same figure identifies the main sections of each process alternative (see Appendix A for further details). On the basis of data on several existing plants, a cyclohexanone production potential of 100,000 t/y was

Table 2. Selected Input/Output Data Calculated for the Alternative Process Options (pr.: Product)

Process option	Benzene kg/kg pr.	Oxygen (air) kg/kg pr.	Water kg/kg pr.	Other Raw mat. kg/kg pr.	Fuel kg/kg pr.	Electricity kJ/kg pr.	Co-products kg/kg pr.	Overall yield
A	1.07	0.47	1.34	0.31	0.45	4248	1.37	74.5%
B	0.99	–	0.18	0.02	0.31	1031	–	80.2%
C	0.98	0.36	0.001	0.61	0.34	578	0.65	81.0%

Overall yield = (mol of cyclohexanone produced)/(mol of benzene fed to the process).

considered. A 99% minimum purity was assumed for the final product (cyclohexanone). Preliminary sizing of process equipment and complete quantification of material balances were also performed. Energy balances were completed for all the defined options, identifying the consumptions of fuel and electrical power. The fugitive emissions were estimated by average emission factors for the expected leak points in the process flow diagram (e.g., seals, joints, valves, etc.),[2] and by evaporation models in the wastewater treatment units.[39] The emission of micropollutant from the utilities (e.g., power generation, wastewater treatment, etc.) were evaluated by emission factors from available databases.[2,39,40] Economic data were also retrieved or assessed. Economic parameters (e.g., material, energy and operative costs, capital costs) were evaluated by average unitary costs.[41–43] The specific equivalent number of employees necessary for process activities was the result of an expert judgment based on existing or similar plants. The preliminary sizing of the more important pieces of equipment allowed the estimation of the unit inventories required in the inherent safety analysis. Table 2 reports selected examples of input and output data obtained.

Methodology Proposed for Sustainability Assessment

Assessment methodology

The flow diagram reported in Figure 3 summarizes the sustainability assessment procedure applied in this study to evaluate and compare the performance of alternative process flow diagram (PFD). The methodology used for the assessment was a further development of that proposed in a previous study for the sustainability assessment of waste disposal processes.[44] In particular, the critical points concerning the effective application of the method were revised and integrated: a dynamic stage for the definition of the starting set of KPIs was introduced, a Monte-Carlo based approach was suggested to check the sensitivity of results, and a simplification stage was added to improve the presentation and the analysis of the sustainability footprint.

The main goal of the procedure is the comparison of a finite number of alternative design options, identifying the preferable configurations and recognizing the design choices more critical with respect to the expected sustainability performance. As a matter of fact, preliminary design typically concerns a relatively limited number of possible alternatives. Optimization of the critical process parameters is usually addressed in a successive design stage by application of suitable optimization techniques. These include Pareto optimization (e.g., see Azapagic and Clift[45,46]), as well as approaches based on aggregated values (e.g., see Chen et al.,[21,28] Azapagic and Clift[47]). Although the proposed KPIs may be used in objective functions, the optimization stage falls beyond the scope of this study.

Figure 3 reports the main steps of the assessment procedure. In the first step, the reference basis and the process boundaries are defined. Process boundaries include all the process units and all the pertinent utilities present onsite (e.g., boilers, wastewater treatment). For nondedicated utilities, only the impact quote allocable to the process of interest is considered.

In the second step, a specific set of primary categories of impact and a correspondent set of key performance indicators (KPIs) needs to be defined. An innovative procedure based on the customization of a ''tree of impacts'' is proposed and will be discussed in detail in the next section.

In step 3, the site-specific reference values for normalization ad aggregation of KPIs are defined considering an expected target area for each impact category.[44] The target

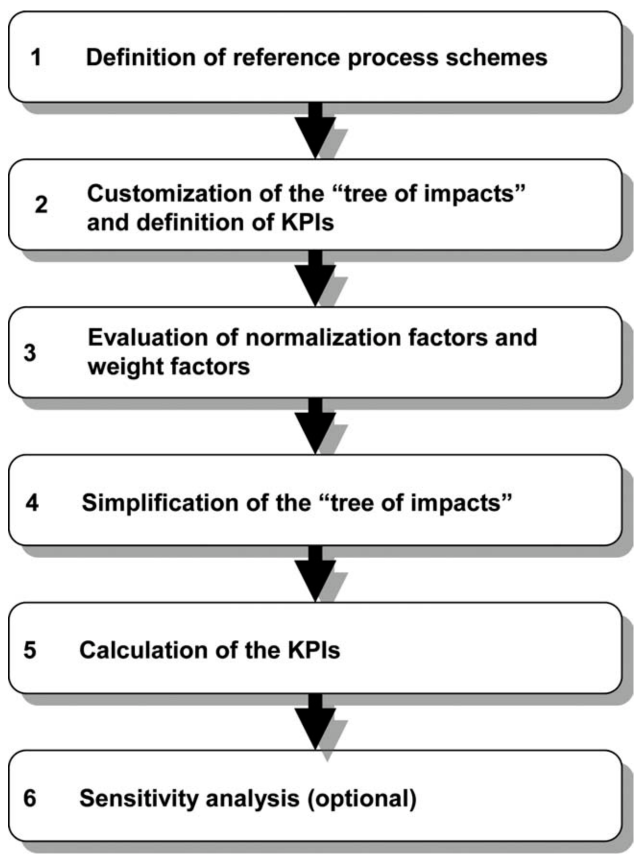

Figure 3. Conceptual flow-chart of the proposed assessment procedure.

area is the area that is loaded and/or affected by the impact of concern. The external normalization factor is assessed accounting the impacts of the industrial facilities already present in the area. Under these assumptions, the normalized indices used in the approach are a direct measure of the relevance of the additional impact of the process to the local site conditions. In this step, the weight factors are also defined for each branch of the tree. The weight factors proposed in Figure 6 were evaluated according to the distance from target values set at national and local level for growth and impact reduction using the procedure described by.[44] Thus, the values of the weight factors used are proportional to the annual reduction rate required for each specific impact by the sustainability policy.

In step 4, the ''tree of impacts'' developed in step 2 may be simplified by the application of cut-off criteria aimed at the elimination of the impact categories which are not relevant for the processes of concern. The simplification step has, thus, an important role in the ''pre-analysis'' of the results. It is based on the estimation of the order of magnitude of the indicators, evaluating impacts with a lower level of detail than what is later necessary for the actual analysis and aggregation. The procedure and the criteria will be discussed in the section ''Simplification of the tree of impacts''.

In the fifth step of the procedure, the values of the primary KPIs, addressing single key impact categories, are calculated for each option. A limited number of aggregated indicators may be obtained from the array of normalized indicators (Figure 6). A staged multi-criteria weighted summation procedure[44] may be used to carry out the aggregation. The ''sustainability fingerprint'' of an option is, thus, described by a multilevel hierarchy of the KPI values, defined according to the tiers of the ''tree of impacts''.

Clearly enough, the introduction of weight factors in step 4 is a nontechnical stage of the analysis that may introduce a bias in the results. Thus, after the calculation of the indicators, a sensitivity analysis was carried out to understand how the aforementioned assumptions influence the final results (step 6).

Customization of the tree of impacts: dynamic definition of the KPI set

A systematic procedure based on the definition of a ''tree of impacts'' (Figure 5a) was proposed for the identification of a generalized set of key performance indicators (KPIs). The development of a tree-like structure was inspired to similar representations of a hierarchic structure extensively applied in safety, decision making and computer technology (see e.g. Mannan,[48] Goodwin and Wright,[49] de Ville,[50] etc.). The ''tree of impacts'' is defined as a hierarchic structure built according to the identification of impact categories of concern in the perspective of process sustainability assessment. Globally, the ''tree of impacts'' provides an organized representation of the concerns of the sustainability policy and of the interests of the stakeholders. The general structure of the tree is independent from the specific process that is analyzed.

The basic structure of the tree of impacts is proposed in Figure 4. As shown in the figure, this consists of three tiers of indicators. The structure was inferred combining the classification of impacts metrics proposed in former approaches to the problem.[1,15,24,51,52] The root of the tree (first tier) is the impact target selected for the analysis (i.e., the overall impact on sustainability). The second tier of indicators addresses the three domains of sustainability.[1,5,15] At the third tier, the domains are further specified in subdomains of concern. Environmental impacts are classified according to emissions to distinct environmental media (air, water and soil), and to the use of valuable resources (inclusive of materials I/O flows, energy I/O flows, land, etc.).[1,15,24] Impacts on the society are classified as internal or external to the facility (i.e., system of concern).[15,24] With respect to the economic impacts, no standard subdomains are proposed, since all the relevant components for industrial processes (e.g., profit, value, investments, etc.[15]) can be generally described by a single monetary indicator.[18,21,24,51] The definition of this standard basic structure for the tree aims at providing a common taxonomy in the assessment and to promote completeness in the definition of the KPIs.

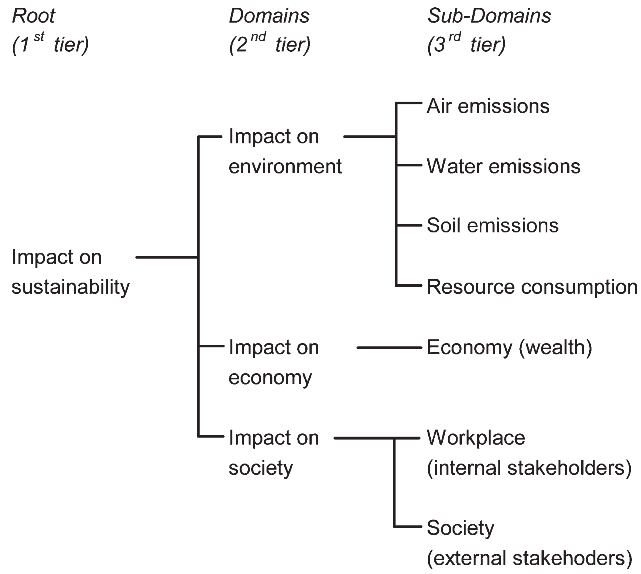

Figure 4. Basic structure of the ''Tree of Impacts''.

Above the basic three structures, a further branching level is present (fourth tier of indicators). The fourth tier of the tree of impacts is used to identify the system and the site specific sustainability concerns. In tier 4, each set of impact categories is customized by a systematic review of the disaggregated contributions to the subdomain (tier 3 category indicator) of concern. A suitable tier 4 impact category should represent the potential outcomes of choices/elements implemented in the design activity of concern (i.e., preliminary PFD definition). A structured brainstorming shall be used for the identification of the potential impact mechanisms and, consequently, of the relevant impact categories. Suitable tools include the OECD approach to safety KPI definition,[53] the application of *system dynamics*[54,55] and the use of guideword-based approaches adapted from process hazard identification techniques[48,56]). An example of the latter technique is provided for the leading case in section ''Results and discussion''. Appendix B reports a list of possible impact categories for tier 4 of the tree. The adoption of a structured approach promotes the flexible selection of a systematic set of impact categories representing the available knowledge and the specific features of the problem analyzed. The hierarchy provided by the tree of impacts can be used as set of guidewords, and provides a systematic and auditable representation of the outcomes.

The impact categories at tier 4 are usually suitable to be defined as primary. A primary impact category (a leaf of the tree of impacts) is an impact category non further developed, since a suitable KPI can be defined to quantify the impact. A suitable primary KPI should satisfy the following attributes:

1. it introduces a quantitative metric;
2. it is directly linkable to the specific characteristics of the assessed options (e.g., midpoint indicator);
3. it has additive characteristics, thus, allowing for normalization;
4. it introduces, as far as possible, a well-known or consolidated metric.

If no practical metric can be defined for a given impact category, a higher level tier of the tree of impacts should be developed for that category, progressing recursively until one or more than one suitable KPI can be defined. However, the use of comprehensive metrics should be preferred, in order to limit need for aggregation steps. Even if a primary KPI is identified and used in the aggregation at a later stage, the interpretation of the results may be better supported by the introduction of optional indices for possible impact subcategories. An example of these subindices is discussed in the following for the category ''inherent safety''.

As a matter of fact, the definition of metrics for the primary categories may be conditioned by the availability of data for the evaluation of the normalization factors. The current methodology asks for the definition of sound references for the normalization of indicators. The data sources for normalization factors (databases and statistics on industrial activities, emissions, occupation, welfare, accidents, etc.) frequently report generic and aggregated data, hindering the applicability of excessively detailed metrics. Nevertheless, the level of detail of primary KPIs can be enhanced by the definition of relevant subindices. This operation is primarily aimed at favoring interpretation of the results, assessing specific contributions to the primary KPI. Clearly enough, the subindices should be subparameters or contributors of the primary KPI metric.

Figure 6a reports the tree of impacts proposed for the leading case. As shown in the figure, several metrics were defined for the relevant subdomains, according to the impact categories introduced in Appendix B. In the case of inherent safety, two relevant subindices were defined: the *potential hazard index* (PI), and the *inherent hazard index* (HI) (Figure 9). While the HI, featuring worst credible accidents, was actually used in the aggregation, the intermediate index PI was finalized to the better analysis of the results, by the identification of the worst case accident potential (see Tugnoli et al.[57] for further details). The calculation of partial subindices yielding the contribution of different plant section to the overall category index (e.g., Figure 8 of the leading case) is another example of subindex customization, enhancing the interpretation of the analysis outcomes.

Simplification of the tree of impacts

The tree of impacts defined at step 2 of the assessment (Figure 6a) may be simplified, cutting the primary impact categories not relevant for the specific problem that is assessed (Figure 5b). This optional simplification has an important role in the ''pre-analysis'' of the set of options, easing the presentation and the interpretation of the preliminary results. Clearly enough, this preanalysis is an optional step of the assessment. Although the holistic perspective of sustainability calls for a widely inclusive assessment, time and resources can be saved in the evaluation of KPIs if the nonrelevant impacts are removed from the assessment (i.e., simplifying the tree). In many practical cases, the impact categories which are negligibly affected by all the assessed options can be easily identified by a swift estimation of the order of magnitude of the impact metrics. This can be obtained by a lower detail application of the same procedures used for the detailed analysis or by alternative shortcut methods. A simplification approach for the identification of relevant impact categories is presented in Figure 5b for the leading case. For each KPI, the higher-order of magnitude among the options is compared with the corresponding normalization factor, to yield the order of magnitude of the normalized KPIs. Figure 7 demonstrates that differences up to several orders of magnitudes may be present among the normalized KPIs. Thus, it is reasonable to retain for further assessment only the impact categories having a higher-order of magnitude. A suitable cut-off criteria should be heuristically identified accounting for the contribution of both the uncertainty on estimated KPI values and the maximum difference between two normalized indicators that can be subverted in aggregation (i.e., equal to the order of magnitude of weight factors multiplied by -1). In the leading example discussed in the following, an uncertainty of one order of magnitude was estimated for the preliminary indicators used in the simplification stage. Since the weight factors used in aggregation do not differ of more than two-orders of magnitude, differences in the normalized KPIs larger than two-orders of magnitude are not expected to modify ranks of the aggregated indicators. Thus, as shown in Figure 7, the practical cut-off criteria used in the leading case retain only the categories within the upper three-orders of magnitude. Clearly enough, more conservative cut-off values can be adopted. Figure 6b lists the key impact categories relevant for the analyzed process options.

It is worth noticing that the weight factors defined at step 3 of the assessment procedure (Figure 6b) are not rescaled to sum up to one after the simplification of tree branches: the fraction allocated to the impact categories which are significant for the processes analyzed is maintained.

Sensitivity analysis of aggregated KPIs

Although all the parameter contributing to the evaluation of KPIs may be affected by uncertainties and approximations, the weight factors, due to their evaluation procedure and to the direct influence in the values of aggregated KPIs, require specific attention.[23,58,59] A statistical approach is proposed to analyze the sensitivity of the aggregated KPIs to the weight factors assumed in the assessment. Due to the

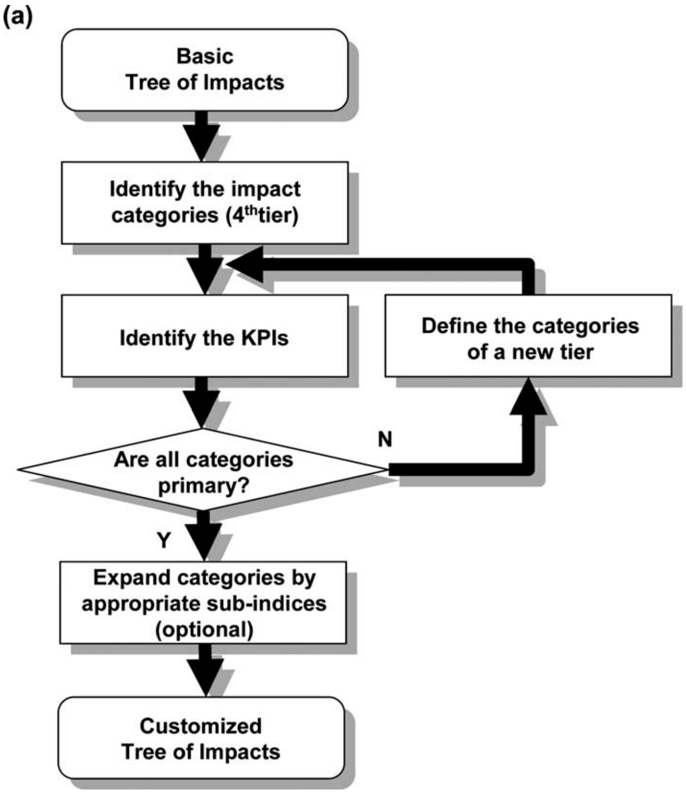

Figure 5. Conceptual diagram of the proposed tree customization procedure (a), and tree simplification procedure (b) (OOM: order of magnitude).

mathematical structure of the procedure, large variations in the values of weight factors may significantly change the numerical value of the aggregated indices. Hence, the large confidence intervals that can be associated with the aggregated values discourage an effective ranking based on straight values. However, the analysis of index differences, rather than of the actual index value, yields more robust results, since it better evidences the effect of the relative variation of the weight factors.[23,58] Clearly enough, only the relative performance or, more simply, the rank of the compared options is obtained by this technique. However, this is usually the result of practical interest in design activities. Thus, the sensitivity analysis method proposed was primarily oriented to explore, for any given aggregated index, the variation of the relative ranking of the options in dependence of the uncertainties in the weight factors. The application of a similar sensitivity approach to explore the actual range of confidence in aggregated values and the effect of uncertainty in primary KPI assessment is possible, as well, within the limits discussed earlier.

First, a value distribution is associated with each weight factor used in the aggregation. Ideally, the shape and the range of these distributions should be proposed during the evaluation of the weight factor at step 4 of the method. Distance from future target was used to assess KPI weights; following the approach of a previous study.[44] The identification of the weight factors for the best case ($W_{\min}$), the worst case ($W_{\max}$), and the more likely case (W_{med}), was possible from the corresponding expected target values. A triangular distribution can be easily defined as

$$p.d.f.(x) = \begin{cases} \frac{2\cdot(x-W_{\min})}{(W_{med}-W_{\min})\cdot(W_{\max}-W_{\min})} & if\ W_{\min} \le x \le W_{med} \\ \frac{2\cdot(W_{\max}-x)}{(W_{\max}-W_{med})\cdot(W_{\max}-W_{\min})} & if\ W_{med} < x \le W_{\max} \end{cases} \tag{1}$$

However, the uncertainty that affects target values is frequently unknown or difficult to assess in practical applications. Thus, an alternative shortcut method was defined: a symmetric triangular probability distribution was assumed for all the weight factors and the maximum range was fixed for all as a percentage of the central value (e.g., 50%). The probabilities of the values are then associated with the assumed shape in order to satisfy the consistency condition.

A Monte Carlo simulation yields a straightforward assessment of the probability distribution of the aggregated indices. Clearly enough, the consistency of the weight factor should be maintained in each run: thus, the randomly generated values for each aggregated index are rescaled so to sum up to one prior to index calculation. The relative performance of the alternative options for an aggregated category is evaluated as ''difference of the indices'' ($DI_{i,k1\text{-}k2}$)[23,58]

$$DI_{i,k1-k2} = I_{i,k1} - I_{i,k2} \tag{2}$$

in which (i) refers to the aggregated index of concern (e.g., overall, environmental, etc.) and $k1$ and $k2$ refer to a couple of alternative options. The alternative options are labeled progressively ($k1$, $k2$,...) according to the decreasing value of the i-th index as obtained by applying the base set of weight

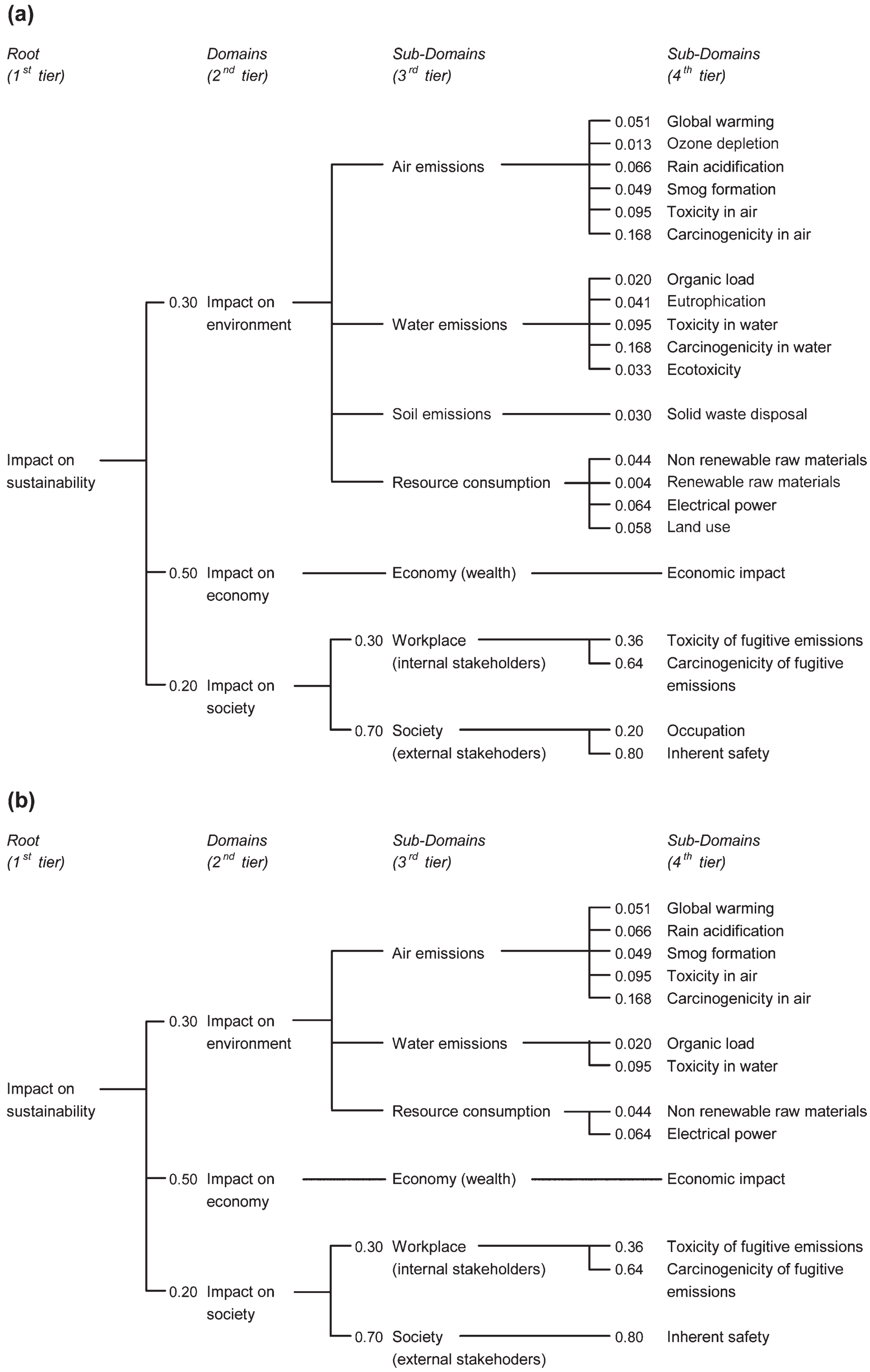

Figure 6. "Tree of Impacts" obtained for the leading case study (a) initial tree, and (b) simplified tree obtained from simplification procedure.

factors. A change in the rank of the options results in a change of sign in the index difference ($DI_{i,k1\text{-}k2}$). The application of Monte Carlo runs allows an easy assessment of the distribution results for differences of the aggregated indices and, thus, of the likelihood of rank change among the options. Moreover, the sensitivity of the results can be explored repeating the procedure for several values of the maximum range in weight factor distribution, as illustrated in Figure 13.

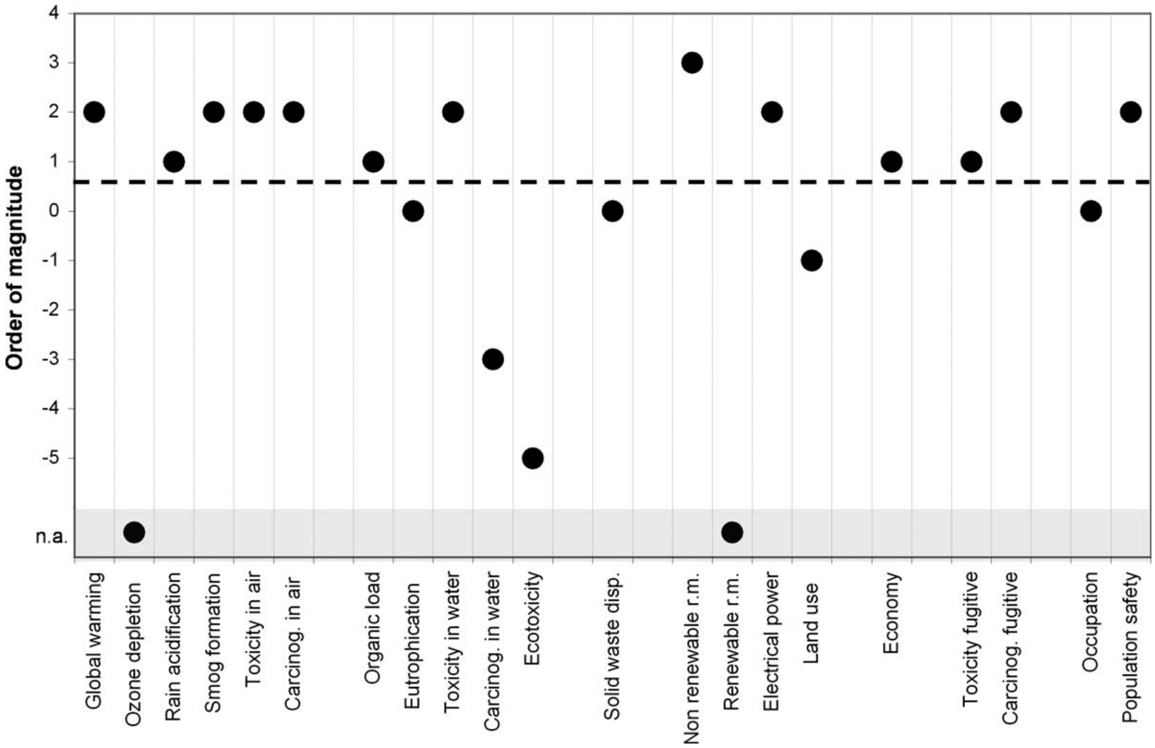

Figure 7. Tree simplification procedure: exclusion of nonrelevant impact categories (n.a.: not applicable).

Results and Discussion

Leaves of impact tree: primary impact indicators

A guideword-based approach was used for the identification of impact categories at the fourth tier (first step in Figure 5a). The relevant elements and parameters manipulated by design choices in PFD definition were screened vs. the potential to affect any of the impact categories at third tier. The matrix reported in Appendix C (Table C1) contains the results of this analysis and the impact categories identified.

According to the procedure illustrated in Figure 5a, suitable KPIs are identified for each impact category at tier 4 (Figure 6a). Midpoint potential impact indicators derived from the literature were selected for the assessment of all the environmental impacts, in accordance with the available data (Table B1). By converse, all the parameters influencing the economic impact of the process options (e.g., capital costs, revenues, raw material cost, employee cost, etc.) may be effectively encompassed by a single metric. Thus, this value of the costs and revenues along the lifecycle of the plant (installation and operation) was adopted.[44] A few indicators were identified as of particular relevance for societal impact of process options in the design phase, reflecting a lack of standardized approaches in the analysis of societal issues in design activities. The number of parameters directly influencing social aspects considered in the method is limited, due to the specific aim of the application. Nevertheless, the open structure provided by the tree of impacts easily allow for the introduction of other indicators beyond the ones considered in the leading case.

As previously discussed, the impact tree was simplified, eliminating the impact categories of minor concern, according to the procedure illustrated in Figure 5b. The order of magnitude of the impacts was estimated by a simplified analysis of the PFD. For example, the "non-renewable raw material" KPI is expected to be mainly dependent on the amount of input raw materials to the process (primarily benzene). This input should be, for all the options, of the same order of magnitude of the product output, due to relatively high overall yield (compare to actual results in Table 2). Hence, the order of magnitude for the normalized KPI is evaluated equal to 3 (i.e., $\sim 10^8$ kg_{eq}/y of benzene vs. $\sim 10^5$ kg_{eq}/(y·km^2) of the relevant normalization factor), even neglecting the contribution from fuel materials. Similarly, in the case of social indicators the order of magnitude of the normalized occupation KPI results equal to 0: the expected number of workers employed in chemical plants of similar type and size is of about $\sim 10^1$ persons and the normalization factor for the "occupation" category was assumed of $\sim 10^1$ persons/km^2, The same approach can be repeated for all the categories. Figure 7 reports the worst case identified for each category among the three possible options.

The simplified tree of impacts is reported in Figure 6b. Table 3 reports the values of the primary impact indicators calculated by a detailed analysis of the three process options. The differences in the values of these KPIs directly reflect the performance achieved by the process and design choices. For example, in the leading case the proposed alternative options require different thermal inputs in reaction and separation units. Several indicators capture the consequences of this factor on the sustainability footprint: the consumption of non-renewable material (via increased fuel use), the economic impact indicator (via fuel costs), and the environmental impact indicators, that are strongly dependent on

Table 3. Non-Normalized Values of 4th Tier Indicators (Primary Impact Categories) and Normalization Factors Used in the Assessment

	Unit	Option A	Option B	Option C	Norm. Factor
Environment					
Air Emissions					
Global worming	kg_{eq}/y	$2.58 \bullet 10^{+08}$	$1.76 \bullet 10^{+08}$	$1.97 \bullet 10^{+08}$	$1.16 \bullet 10^{+06}$
ARP	kg_{eq}/y	$8.60 \bullet 10^{+04}$	$5.48 \bullet 10^{+04}$	$6.23 \bullet 10^{+04}$	$4.83 \bullet 10^{+03}$
MIR	kg_{eq}/y	$1.11 \bullet 10^{+06}$	$2.85 \bullet 10^{+04}$	$9.61 \bullet 10^{+04}$	$5.63 \bullet 10^{+03}$
Air Toxicity	kg_{eq}/y	$2.99 \bullet 10^{+07}$	$2.11 \bullet 10^{+07}$	$2.44 \bullet 10^{+07}$	$3.77 \bullet 10^{+05}$
Air Carcinogenicity	kg_{eq}/y	$1.61 \bullet 10^{+04}$	$2.17 \bullet 10^{+04}$	$1.77 \bullet 10^{+04}$	$1.01 \bullet 10^{+02}$
Water Emissions					
Organic load	kg_{eq}/y	$2.48 \bullet 10^{+03}$	$1.33 \bullet 10^{+00}$	–	$1.79 \bullet 10^{+02}$
Water toxicity	kg_{eq}/y	$2.17 \bullet 10^{+04}$	$1.65 \bullet 10^{+03}$	–	$2.80 \bullet 10^{+02}$
Resource consumption					
Raw materials	kg_{eq}/y	$3.81 \bullet 10^{+08}$	$2.65 \bullet 10^{+08}$	$2.59 \bullet 10^{+08}$	$3.51 \bullet 10^{+05}$
Electrical power	kWh/y	$1.21 \bullet 10^{+08}$	$2.91 \bullet 10^{+07}$	$1.63 \bullet 10^{+07}$	$1.10 \bullet 10^{+06}$
Economy					
Economic impact	€	$1.69 \bullet 10^{+07}$	$-1.28 \bullet 10^{+08}$	$-5.85 \bullet 10^{+07}$	$3.40 \bullet 10^{+07}$
Society					
Workplace					
Fugitive toxic	kg_{eq}/y	$1.85 \bullet 10^{+06}$	$3.25 \bullet 10^{+04}$	$4.23 \bullet 10^{+05}$	$3.77 \bullet 10^{+05}$
Fugitive carcinogen	kg_{eq}/y	$1.01 \bullet 10^{+03}$	$8.34 \bullet 10^{+03}$	$4.23 \bullet 10^{+03}$	$1.01 \bullet 10^{+02}$
External society					
Inherent safety	km^2/y	$1.71 \bullet 10^{-03}$	$2.90 \bullet 10^{-04}$	$1.87 \bullet 10^{-03}$	$6.00 \bullet 10^{-06}$

emission of combustion exhausts (global warming, rain acidification, etc.). Thus, the more energy demanding options (e.g., option A) may be recognized by their final impacts and discouraged. The outcomes of the indicators identify two levels of design optimization aimed to reduce energy demand: (1) improvement of the process (conceptual design), and (2) improvement of the unit design (basic design). Minimizing the heat requirements of the process generally asks for a deep modification of the process, generating alternative options as the three compared here. For the basic material transformation processes, as the leading case presented, the main energy sinks correspond to the reboilers of the larger distillation columns (high-vapor flows) or to the feed vaporizers of vapor-phase reactors. Only changes in the chemistry of the process allow the limitation of separation severity (higher conversion and selectivity) and milder operating conditions (more active catalysts). Option B is a good example of the limitation of the requirements for separation, since the recycle loop effectively processes a non separated mixture. On the other hand, the design of efficient and low-emission fuel fired boilers, furnaces and integrated energy networks (e.g., HEN[2]) can reduce impacts at the level of equipment definition. Clearly enough, any proposed improvement should be assessed by the recalculation of the indicators, in order to monitor the effect of changes on process performance and to check the effect of possible impact shift phenomena (e.g., increase of costs, increase of possible leak points, etc.).

The impacts coming from specific sections of the plant can be easily identified. For example, Figure 8 shows that the carcinogenic emissions are mainly expected because of micropollutants from energy production,[40] although particular attention should be devoted to fugitive emissions from process lines rich in benzene (affecting internal stakeholders, Table 3). Thus, in the detailed design of relevant sections in options B and C, possible sources of fugitive emissions should be limited (e.g., avoiding flanged connection, using improved sealing systems, etc.). Similar conclusions may be drawn for sections with toxic and smog-promoting compounds.

The safety performance in the societal domain of the leading case provides another good example of the design influence on the process impacts. Table 3 reports the final values of the inherent hazard index (HI),[57] while Figure 9a provides a breakdown for single sections and units. Severe accidental scenarios are related to units which have high inventories or which process large streams of toxic or flammable materials. Moreover, the operative conditions of the unit and the properties of the substance play a major role in the expected severity of the scenarios. An auxiliary index, the potential hazard index (PI),[57] allows focusing on the severity of the possible accident scenarios (Figure 9b). Examples of critical units are the preparation of reagents (E1) in the cyclohexane production *(i-option A)*, the oxidation reactors (R2) of cyclohexane oxidation *(ii-option A)* and distillation columns in the separation sections (S1) of cumene synthesis *(i-option C)*. Again, the possibility of safety improvement by design is very different among the cases. In option A, the hazards mainly depend on the process (materials, reaction conditions and conversion, etc.) and no practical plant design action can improve inherent safety. Differently, in option C, also design choices aimed to reduce inventories of the separation units (e.g., intensified columns, improved separation scheme, alternative separation technologies, etc.) may be effective in reducing damage distances.

The HI index accounts for both the severity and the safety score of the units, addressing the worst credible accidents. Thus units very prone to loss of containment, as the heat exchangers and the pumps also assume a critical role. Beside the reduction of severity, the reliability of the equipment (e.g., adopting high-quality units in the hazardous operations) can be improved to enhance safety performance. Moreover, pressurized units (e.g., benzene alkylation section *(i-option C)*) result critical, since they may result in large damage distances (potential to release large amounts of

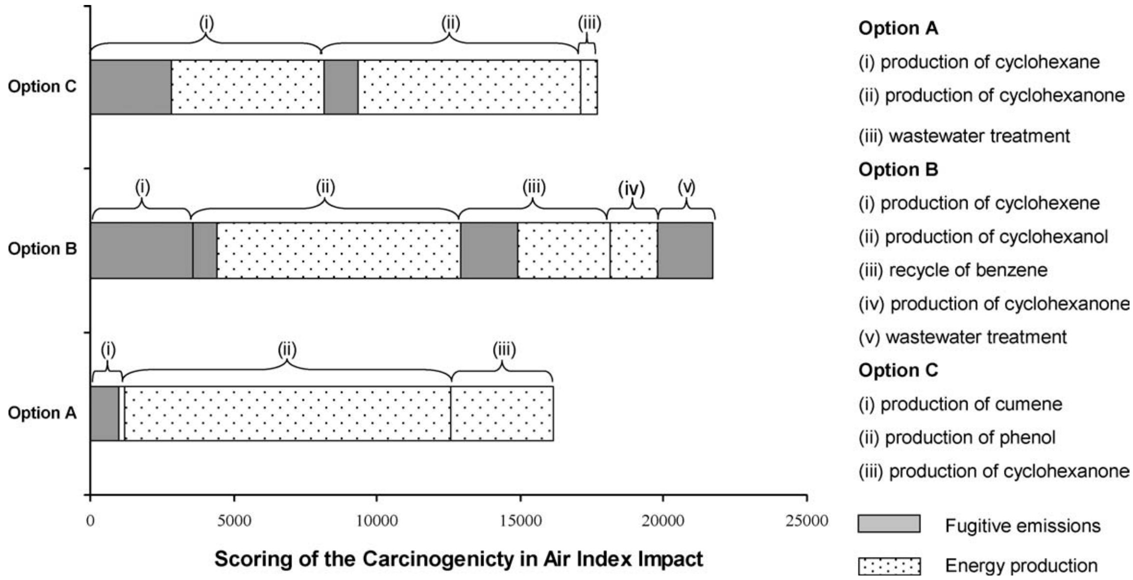

Figure 8. Non normalized values of the 4th tier indicator for air carcinogenicity, contribution of the single steps of the process.

flashing liquids), even in the case of small leaks. The phenol hydrogenation section (*iii-option C*), that contains few units and operates at low pressure, is an effective example of an inherently safer plant section that is recognized by this strategy. In some cases (e.g., ii-option A, ii-option B) safety performance is not dominated by a single critical unit, thus, the improvement of safety requires a general enhancement of equipment safety performance.

Normalization of the KPIs: the impact footprint

Figure 10a reports the normalized values of the single impact indicators calculated for the leading case. The adoption of a site-specific approach in the normalization procedure required the selection of a reference site for the analysis. This was arbitrarily chosen in the outskirts of an industrial town in northern Italy. Emission and statistic databases[60–63] allowed the definition of the values of the normalization factors for the chosen site (Table 3).

The normalized values point out that a few impact categories are actually responsible for the major impacts. As expected for the basic material transformation process, the use of resources is the main impact category for all the process options. The values of the indicators reflect the differences among the proposed options in the consumption of raw materials (overall yield), the production of valuable co-products (e.g., acetone in option C), the fuel use for thermal energy (natural gas) and the need of auxiliary materials (e.g., NaOH, H_2SO_4, etc.). Similarly, impact indicators of greenhouse gases and potentially carcinogen compounds confirm that the thermal energy production is a main environmental concern. The design choice to fire the boilers by natural gas has proved to be successful in limiting environmental impacts on acidification and smog formation categories. The complexity of the process, the presence of several pressurized units and the large inventories of flammable and toxic liquids yields high values of the inherent safety index.

By converse, some process features, although very significant for specific impacts, appear to have a secondary influence on the differences in the sustainability footprint among the options. An example is the emissions to water, as evident in Figure 10a.

The normalized economic indicator shows a potential impact that is a couple of orders of magnitude lower than the other indices. This is in line with the general results obtained for commodity production processes, where the saving margins are well-known to be limited if compared to the capital investments, yielding low-present values for the initiative. Thus, design improvements should primarily aim at the minimization of capital costs, simplifying the process schemes and pursuing the design of smaller and simpler units of equipment, as demonstrated by option B. Also the improvement of yields and the reduction energy consumption have a positive impact on economical factors, having moreover a synergetic effect on the environmental performance.

Aggregation of the KPIs: the sustainability footprint and overall performance indicators

Although the analysis of primary KPIs provides an insight on specific impacts from the process alternatives, Figure 10 evidences as risk-shift phenomena result in a change of rank among the process options when passing from an impact category to another. By converse, the aggregated KPIs introduce trade-offs among the impact categories, yielding information on the combined extent of several impact potentials. The weight factors defined in Figure 6 allow for a staged aggregation of the primary KPIs: in the first stage the environmental and societal primary KPIs (at 4th tier in Figure 6) are aggregated to yield an environmental and a societal KPI (2nd tier); in the second stage, the KPIs at the 2nd tier are further aggregated to yield the value of the 1st tier overall index. Although the structure of the tree of impacts includes

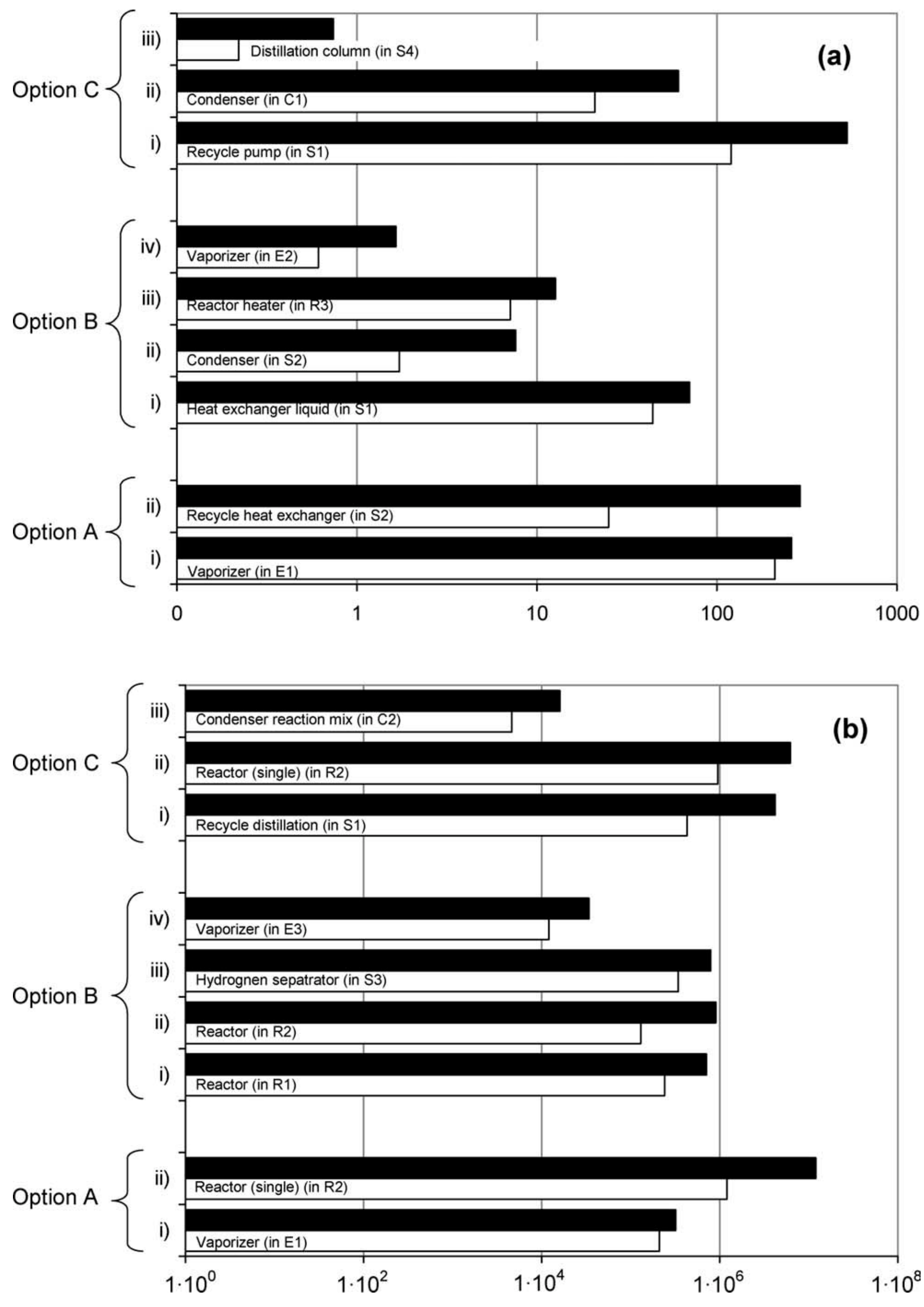

Figure 9. Results from the analysis of inherent safety KPIs.

(a) inherent hazard index (HI), and (b) potential hazard index (PI). Black bars refer to a process section; white bars to the unit with the greater score for that section.

also 3rd tier indicators, in this case study the results at this tier, if compared with 4th tier indicators, did not provide additional elements useful for the interpretation of the impact fingerprints and were not reported in the following discussion for the sake of brevity.

Figures 10b and 11 report the sustainability KPIs obtained from the aggregation stages. Environmental and societal impacts result to be the dominating issues, as shown in Figure 11. Option B clearly results in improved societal and economic performances, but the environmental impact is quantified as slightly higher than for option C. Figure 12 reports the contribution of the single process sections to the final value of the environmental index. The contribution of the benzene feedstock (i.e., a specific material resource use) accounts for about one quarter of the environmental impact in all process alternatives. This contribution can be partially reduced further improving the overall yield of the process by innovative reaction and separation strategies. However, the impact related to feedstock material can be drastically reduced only by substituting benzene with a ‘‘greener’’ raw

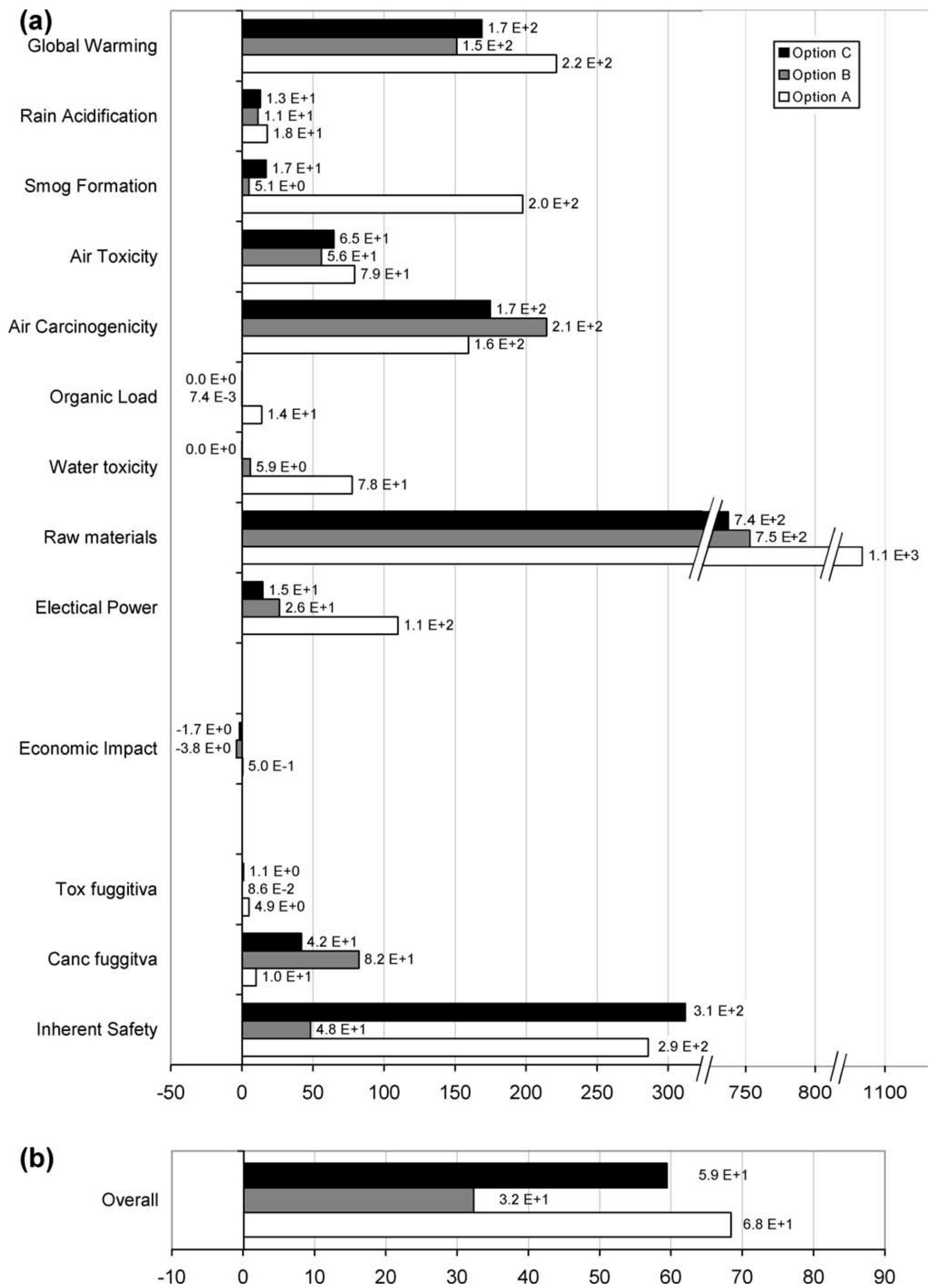

Figure 10. Key Performance Indicators: normalized values for indicators at 4th tier (a) and aggregated indices at 1st tier.

material (e.g., from renewable resources). The need for wastewater treatment in process option A significantly contributes to the environmental impact. However, changes in the wastewater technology are not likely to improve the performance of option A, since the environmental impact is the higher independently of the impact score attributed to wastewater treatment.

Choices in the account of the impacts should be considered when discussing the results. For example, in Figure 12 the production of cumene in option C shows larger environmental impacts than phenol production. However, in cumene production the consumption of propene raises the impact value; while in phenol production the byproduction of acetone (accounted as a material consumption multiplied by −1) lowers the value.

The sustainability KPIs can be aggregated by the weight factors reported in Figure 6, obtaining an overall sustainability index. As observed in Figure 11, the environmental indices for the process options considered have quite similar values, while the societal and economic performance show larger variations. Alternative B shows the better performances on both the latter aspects, thus, resulting preferable from

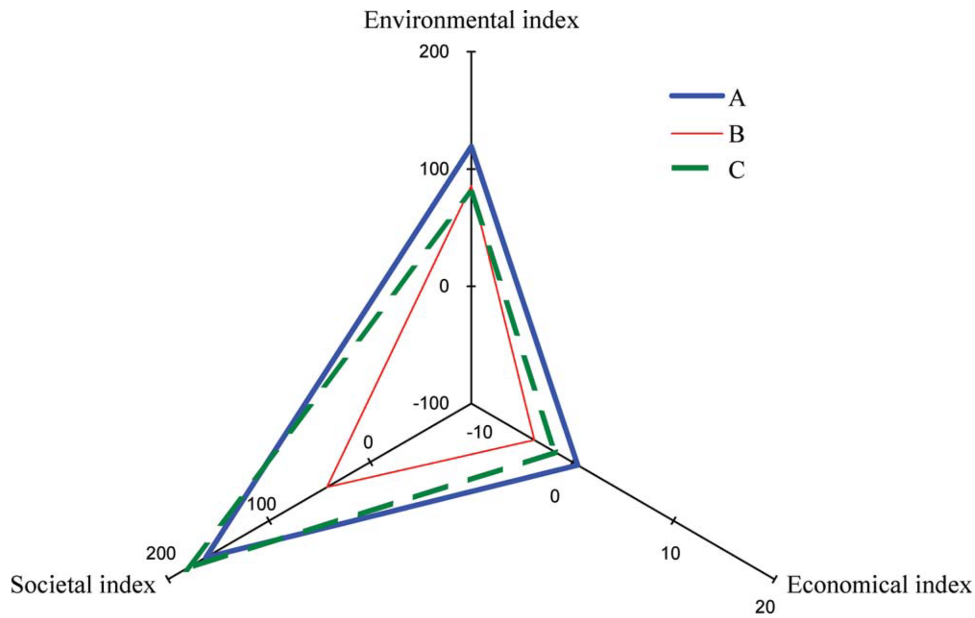

Figure 11. Footprint of the indices at 2nd tier for the options considered in the leading case.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the point of view of the integrated sustainability performance. As discussed earlier, this result has been achieved through design choices oriented at the efficient use of raw materials, the reduction of energy requirements, the larger adoption of atmospheric operations and the simpler process scheme. In particular, the proposed KPIs pointed out a significant role of raw material consumption in determining the final value of the environmental index, ranking units in accordance to the green chemistry indices in Table 1. However, the KPI assessment evidenced further aspects in the positive performance of option B well beyond the raw material consumption: safety performance, economy, and fuel consumption and exhaust emissions, not accountable by indices like RME.

Sensitivity and uncertainty analysis

The Monte-Carlo method proposed for sensitivity analysis was applied in order to explore the effects of the chosen weight factors on the aggregated indices. The "Crystal Ball"

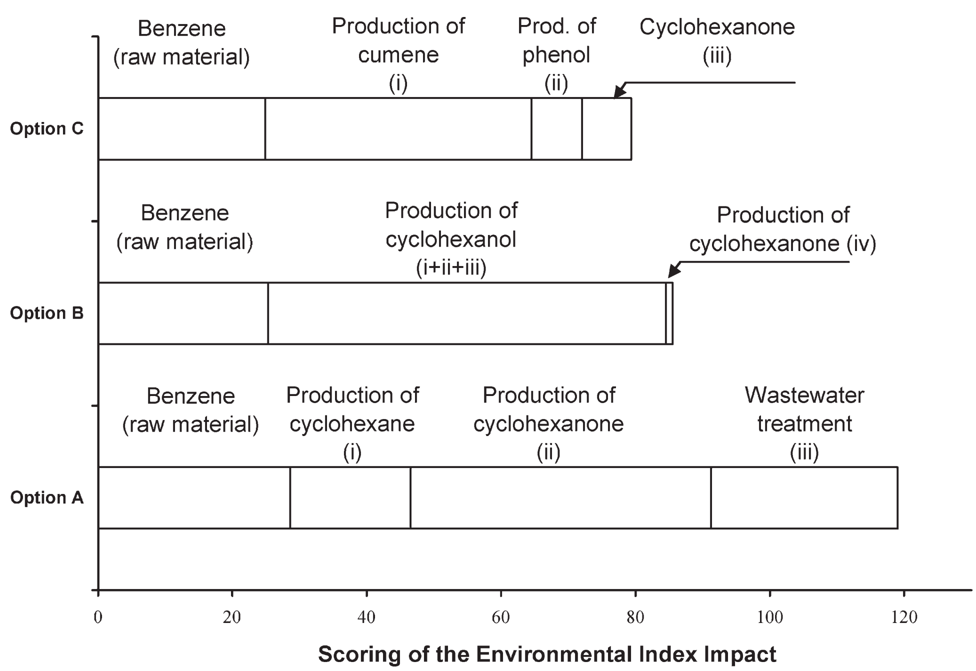

Figure 12. Environmental impact index, contribution of the single steps of the process.

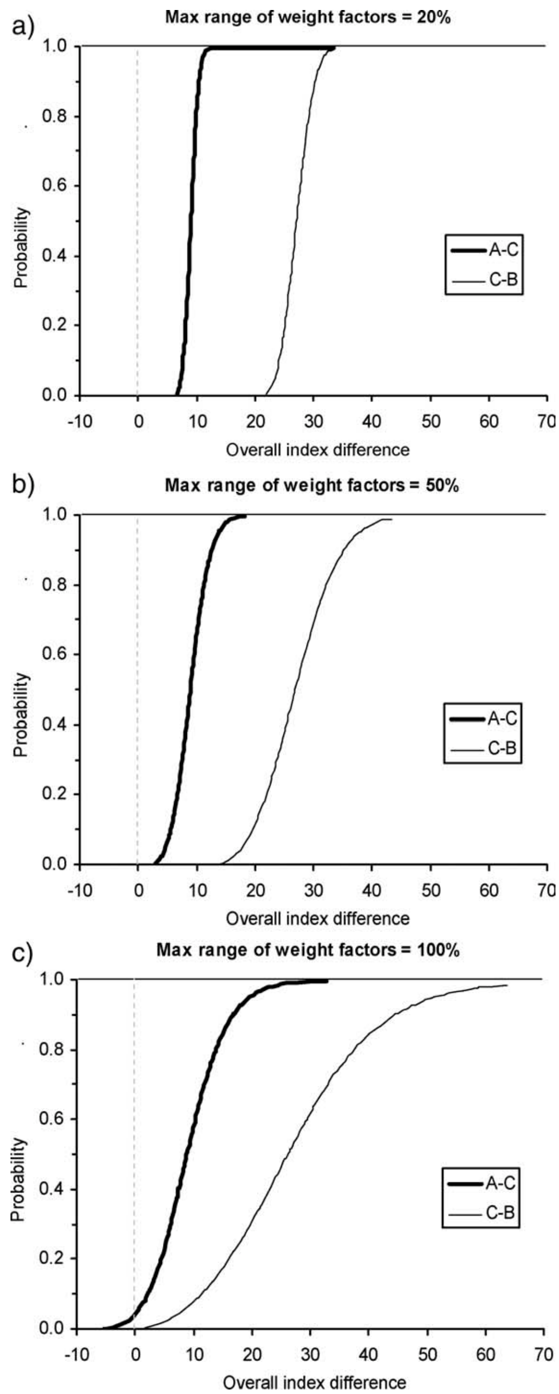

Figure 13. Example of result from sensitivity analysis: difference of the values of overall impact index for options A-C and C-B for maximum range of the weighting factor distribution 20% (a), 50% (b), and 100% (c) of the central value.

software by Decisioneering was used to implement the procedure.

Figure 13 shows the cumulative probability of the overall index difference for options ''A minus C'' and ''C minus B''. The graphs were obtained applying increasing values of maximum range for the triangular distribution of the weight factors. The analysis confirms all the observations drawn in the discussion above even for moderate variations of the value of the weight factors. Only for variations of the weight factors as high as 100% of the initial value (i.e., distribution ranging from zero to double of the central value), a change in sign of the difference index starts to get appreciable. By converse, the same variation of the weight factors (i.e., 100%) would have a dramatic effect on the actual value of the overall indicators (e.g., for option A, B and C the 90% confidence range would be, respectively ±52%, ±66%, ±58% of the median value). Such a spread well justifies the use of the proposed difference method in assessing the rank of options.

Noticeably enough, for the weight factors considered (Figure 6), a 100% variation may introduce local variations of the ranking of the weight factor (compatible with the uncertainty expected on the value), but is unlikely to subvert the general definition of the top impact reduction priorities. Thus, e.g., the weight for toxicity may assume values greater than carcinogenicity, but the originally top ranked environmental impact categories (e.g., carcinogenicity, toxicity, global warming, rain acidification, etc.) are not likely overcome by those of lower concern for the area (e.g., renewable raw materials, ozone depletion, organic load, etc.). Altogether, Figure 13 shows that the identified rank of preference for the options is confirmed up to variations of the weight factors that maintain the general ranking of impact reduction priorities of concern for the area.

Conclusions

An innovative procedure was defined for the sustainability analysis of design options in the early stages of process development (conceptual and basic design). The approach is based on the systematic development of a ''tree of impacts'' that yields a comprehensive set of key performance indicators, dynamically defined according to the impact issues of concern for the process. The procedure was applied to a leading case, consisting in the sustainability assessment of three alternative design options for industrial production of cyclohexanone. The robustness of the ranking procedure was confirmed by a specific Montecarlo analysis that evidenced that no inversion of ranking is possible within credible ranges of weight factors. The breakdown provided by the hierarchic structure of the approach allowed focusing on both the overall ranking of alternative process options and on specific issues of single processes. The analysis, thus, provides a guidance addressing design improvement, and captured the different issues related to cyclohexanone production, considering safety, environmental and economic impacts at once.

Acknowledgments

Financial support from the 7th Framework Program of the European Commission under the iNTeg-Risk project (CP-IP 213345-2), as well as from the Italian MIUR under the PRIN2007 program is gratefully acknowledged.

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Appendix A

Option A: Synthesis via oxidation of cyclohexane

Process option A represents a chemical process for synthesis of cyclohexanone based on the oxidation of the intermediate cyclohexane. The first industrial application of this process dates back to the 1940s. This process is notorious for the Flixborough accident,[48] where a vapor cloud explosion took place following the loss of containment in the cyclohexane oxidation reactors.

Two main sections are identified in the process scheme (Figure 2a):[37,38,64]

i. Synthesis of cyclohexane (hydrogenation of benzene).
ii. Synthesis of cyclohexanone (oxidation of cyclohexane).

In the first section (*i*), benzene is vaporized and mixed with hydrogen (in excess with respect to stoichiometric ratio) and cyclohexanol vapors.[65] The mixture is fed to a catalytic rector (R1) where the following reaction takes place:

$$C_6H_6 + 3H_2 \xrightarrow[Ni,Pd,Pt]{300^\circ C,\ 20\div30MPa} C_6H_{12} \tag{A1}$$

Since the reaction is exothermic, the reactor is operated with inter-cooled stages. Benzene conversion is almost complete. The hydrogen in the reactor output is separated by condensation of the other components (C1) and recycled back to the reactor feed. A fraction of the cyclohexane is recycled to the reactor as thermal inert.

In the second process section (*ii*), the cyclohexane stream is fed to a series of oxidation reactors (R2), operated in liquid phase with air. The overall reaction system can be described as

$$C_6H_{12} + O_2 \xrightarrow[1.5\div4MPa]{175\div220^\circ C} C_6H_{11}OOH \tag{A2}$$

$$C_6H_{11}OOH \rightarrow C_6H_{10}O + H_2O \tag{A3}$$

$$C_6H_{11}OOH \rightarrow \frac{16}{17}C_6H_{12}O + \frac{6}{17}H_2O + \frac{6}{17}CO_2 \tag{A4}$$

$$C_6H_{11}OOH \rightarrow side\ products \tag{A5}$$

The first reaction stage (A2) produces cyclohexyl-hydroperoxide. The peroxide may undergo decomposition yielding the desired products (cyclohexanone and cyclohexanol) (A3,A4), as well as other undesired side-products (A5).[54]

The formation and further oxidation of the undesired side-products largely complicate product purification. In order to prevent the phenomenon, peroxide decomposition is segregated in a dedicated nonoxidative reactor (R3). For the very same reason, in the oxidation reactors the conversion of cyclohexanone is maintained low ($2 \div 5\%$). Thus, separation

Table B1a. Part 1. Preliminary Database of Primary Impact Categories and Suitable KPIs

Impact category	Process data required	Reference normalization data	Suitable metrics (KPIs)
Air emissions			
Global warming	Air emissions of greenhouse gases and organic compounds, e.g. form i) boiler stacks, ii) potential fugitive emission sources, iii) vents and waste incinerators	Emissions of greenhouse gases from industrial sites and power plants[60,61,74,75]	Equivalents of CO_2 of the gas emissions per year[76]: a) Time horizon 20 years b) Time horizon 100 years c) Time horizon 500 years
Ozone depletion	Air emissions of ozone depleting compounds, e.g. form i) potential fugitive emission sources, ii) vents and stacks	Emissions of ozone depleting compounds from industrial sites and power plants[60,61,74,75]	Equivalents of CFC-11 (change in stratospheric ozone concentration) of the gas emissions per year[2,18]
Rain acidification	Air emissions of acid compounds, e.g. form i) boiler stacks, ii) potential fugitive emission sources, iii) vents and waste incinerators	Emissions of acid gases (SO_x, NO_x, etc.) from industrial sites and power plants[60,61,74,75]	Equivalents of SO_2 (max H^+ release) of the gas emissions per year[2,18]
Smog formation	Air emissions of volatile organic compounds (VOC), e.g. form i) boiler stacks, ii) potential fugitive emission sources, iii) vents and waste incinerators	Emissions of volatile organic compounds from industrial sites and power plants[60,61,74,75]	Equivalents of the emission of VOC per year of: a) maximum incremental reactivity of the VOC[77] b) photochemical ozone creation potential (POCP) in ethylene equivalents
Air toxicity	Air emissions of toxic compounds, e.g. form i) boiler stacks, ii) potential fugitive emission sources, iii) vents and waste incinerators	Air emissions of toxic compounds from industrial sites and power plants[60,61,74,75]	Toxicity equivalents of the gas emissions per year: a) equivalents of toluene ($1/LC_{50,inh}$)[21,44] b) equivalents of lead (Human Toxicity Potential)[18]
Air carcinogenicity	Air emissions of carcinogenic compounds, e.g. form i) boiler stacks, ii) potential fugitive emission sources, iii) vents and waste incinerators	Air emissions of carcinogenic compounds from industrial sites and power plants[60,61,74,75]	Equivalents of benzene of the gas emissions per year: a) cancer potency slope factor (inhalation)[21,44]

The table also reports the required process and suggested normalization data type.

(S1) and recycle of the nonreacted cyclohexane is fundamental for the process. The cyclohexane in the exhaust gas stream is condensed (C2) and recycled back to the reactor.

The liquid output of the reactor is sent to a column (S1) in order to separate the bulk of unreacted cyclohexane to be recycled. A decanter removes water and soluble low-boiling acid side-products. The bottoms of the column, rich in peroxide are sent to the decomposition reactor (R3). The decomposition of the hydroperoxide requires mixing with an alkaline solution. The aqueous fraction of the reactor output is separated in a decanter (S2). This aqueous stream contains high-boiling acids yielded by the side-reactions in the oxidation reactor and needs to be treated in order to be disposed. In the process scheme analyzed, the stream is neutralized and the organic fraction is removed by electro-oxidation (WT2). The resulting salt solution is a marketable product (e.g., deicing applications). The oily phase from the decanter is distilled (S3), and the fraction of cyclohexane still present is separated and recycled back to the oxidation reactor (R2). Cyclohexanone is vacuum-distilled from the bottoms of the former column. A further distillation step removes high-boiling products from cyclohexanol.

Additional cyclohexanone can be obtained by dehydrogenation of the produced cyclohexanol.[38] Cyclohexanol is vaporized (E2) and converted in a gas-phase catalytic process (R4).

$$C_6H_{11}OH \underset{0.1\div 0.15MPa}{\overset{250\div 450^\circ C}{\longrightarrow}} C_6H_{10}O + H_2 \qquad \text{(A6)}$$

The reaction is endothermic and has a yield of about 80%. The stream leaving the reactor is cooled (C3), hydrogen is separated and the condensable fraction is vacuum-distilled (S4) to recover the desired cyclohexanone.

Process B: Synthesis via hydration of cyclohexene

This option is representative of a different chemical way, based on cyclohexene as intermediate. The technology for selective hydrogenation of benzene and hydration of cyclohexene was developed in the 1970s, but first industrial application appeared only in 1990s, by Asahi.[38]

The reference process scheme designed and analyzed in current study can be divided in four main sections (Figure 2b):

i. Synthesis of cyclohexene (hydrogenation of benzene).
ii. Synthesis of cyclohexanol (hydration of cyclohexene).
iii. Recycle (dehydrogenation to benzene).
iv. Synthesis of cyclohexanone (dehydrogenation of cyclohexanol).

The first section (*i*) is based on the exothermic reaction:

$$C_6H_6 + 2H_2 \underset{4MPa}{\overset{140^\circ C}{\longrightarrow}} C_6H_{10} \qquad \text{(A7)}$$

The reaction occurs in liquid slurry phase and the heat of reaction is removed by external exchangers (R1). Nonreacted hydrogen is recycled. Conversion is not complete (ca. 50%), and selectivity is limited (35% yield), the main byproducts

Table B1b. Part 2. Preliminary Database of Primary Impact Categories and Suitable KPIs

Water emissions			
Organic load	Liquid emissions of organic compounds, e.g. from i) water discharges, ii) fugitive emission sources	Water emissions of organic compounds from industrial sites and power plants[60,61,74,75]	Total oxygen demand of the water emissions per year[20]
Water toxicity	Liquid emissions of toxic compounds, e.g. from i) water discharges, ii) fugitive emission sources	Water emissions of toxic compounds from industrial sites and power plants[60,61,74,75]	Toxicity equivalents of the water emissions per year: a) equivalents of toluene (1/ $LD_{50,orl}$)[21,44] b) equivalents of lead (Human Toxicity Potential)[18]
Water carcinogenicity	Liquid emissions of carcinogenic compounds, e.g. from i) water discharges, ii) fugitive emission sources	Water emissions of carcinogenic compounds from industrial sites and power plants[60,61,74,75]	Equivalents in benzene of the water emissions per year: cancer potency slope factor (oral)[21,44]
Eco-toxicity	Liquid emissions of eco-toxic compounds, e.g. from i) water discharges, ii) fugitive emission sources	Water emissions of eco-toxic compounds from industrial sites and power plants[60,61,74,75]	Equivalents for aquatic eco-toxicity of the water emissions per year: a) dilution volumes (1/$PNEC_{acquatic}$)[18] b) equivalents of toluene ($PNEC_{toluene}$/$PNEC_{acquatic}$)[21,44]
Eutrophication	Liquid emissions of eutrophication compounds, e.g. from i) water discharges, ii) fugitive emission sources	Water emissions of eutrophication compounds from industrial sites and power plants[60,61,74,75]	Equivalents of phosphate ion (eutrophication potential) in the water emissions per year[18,20]
Soil emissions			
Waste disposal	Stream of solid and liquid wastes, e.g. from i) main process waste products, ii) waste sludge of water treatment, iii) waste package of in/out materials, etc.	Waste production from industrial sites and power plants	Equivalents of municipal solid waste (based on disposal cost) produced per year[24,44]
Resources consumption			
Non-renewable raw materials	Non-renewable raw material input and output of the process including, e.g. i) primary feedstock, ii) auxiliary materials (e.g. NaOH, H2SO4, etc.), iii) fuels, iv) valuable co-product outputs	National consumption of fossil fuels and non-renewable materials in industrial sites and power plants[78]	Equivalents of crude oil (unitary costs) of the raw material resource per year[44]
Renewable raw materials	Renewable raw material input of the process including, e.g. i) primary feedstock, ii) auxiliary materials, iii) fuels, iv) valuable co-product outputs	Agricultural production of renewable materials[62]	Equivalents of area (e.g. 1/(agricultural yield)) of the raw material resource per year[34]
Electric power	Electrical energy consumption, e.g. by main compressors, pumps, stirrers, and electro-operations (e.g. electro-oxidation)	National consumption of electrical energy in industrial sites and power plants[78]	Electrical energy use (kWh) per year
Land use	Long term occupation of the land, e.g. by i) plant, ii) plant auxiliary services and buildings	Land occupation by industrial sites and power plants	Spatial area occupied by the facility[34,44]

The table also reports the required process and suggested normalization data type.

being cyclohexane (traces of methyl-cyclopentane are also produced).[38] The liquid mixture leaving the reactor is filtered (S1) and sent to a two-step hydration process (R2), where the overall reaction occurs (*ii*)

$$C_6H_{10} + H_2O \leftrightarrow C_6H_{11}OH \tag{A8}$$

In a first reactor cyclohexene is attacked by a sulfuric acid solution yielding an hydrogen sulfate salt. In a second reactor water is added to decompose the salt. The overall conversion of cyclohexene is about 55%, and the selectivity toward cyclohexanol is about 95% (cyclohexanone is the main side-product).[38] The mixture is sent to a separation section (S2, distillation columns and decanters) where several streams are produced: cyclohexanol (to be fed to the dehydrogenation section), sulfuric acid and water (to be recycled back to the corresponding phases of hydration reactors), a mixture of benzene, cyclohexane and cyclohexene (to be sent to the dehydrogenation section) and streams of other impurities (e.g., phenol). As a matter of fact, benzene, cyclohexane and cyclohexene form azeotropic mixtures that are practically not separable without restoring to extractive distillation.[38] In the considered process scheme the separation of the mixture is avoided. The hydrocarbon mixture is, in fact, dehydrogenated back to benzene (*iii*)[66,67]

$$C_6H_{6+2n} \xrightarrow{370^\circ C} C_6H_6 + n\,H_2 \tag{A9}$$

The reaction is endothermic and requires a multiple stage reactor to provide the required heat (R3).

Table B1c. Part 3. Preliminary Database of Primary Impact Categories and Suitable KPIs

Economy (wealth)			
Economic impact	Annual savings (e.g. form product sale), operative costs (e.g. raw materials, fuels, auxiliaries, electrical power, employees, etc.), capital costs (e.g. plant cost)	Gross domestic product (value added) by the industrial sector[62]	a) Actualized value (monetary) of total costs and savings in the process life b) Actualized value (monetary) of operative costs and savings in the process life
Workplace			
Toxicity of fugitive emissions	Fugitive emissions of toxic compounds concerning areas potentially occupied by operators, e.g. i) non stack or safely vented discharges, ii) potential fugitive emission sources (valves, seals, etc.)	Air emissions of toxic compounds from industrial sites and power plants[60,61,74,75]	Toxicity equivalents of the gas emissions per year: a) equivalents of toluene (1/$LC_{50,inh}$)[21,44] b) equivalents of lead (Human Toxicity Potential)[18]
Carcinogenicity of fugitive emissions	Fugitive emissions of carcinogenic compounds concerning areas potentially occupied by operators, e.g. i) non stack or safely vented discharges, ii) potential fugitive emission sources (valves, seals, etc.)	Air emissions of carcinogenic compounds from industrial sites and power plants[60,61,74,75]	Equivalents of benzene of the gas emissions per year: cancer potency slope factor (inhalation)[21,44]
Society			
Occupation	Work hours required for process operation (e.g. control room crew) and regular maintenance operations.	Employees in the industrial sector[63,79]	Equivalent number of employees (total standard work hours)
Inherent safety	Preliminary design of the units, operative conditions, inventories in the units, flows of the main lines	Average risk to human life from major industrial accident.[63,79]	Equivalent area potentially affected by accidents per year.[57]

$LC_{50,inh}$: lethal concentration for 50% of the sample, inhalation; $LD_{50,orl}$: lethal concentration 50% of the sample, oral; $PNEC_{acquatic}$: predicted no effect concentrations for plants and animals that live in that aquatic environment; +: further assumptions introduced in this study.
The table also reports the required process and suggested normalization data type.

Hydrogen and benzene are purified (S3) and recycled to section (1).

The final section of the process (*iv*) requires dehydrogenation of cyclohexanol to the desired product cyclohexanone. This section is similar to the process step described above in option A (Eq. A8).

Process C: Synthesis via hydrogenation of phenol

The hydrogenation of phenol is currently the process option more common for cyclohexanone production. The process scheme defined for the current assessment can be divided in three main sections (Figure 2c):

i. Synthesis of cumene (alkylation of benzene).
ii. Synthesis of phenol (oxidation of cumene).
iii. Synthesis of cyclohexanone (hydrogenation of phenol).

In section (*i*), cumene is produced by the alkylation of benzene with propene[68,69]

$$C_6H_6 + C_3H_6 \underset{1.5\div 3.5Mpa}{\overset{250^{\circ}C}{\longleftrightarrow}} C_9H_{12} \tag{A10}$$

The reaction is exothermic and is operated in the gas phase and with an excess of benzene (supported acid catalysts) (R1). Average conversion of propene is about 94%. The stream leaving the reactor is condensed and separated by several distillation stages (S1) Streams of benzene and propylene are recovered and recycled back to the reactor. A stream of cumene at the desired grade of purity is finally obtained. Side-products (dipropylbenzene isomers, methylpentene, etc.) are separated.

Phenol is obtained by oxidation of cumene with air (*ii*).[70,71] It is a well known two-stage process: in the first step cumene is oxidized to cumyl-hydroperoxide in liquid phase (R2), and in the second step, the hydroperoxide is decomposed to phenol and acetone (R3). The selectivity of the oxidation step toward cumyl-hydroperoxide is about 89.5% and some side-products are formed. The operation is performed in a series of reactors operating at 0.6÷0.65 MPa and 105÷115°C, where the temperature is controlled by external coils. The product stream contains about 32% of cyclohexanone. This stream is concentrated in a vacuum column (S2), and the most of cumene is separated and recycled back to the reactors. The concentrated solution of cyclohexyl-hydroperoxide is sent to the decomposition reactor (0.1÷0.15 MPa, 115°C, catalyzed by aqueous sulfuric acid). The reaction is exothermic and the heat of reaction is removed by evaporation and condensation of acetone. The output stream of the reaction is washed and decanted, to remove sulfuric acid. The oily phase is separated in a train of distillation columns (S3) to yield pure phenol (99.96% in weight). In particular the separation of some compounds, like α-methylstyrene, requires an extractive distillation. Acetone is also purified in a dedicated column.

Phenol hydrogenation (*iii*) is operated in gas phase (0.1÷0.2 MPa, 145°C, palladium catalyst).[38,72] This requires the vaporization of the feed mixture (E2), and the condensation

Table C1. Part 1. Example of Structured Matrix for Identification of Impact Categories

Element / parameter manipulated by design	Guideword	Threat / Impact mechanism	Impact category	Code
Materials	A) Air emissions	Greenhouse gas	Global warming	A1
		Damage stratospheric ozone layer	Ozone depletion	A2
		Acidifying agents or precursors of acidifying agents	Rain acidification	A3
		Promote/induce photochemical smog	Smog formation	A4
		Short term damage to human beings	Toxicity in air	A5
		Long term damage to human beings	Carcinogenicity in air	A6
		Short/long term damage to non-human beings (consider a single critical target in eco-system: water species)	*Account in B*	*See B5*
	B) Water emissions	Carbon content in water	Organic load	B1
		N/P content in water	Eutrophication	B2
		Short term damage to human beings	Toxicity in water	B3
		Long term damage to human beings	Carcinogenicity in water	B4
		Short/long term damage to non-human beings (consider a single critical target in eco-system: water species)	Ecotoxicity	B5
	C) Soil emissions	Carbon content in soil —> leach to water	*Account in B*	*See B1*
		N/P content in soil —> leach to water	*Account in B*	*See B2*
		Short term damage to human beings —> leach to water	*Account in B*	*See B3*
		Long term damage to human beings —> leach to water	*Account in B*	*See B4*
		Short/long term damage to non-human beings (consider a single critical target in eco-system: water species)	*Account in B*	*See B5*
		Discharge of materials (wastes) to soil	Solid waste disposal	C1
	D) Resource consumption	Materials of non renewable origin (e.g. oil, natural gas, minerals, etc.)	Non renewable raw materials	D1
		Materials of renewable origin (e.g. corn, wood, etc.)	Renewable raw materials	D2
	E) Economy (wealth)	Monetary value of the material	Economic impact	E1
		Disposal cost of materials	Economic impact	E1
	F) Workplace	Short term damage to human beings on the workplace	Toxicity of fugitive emissions	F1
		Long term damage to human beings on the workplace	Carcinogenicity of fugitive emissions	F2
	G) Society	Short term damage to human beings by continuous emissions to air/water/soil	*Account in A/B/C*	*See A5, B3*
		Long term damage to human beings by continuous emissions to air/water/soil	*Account in A/B/C*	*See A6, B4*
		Accidental release of hazardous/energetic (instable, reactive, etc) material	Inherent safety	G2

of the product stream (C2). The noncondensed gas is recycled back to the reactor. The condensate is vacuum-distilled (S4) to remove cyclohexanol (the selectivity to cyclohexanol is about 4% in the reactor), which can be actually sold on the market. Cyclohexanone is distilled in a second vacuum column. The bottoms of the column are flashed to remove high-boiling compounds and are recycled to the reactor.

Appendix B

Table B1 provides a reference list of the primary impact categories relevant for the analysis of industrial process options. The same table evidences possible KPIs to be employed for the quantification of the category and the input and normalization data required. The database is not meant to be exhaustive, and further suitable metrics can be introduced. A more extensive list of suitable KPIs is currently under development as part of the IntegRisk Project funded by the European Commission under the 7th Framework Program (CP-IP 213345-2).[73]

Appendix C

Table C1 provides an example of a structured matrix used for identification of relevant impact categories. The identification procedure consists in pointing out the potential impacts on sustainability deriving from the elements and parameters manipulated and defined in design activities. The brainstorming team considered the following components as relevant design elements/parameters for the cyclohexanone plant case (1) materials, (2) units/machines, (3) utilities, and (4) process as network of units. The design elements were systematically screened in their impact potential considering the 3rd tier impact categories as guidewords. The possible threats were identified according to the knowledge of the

Table C1. Part 2. Example of Structured Matrix for Identification of Impact Categories

Units / Machines	A) Air emissions	Air emissions of fugitive origin	*see A (materials)*	
	B) Water emissions	Water emissions of fugitive origin	*see B (materials)*	
	C) Soil emissions	Soil emissions of fugitive origin	*see C (materials)*	
	D) Resource consumption	Material resource consumption for the operation/maintenance	*see D (materials)*	
		Thermal energy resource consumption	*see D (utilities)*	
		Electrical energy resource consumption	Electrical power	D3
		Space	Land use	D4
	E) Economy (wealth)	Investment for acquisition	Economic impact	E1
		Cost for operation/maintenance	Economic impact	E1
	F) Workplace	Fugitive emission of hazardous materials	*see F (materials)*	
	G) Society	Personnel required for operation/control	Occupation	G1
		Accidental release of hazardous material/ energy (pressure, heat, projectiles, etc)	Inherent safety	G2
Utilities	A) Air emissions	Air emissions of fugitive origin	*see A (materials)*	
	B) Water emissions	Water emissions of fugitive origin	*see B (materials)*	
	C) Soil emissions	Soil emissions of fugitive origin	*see C (materials)*	
	D) Resource consumption	Material resource consumption for the operation/maintenance	*see D (materials)*	
		Electrical energy resource consumption	Electrical power	D3
		Space	Land use	D4
	E) Economy (wealth)	Investment for acquisition	Economic impact	E1
		Cost for operation/maintenance	Economic impact	E1
	F) Workplace	Fugitive emission of hazardous materials	*see F (materials)*	
	G) Society	Personnel required for operation/control	Occupation	G1
		Accidental release of hazardous material/ energy (pressure, heat, projectiles, etc)	Inherent safety	G2
Process (unit network)	A) Air emissions	Outputs to air (e.g. vents, stacks)	*see A (materials)*	
	B) Water emissions	Outputs to water	*see B (materials)*	
	C) Soil emissions	Outputs to soil / solid waste disposal	*see C (materials)*	
	D) Resource consumption	Input materials	*see D (materials)*	
		Thermal energy input	*see D (utilities)*	
		Electrical energy input	Electrical power	D3
		Soil occupation	Land use	D4
	E) Economy (wealth)	Other investment expenses	Economic impact	E1
		Other operative costs	Economic impact	E1
	F) Workplace	Fugitive emission of hazardous materials	*see F (materials)*	
	G) Society	Personnel required for operation/control	Occupation	G1
		Accidental release of hazardous material/ energy (pressure, heat, projectiles, etc)	Inherent safety	G2

brainstorming team and the pertinent 4th tier impact categories were defined accordingly. In some cases, impact mechanisms were simplified to single components (e.g., water species in lieu of the whole ecosystem), or included in other categories (e.g., soil emissions leached to water) due to practical considerations on the definition of KPIs.

Manuscript received Jun. 3, 2010, and revision received Sept. 29, 2010.