Decision Framework for Chemical Process Design Including Different Stages of Environmental, Health, and Safety Assessment

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In recent years, many chemical companies have adopted the concept of sustainable development as a core business value. In this context and with focus on early phases, we present a novel design framework that comprises four stages of process modeling and multiobjective evaluation considering monetary and nonmonetary aspects. Each stage is characterized by the available information as a basis for process modeling and assessment. Appropriate modeling approaches, and evaluation indicators for economy, life-cycle environmental impacts, environment, health, and safety (EHS) hazard, and technical aspects are selected for each defined stage. The proposed framework is demonstrated on the design of a methyl methacrylate (MMA) process: considering 17 synthesis routes, the framework is mimicked step-by-step, to select the route with the best multiobjective performances, and to produce an optimized process flowsheet. As a validation of the framework, evaluation profile of six routes over all stages are compared, and crucial points are identified that should be estimated considerably well in early stages of the framework. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1037–1053, 2008

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Introduction

In recent years, many chemical companies have adopted the concept of sustainable development as a core business value. The basis of decision-making has been extended to cover various aspects in addition to the economic performance, and chemical companies need to reflect such paradigm shift in their entire business. In chemical process design incorporation of sustainable development criteria is crucial, in particular consideration of the potential impacts on the environment, workers' health, and safety (EHS) aspects.

Various methods have been proposed for including nonmonetary aspects into the process design procedure. With respect to safety and health, methods for detailed hazard analysis of plants are available such as Fault Tree Analysis (FTA),[1] Failure Mode Effect Analysis (FMEA),[2] or HAZard and OPerability study (HAZOP).[3] These well-established methods are in many cases already part of the process design

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procedure, especially in the detailed engineering or early operation phases. For the early design phases, introduction of the concept of "inherent safety"[4] has brought into focus a lot of methods with a different approach, such as the Dow Indices—Dow Fire & Explosion Index,[5] Chemical Exposure Index,[6] and safety and health part of EHS method.[7] Koller et al.[8] reviewed and compared inherent safety and health assessment methods. Their analysis was extended by Adu et al.[9] who also analyzed and compared environmental hazard assessment methods mentioned later.

Environmental indices comprise two different types. One group focuses on the hazard of a substance on flora or fauna caused by an accident or through the use of these substances, e.g., the EU Risk ranking method[10] and environmental part of EHS method.[7] The other type, process-oriented methods, quantifies the extent of the environmental impacts by multiplying potential damage of a substance with its relevant mass. Methods such as atom efficiency,[11] Mass Loss Indices,[12] Douglas method,[13] Environmental Hazard Index,[14] or Environmental Fate And Risk Assessment Tool (EFRAT)[15] focus on the mass leaving the reaction or process systems, and measure their impacts. In some other methods, such gate-to-gate environmental impacts, which are of companies' primary interest, are considered as a part of the overall impacts in a chemical's life-cycle, including raw material productions, use and disposal of the product. Life-cycle assessment (LCA)[16–19] is the base concept for these methods, including WAste Reduction algorithm (WAR),[20] Material Intensity Per Service (MIPS),[21] and Sustainable Process Index[22] method.

Methods aforementioned are targeting at single noneconomic aspects of chemical processes. Integrated design approaches that formulate multiobjective evaluation and optimization of monetary and nonmonetary objectives can be found, i.e., in Sugiyama et al.,[23] Kniel et al.,[24] Azapagic and Clift,[25] and BASF's eco-efficiency analysis.[26]

These methodologies of integrated design have a focus on a specific stage of the whole design procedure. In general, process design typically uses a hierarchical approach[27] and consists of different phases including process chemistry, conceptual design, piloting, detailed design, construction startup, and redesign.[28] So far, three authors reflected such nature of process design, and proposed design frameworks that include different steps of multiobjective evaluation. Hoffmann et al.[29,30] presented a two-step procedure for defining the process structure: in the first step a large number of process alternatives is generated and screened, and in the second step selected ones are analyzed in detail. Application of simple evaluation indicators, instead of rigorous evaluation e.g., net present value (NPV) or full-LCA, has benefit in their method to enable the evaluation of a large number of process alternatives. Chen and Shonnard[31] presented a two-step design framework in which reaction route selection, creation of a base case flowsheet, and its optimization are included. In their framework, EFRAT[15] is the basis to evaluate various environmental impacts occurring from the process while the economic indicator evolves according to design stages, i.e., raw material cost in reaction route selection and NPV in flowsheeting and optimization. Azapagic et al.[32] presented an application of sustainability evaluation indicators covering economic, environmental, and social aspects into different design stages from the project initiation to the final design. Quantitative and qualitative indicators are effectively combined to enable comprehensive process evaluation including social aspects.

In this work, we present a novel framework that comprises four stages of process modeling and multiobjective decision-makings considering monetary and nonmonetary aspects. This framework targets the early design phase, i.e., process chemistry and conceptual design phases, and includes two sub-stages within a phase. Each stage is characterized by the available information as a basis for process modeling, assessment, and the tasks that have to be solved. Appropriate modeling methods and a comprehensive set of evaluation indicators are selected for each stage, including quantitative indices for economy, life-cycle environmental impacts and EHS hazard, and qualitative consideration of technical aspects. Particular features are estimation of gate-to-gate costs and environmental impacts in early phases by proxy indicators, and evaluation of EHS hazard over all defined stages. Based on the evaluation results, multiobjective decision-making is performed systematically at each stage. The proposed framework is demonstrated on the design of a methyl methacrylate (MMA) process: considering 17 MMA synthesis routes as a starting point, the framework is mimicked step-by-step, to produce an optimized process flowsheet of the route with the best multiobjective performance. As a validation of the framework six reaction routes, including ones that were judged inferior at earlier stages, were modeled and evaluated up to the level of the last stage, i.e., rigorous process simulation. By comparing the evaluation profile of six routes over different stages, we identified several factors that were unforeseen at earlier stages but caused significant updates of the evaluation results at later stages.

Design Framework

Figure 1 shows the overview of the proposed framework. This framework includes four design stages which are commonly part of early phases of grass root design. Stage-gate approach is taken in this framework: at each stage alternatives of reaction routes and/or process technologies are modeled and evaluated, and promising options survive to the next design stage. At each defined stage, indicators for multiobjective evaluation are selected and attached. These indicators cover the following three aspects: economic performance, life-cycle environmental impacts, and EHS hazard. Within one evaluation aspect, an appropriate indicator is defined according to changing analysis scope at each stage. In *Process Chemistry* stages where only reaction information is available, proxy indicators that estimate efforts in separation/waste treatment processes are defined. Technical aspects are included as a supplement indicator to the multiobjective indicators discussed earlier.

It is assumed that before the first stage of the framework is executed, product type, quality, and production scale are fixed by management decisions. In *Process Chemistry I*, only reaction stoichiometry is available, and modeling/evaluation of routes is based on ideal performance of the reaction, i.e., 100% yield. Since the level of modeling is too simple and evaluation results are too far from the actual performance, no decision is forced to be taken at this decision stage "D1."

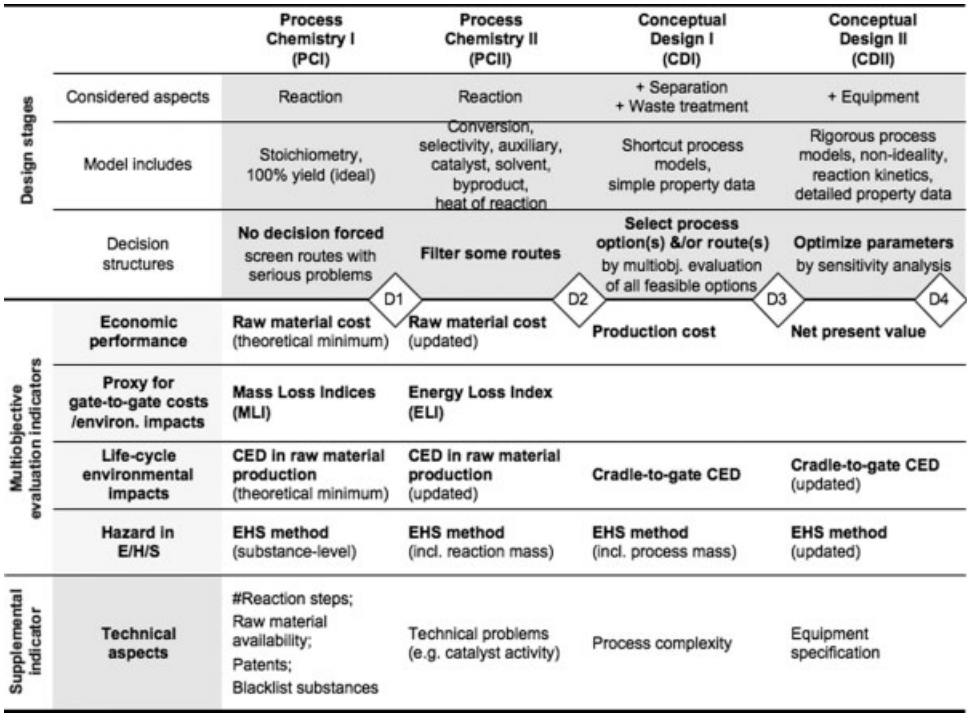

Figure 1. Overview of the framework: definition of design stages and appropriate modeling approaches as well as evaluation indicators attached to each stage.

Technical issues, however, can well be a killing factor here for, e.g., a reaction route involving "blacklist substances," which are forbidden to be used in the company. In *Process Chemistry II*, reaction mass and heat balances and rough operating conditions become available by, e.g., laboratory experiments. Based on this actual reaction information, routes are modeled, evaluated, and inferior ones are screened out at decision stage "D2." From here on, multiobjective evaluation results are the basis of decision-making at each stage. In both Process Chemistry stages, experiments and/or literature survey are typical mechanisms for acquiring information, and chemists are the major player. Process engineers come into play in *Conceptual Design* (CD) stages where the whole process including reaction, separation, waste treatment, and equipment specification is analyzed using process simulators. Along the last two stages process models evolves from shortcut to detailed levels. Route(s) and/or process option(s) are screened at decision stage "D3," and the selected process option is further analyzed and optimized at "D4."

Process models

Process Chemistry Stages. Figure 2a shows the model structure in Process Chemistry stages. The reaction mass and energy balances [flows F_2, F_3 (kg/h), and F_7 (MJ/h)] comprise the reaction unit, and the separation is a pseudo unit that isolates the product (flow F_4) from reaction-outlet mixture (flow F_3). When a reaction route has more than two steps, the model in Figure 2a is connected step-by-step to form the overall process model. In Process Chemistry I, modeling of the reaction unit is based on stoichiometry of the main reaction that is assumed to proceed with 100% yield. Separation removes only coupled products (flow F_5), and there is no recycle flow (flow F_6). In Process Chemistry II, the reaction model includes conversion, selectivity to product/byproducts, reaction temperature and pressure, type of auxiliaries, solvent, catalyst, and ratio of them to reactants. A pseudo separation unit recycles all unreacted raw materials to the reactor (flow F_6), separates coupled products (CPs) and byproducts (flow F_5), and isolates the main product (flow F_4). This ideal separation unit also recycles the remaining materials, e.g., auxiliaries, solvent, and catalyst to the reactor, and thus no fresh ones are included in the overall inlet (flow F_1). For the assessment, mass and energy flows are normalized to the amount of the product, and the perspective is on the overall process except in the proxy indicator calculation (Section Evaluation Indicators) where evaluation scores are first obtained on individual reaction steps and afterward are summed up.

Conceptual Design Stages. The model structure in *Conceptual Design I/II* is shown in Figure 2b with a typical separation sequence as an example. This model is an extension of the one at Process Chemistry stages shown in Figure 2a, and corresponding flows are indicated by primes. When there are multiple reaction steps, the overall process is composed by repeating the model in Figure 2b as a train of reaction and separation sequences. In evaluating processes at CD stages, the perspective is on this overall process model. Reaction model in Conceptual Design I (CD I) is at the same level as in the previous stage but with new reaction information if obtained by further experiments. The separation part is largely refined at CD I by considering unit-operation structure and physical properties of substances. With this update, new information is made available: loss of valuable materials within

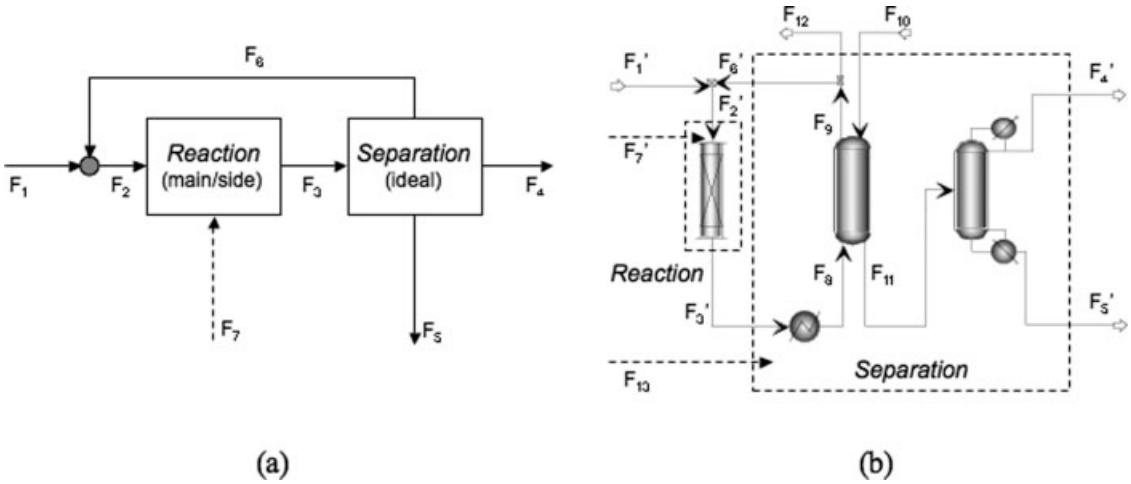

Figure 2. Structure of the process models at (a) Process Chemistry I/II and (b) Conceptual Design I/II.

Solid arrows represent material flows, and dotted arrows indicate energy flows.

the process, e.g., raw materials, product, or solvents, for which 100% recovery were assumed before, to output flows, e.g., purge (flow F_{12} in Figure 2b), or waste stream (flow F_5'); separation agents (flow F_{10}); and energy utilities, e.g., steam (flows F_7' and F_{13}). The process model at CD I is based on simple data and methods, e.g., average relative volatility and Fenske/Gilliland/Underwood methods for distillation. Such short-cut models become more rigorous at Conceptual Design II (CD II) by considering reaction kinetics and/or azeotropic mixture. Equipments can be sized for the overall process, which is the basis for the investment cost estimation.

Evaluation indicators

Economic Evaluation Indicators. According to Figure 1 at Process Chemistry stages as economic evaluation indicator raw material cost $E^r_{\mathrm{PCI/II}}$ [\$/(kg product)] of route r is used:

$$E^r_{\mathrm{PCI/II}} = \sum_{i=1}^{a} C_i m_i^{\mathrm{In}} \tag{1}$$

where a is the number of raw materials, C_i (\$/kg) is the cost or price of material i, m_i^{In} [kg/(kg product)] is mass flow of material i per amount of product (hereafter called specific mass flow) in the input of the overall process (Figure 2a: flow F_1). In Process Chemistry I, this mass input is based on the ideal reaction performance, i.e., 100% yield, and thus the minimum raw material cost is obtained. When this minimum raw-material cost exceeds the targeted product price, such routes can be safely discarded. In Process Chemistry II, more detailed information becomes available, and m_i^{In} is updated.

In CDI where mass and energy balances include separation processes, production cost E^r_{CDI} [\$/(kg product)] is used as an economic indicator:

$$E^r_{\mathrm{CDI}} = \sum_{i=1}^{a+b} C_i m_i^{\mathrm{In}} + \sum_{j=1}^{c} C_j m_j^{\mathrm{out}} + C_{\mathrm{L}} \tag{2}$$

In the first term, a is the number of raw materials (in Figure 2b: flow F_1'), and b is the number of other input materials and energy carriers such as solvents, auxiliaries, separation agents, or steam (flows F_7', F_{10}, and F_{13}). The second term is the treatment cost of output flows (flows F_5', F_{12}) where c is the number of substances to be treated, C_j (\$/kg) is the treatment cost of substance j, and m_j^{Out} [kg/(kg product)] is the corresponding output specific mass flow. Labor cost C_{L} [\$/(kg product] represents the third term. Raw material cost, i.e., summation up to material a in the first term, is updated as compared to the previous stage. The remainder in this term, i.e., summation up to b, is newly added at this stage based on the following information: fresh auxiliaries, catalysts, or solvents for which 100% recovery was assumed before and loss data are available now; separation agents; energy utilities. The second and the third terms are new as well at this stage.

At the last stage CDII, NPV is used as economic evaluation indicator E^r_{CDII} (\$):

$$E^r_{\mathrm{CDII}} = \mathrm{INV} + \sum_{t=1}^{N} \frac{\mathrm{CF}_t}{(1+d)^t} \tag{3}$$

where INV (\$) is the investment cost, CF_t (\$/year) is the annual cash flow of a process in year t, d is the discount rate of the project, and N (year) is the projected plant lifetime. Precise quantification of investment cost is possible only at this stage where equipments can be sized based on physical models. Cash flow CF_t is the net profit from revenues after subtracting production cost. Additional costs, e.g., depreciations, can be included in CF_t depending on the company's accounting systems, and typical formulation of the cash flow term can be found elsewhere.[33] At this stage of process design, several economic indicators are applicable, and among others appropriateness of dynamic cost calculation by using NPV is illustrated by Pintaric and Kravanja.[34]

Indicators for Life-Cycle Environmental Impacts. Figure 3 shows the production of a chemical as a part of its life-cycle. Within the proposed framework, cradle-to-gate perspective is sufficient, because decisions taken within the framework do not affect environmental impacts after the process, e.g., use or disposal of the chemical product. Life-cycle

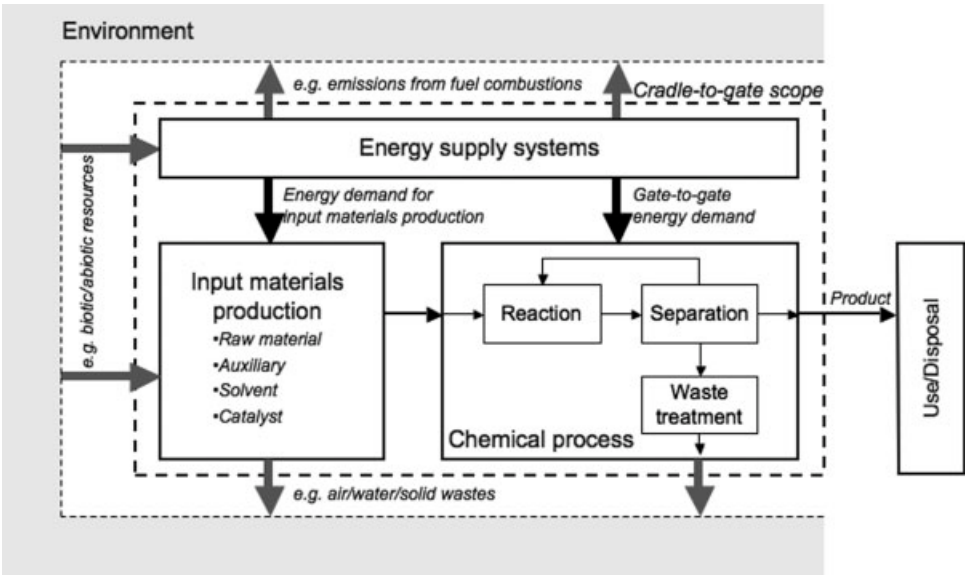

Figure 3. The production of a chemical as a part of its life-cycle.

environmental impacts of this system can be represented by the following three types (indicated as gray arrows in Figure 3): input to the production and energy supply system from the environment, e.g., biotic/abiotic resources; outlet from the production systems, e.g., air/water/solid wastes; and from energy supply systems, e.g., emissions from fuel combustions to the environment. These environmental impacts are proportional to the energy demands from the input materials production and the process under design (shown as thick black arrows in Figure 3). The sum of these two energy demands which is equivalent to the well-established cumulative energy demand (CED)[35] is the evaluation indicator for the life-cycle environmental impacts that we use in the framework.

As shown in Figure 1, the evaluation indicator of route/process r considering life-cycle environmental impacts using CED, L_s^r [(MJ equiv)/kg product)], is updated/extended at each design stage s. The calculation of this indicator is similar to the economic evaluation. Raw material CED and cradle-to-gate CED are calculated with Eqs. 1 and 2, respectively, by replacing C_i, cost or price of material i, by CED_i (MJ equiv)/kg], overall amount of primary energy sources required to bring material i to the entrance of the process under design or to treat material i leaving the process. Labor cost term in Eq. 2 is omitted when calculating cradle-to-gate CED. Values of CED_i can be obtained from LCA databases such as *ecoinvent*.[36] In ecoinvent, CED_i is presented by Joule-equivalent, which is converted from the amount of primary energy in different mass or volume units, e.g., crude oil in kg, natural gas in Nm^3 by using the lower heating values of each energy source. In the framework, CED can be replaced with another impact category that is favored or is more appropriate in other design cases.[37,38]

Proxy Indicator for Gate-to-Gate Cost/Environmental Impacts. For Process Chemistry I, several proxy indicators are applicable, e.g., atom efficiency by Sheldon[11] or MLI by Heinzle et al.[12] These indicators are based on the same idea to measure how much unwanted substances are produced in the reaction. In this framework, MLI is selected as an indicator which is the mass ratio of all substances except for the product. The proxy indicator of gate-to-gate cost and environmental impacts of reaction route r at Process Chemistry I is expressed as:

$$P_{\text{PCI}}^r = \sum_n \text{MLI}_{\text{CP},n} \tag{4}$$

where $\text{MLI}_{\text{CP},n}$ is the mass ratio of CP to product at nth reaction step. Since at this stage only main reactions are considered on the ideal basis, only CP is considered in MLI here, and its value is the inherent mass of CP per mass of product.

For Process Chemistry II, these mass-based indicators have some drawbacks. Major problem here is that the relation between mass ratios and process energy consumption is not clear. For instance, even if a large amount of byproduct is produced, but this byproduct has much higher boiling point than the product, the separation is rather easy. On the contrary, small amounts of byproduct with a closer boiling point to the product would cause more problems in separation. To overcome such a gap, we have developed a new indicator, energy loss index (ELI).

ELI is an indicator to estimate energy-related efforts associated to the process using reaction information only. With this indicator, utilities to be used in the process, e.g., energy utility and separation agents are forecasted from reaction mass and energy balances that are available at Process Chemistry II. Thus the ELI can be a proxy indicator of gate-to-gate costs/environmental impacts at this stage. ELI of a reaction step is calculated as 0 (low) to 1 (high estimated energy demand) index value in five different categories: presense of water, product concentration, minimum difference of boiling point, inherent waste amount, and reaction energy. In each of these categories, reaction mass information is translated to 0 to 1 index values. Using this ELI concept both gate-to-gate costs and environmental impacts of route r at Process Chemistry II are approximated by:

$$P^r_{\mathrm{PCII}} = \sum_n \sum_{\mathrm{cX}} w_{\mathrm{cX}} \times \mathrm{ELI}_{\mathrm{cX},n} \quad (5)$$

where $\mathrm{ELI}_{\mathrm{cX},n}$ is a calculated ELI value in category cX at nth reaction step, and w_{cX} is a weighting factor of ELI-category cX ranging from 0 to 1. In the case study presented later weighting factors are set equal for each category, i.e., w_{cX} is always 0.2. More details on ELI method can be found elsewhere.[39]

Indicators for EHS Hazard. Various hazard assessment methods have been proposed for each EHS aspect. Adu et al.[9] analyzed such difference of various hazard assessment methods qualitatively and quantitatively, and concluded that there is no advantage or disadvantage in choosing one or the other method. Having identified the difference to other methods,[9] we consistently use EHS method[7] over four stages in this framework. In this hazard assessment method, mobility, fire/explosion, reaction/decomposition, and acute toxicity are included in safety category, irritation, and chronic toxicity are considered in health category, and persistency, air hazard, water hazard, solid waste, and bioaccumulation are sub categories in environmental assessment. For each subcategory an index value ranging from 0 to 1 is assigned to a chemical. Property parameters of a substance are the basis of calculating such index values and priorities among property parameters have been defined.[7] For instance, in fire/explosion subcategory, flash point of a substance is the default parameter used, and its difference to the reaction or process temperature is transferred to the 0 to 1 scale. When flash point is not available less quantitative parameters are used, e.g., risk phrases.[40] The assessment method can be flexibly used for assessing inherent hazards of chemicals, e.g., during laboratory experiments as well as in assessing hazards of tank farms, and a corresponding computational tool for such purposes is available.[41]

In Process Chemistry I, EHS method is used at the substance-level, i.e., index values ranging from 0 to 1 are considered for substances in each reaction route to analyze hazard properties. From Process Chemistry II on, the evaluation is carried out on the process-level where index values are multiplied by corresponding mass.

In Process Chemistry II, safety hazard $\mathrm{SH}^r_{\mathrm{PCII}}$ [kg/(kg product)] of a route r is formulated as:

$$\mathrm{SH}^r_{\mathrm{PCII}} = \sum_{\mathrm{cS}} \max_F \left(\max_i \left(m^F_i I^{\mathrm{cS}}_i \right) \right) \quad (6)$$

where m^F_i [kg/(kg product)] is the specific mass flow of substance i in flow F within process r (see Section Process Models) and I^{cS}_i is the index value of substance i in safety category cS. Reaction temperature is used to calculate I^{cS}_i in mobility and fire/explosion categories, where vapor pressure and temperature difference to the flash point are the basis of calculating index values.

Health hazard of route r at stage Process Chemistry II, $\mathrm{HH}^r_{\mathrm{PCII}}$ [kg/(kg product], is presented as:

$$\mathrm{HH}^r_{\mathrm{PCII}} = \sum_{\mathrm{CH}} \max_i \left(m^{\mathrm{UN}}_i I^{\mathrm{cH}}_i \right) \quad (7)$$

where m^{UN}_i [kg/(kg product)] is unit (UN) mass, i.e., 1 kg of substance i in process r, and I^{cH}_i is the index value of substance i in health category cH. Unit mass is taken as reference because the health hazard is independent of the mass to which the workers are exposed.

Environmental hazard of route r at Process Chemistry II, $\mathrm{EH}^r_{\mathrm{PCII}}$ [kg/(kg product], is expressed as:

$$\mathrm{EH}^r_{\mathrm{PCII}} = \sum_{\mathrm{cE}} \sum_i \left(z \max_F \left(m^F_i \right) I^{\mathrm{cE}}_i \right) + \sum_{\mathrm{cE}} \sum_j \left(m^{\mathrm{Out}}_j I^{\mathrm{cE}}_j \right) \quad (8)$$

where z is the fraction of mass emitted to the environment in case of an accident from the maximum mass present in the overall process, $I^{\mathrm{cE}}_{i/j}$ is the index value of substance i/j in environmental category cE, and m^{Out}_j [kg/(kg product)] is the specific mass flow of substance j leaving the process except for product flow (in Figure 2a: flow F_5), which only includes coupled and by-product at this stage. The fraction z is set as 10% in the case study. Two aspects are considered in the environmental hazard in Eq. 8. In the first term, an accidental situation is assumed where the fraction z of the maximum mass of a substance within a process is emitted to the surrounding environment. In the second term, m^{Out}_j represents the mass that constantly leaves the process to waste treatment. Consideration of the former aspect is the approach of Edwards and Lawrence[42] while the latter aspect is targeted by the method of Koller et al.[7]

In CD stages the EHS assessment is adapted to the extension of the process model as presented in Figure 2b. Safety hazard indicator of route r at CD stages, $\mathrm{SH}^r_{\mathrm{CDI/II}}$ [kg/(kg product)], is thus defined as follows.

$$\mathrm{SH}^r_{\mathrm{CDI/II}} = \sum_{\mathrm{cS}} \max_F \left(\sum_i m^F_i I^{\mathrm{cS}}_i \right) \quad (9)$$

Values of m^F_i are refined from the previous stage (Eq. 6) by the use of improved process model especially in separation part, and substance i in this variable includes newly introduced substances in the process, e.g., separation agents (see Section Process Models).

The health hazard at CD stages of process r, $\mathrm{HH}^r_{\mathrm{CDI/II}}$ [kg/(kg product)], is calculated by using Eq. 7.

Equation 8 is used to calculate the environmental hazard in CD stages $\mathrm{EH}^r_{\mathrm{CDI/II}}$ [kg/(kg product]. Terms of specific mass flows in Eq. 8 are updated as in the safety hazard, and as compared to the stage before substances in the second term are not restricted to coupled and by-product but includes all substances emitted from the process (in Figure 2b: flows F_5' and F_{12}).

Aggregation of Multiobjective Evaluation Indicators. At each design stage from Process Chemistry II on, decisions have to be taken based on multiobjective evaluation results. Among several possible methods for such multiobjective decision-making, e.g., Pareto approach,[43] we use an aggregation approach, i.e., different indicator results are aggregated into a single evaluation score using weighting factors.

To present the aggregation procedure, $X^r_{s,i}$ is introduced which is the evaluation indicator of route or process r at design stage s from Process Chemistry II to CD II in considered category i, i.e., it represents $\{E^r_s, P^r_s, L^r_s, \mathrm{SH}^r_s, \mathrm{HH}^r_s, \mathrm{EH}^r_s\}$ where the different elements are the evaluation indicators for economy, proxy for gate-to-gate cost/environmental

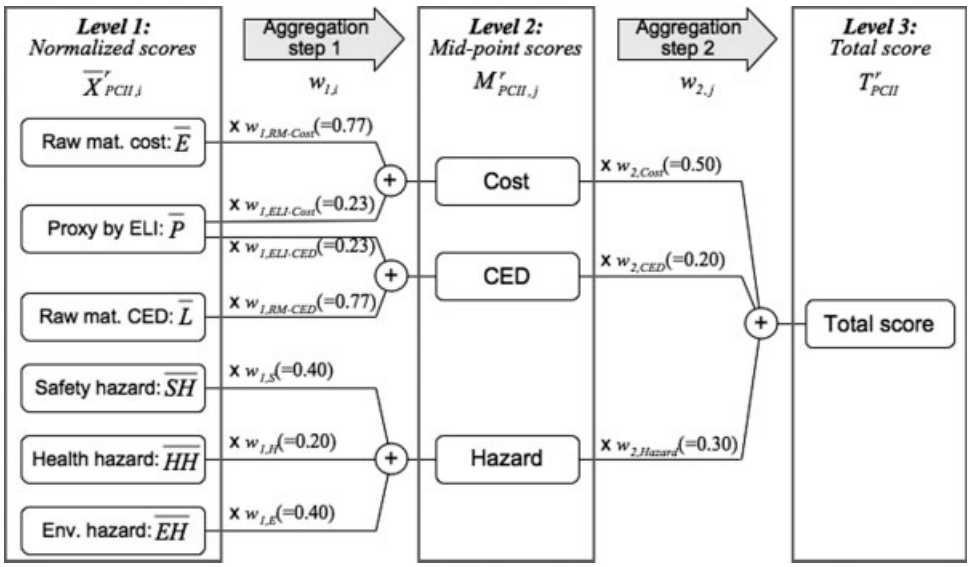

Figure 4. Aggregation scheme at Process Chemistry II.

Values of weighting factors are those used in the case study.

impacts, life-cycle environmental impacts, and hazard in safety, health and environment, respectively. Before aggregation, the evaluation indicator results in each category i are normalized by the maximum (i.e., the worst) indicator value of all routes/processes as follows.

$$\overline{X}^r_{s,i} = \frac{X^r_{s,i}}{\max_r \left(X^r_{s,i}\right)} \tag{10}$$

When applying NPV as an economic indicator at CD II E^r_{CDII} in Eq. 10, which has the opposite scale to raw material or production costs, the scale should be reversed, e.g., by taking the inverse. At each design stage s, all of the normalized evaluation scores are aggregated to a single score in a two step procedure: the first aggregation results in three mid-point scores with regard to cost, CED, and hazard, and the second aggregation in one total score. In aggregation step 1, a mid-point score $M^r_{s,j}$ of route/process r at stage s in category j (cost, CED, and hazard) is obtained by combining normalized scores of related categories i, $\overline{X}^r_{s,i}$, using a weighting factor $w_{1,i}$ ranging from 0 to 1.Thus the mid-point score of cost $M^r_{s,\mathrm{Cost}}$ is expressed as:

$$\begin{cases} M^r_{\mathrm{PCII,Cost}} = w_{1,\mathrm{RM\text{-}Cost}}\overline{E}^r_{\mathrm{PCII}} + w_{1,\mathrm{ELI\text{-}Cost}}\overline{P}^r_{\mathrm{PCII}} \\ M^r_{\mathrm{CDI/II,Cost}} = \overline{E}^r_{\mathrm{CDI/II}} \end{cases} \tag{11}$$

where $w_{1,\mathrm{RM\text{-}Cost}}$ and $w_{1,\mathrm{ELI\text{-}Cost}}$ are weighting factors at aggregation step 1 for raw material cost and gate-to-gate cost estimated by ELI, respectively. At Process Chemistry II $M^r_{\mathrm{PCII,Cost}}$ is a weighted combination of raw material cost and gate-to-gate cost estimate. At CD stages where costs that were estimated at Process Chemistry II are included in the economic evaluation, the $\overline{E}^r_{\mathrm{CDI/II}}$ value is directly used as the mid-point score. In the same way, the mid-point score for CED, $M^r_{s,\mathrm{CED}}$, is calculated as:

$$\begin{cases} M^r_{\mathrm{PCII,CED}} = w_{1,\mathrm{RM\text{-}CED}}\overline{L}^r_{\mathrm{PCII}} + w_{1,\mathrm{ELI\text{-}CED}}\overline{P}^r_{\mathrm{PCII}} \\ M^r_{\mathrm{CDI/II,CED}} = \overline{L}^r_{\mathrm{CDI/II}} \end{cases} \tag{12}$$

where $w_{1,\mathrm{RM\text{-}CED}}$ and $w_{1,\mathrm{ELI\text{-}CED}}$ are weighting factors at aggregation step 1 for raw material CED and gate-to-gate CED estimated by ELI, respectively. As in the mid-point score of cost, $M^r_{\mathrm{PCII,CED}}$ is a weighted combination of raw material CED and estimated gate-to-gate CED, while the $\overline{L}^r_{\mathrm{CDI/II}}$ value is directly used for $M^r_{\mathrm{CDI/II,CED}}$. For hazard, the mid-point score is calculated in the same way at all stages s from Process Chemistry II to CD II:

$$M^r_{s,\mathrm{Hazard}} = w_{1,\mathrm{S}}\overline{\mathrm{SH}}^r_s + w_{1,\mathrm{H}}\overline{\mathrm{HH}}^r_s + w_{1,\mathrm{E}}\overline{\mathrm{EH}}^r_s \tag{13}$$

where $w_{1,\mathrm{S}}$, $w_{1,\mathrm{H}}$, and $w_{1,\mathrm{E}}$ are weighting factors in each hazard aspect at aggregation step 1. These mid-point scores in cost, CED, and hazard are then in aggregation step 2, aggregated to the total score T^r_s of route/process r at stage s:

$$T^r_s = \sum_j w_{2,j} M^r_{s,j} \tag{14}$$

where $w_{2,j}$ is the weighting factor at aggregation step 2 with regard to mid-point category j (cost, CED, hazard) ranging from 0 to 1.

To give an example, aggregation at Process Chemistry II is described with the schematic procedure in Figure 4, which also shows weighting factor values used in the case study. From normalized scores (Level 1 in Figure 4), three mid-point scores in cost, CED, and hazard (Level 2) are calculated in aggregation step 1 using Eqs. 11–13, followed by calculation of the total score (Level 3) using Eq. 14 in aggregation step 2.

Weighting factors reflect designer's or company's idea on the importance of each evaluation category, and their choice

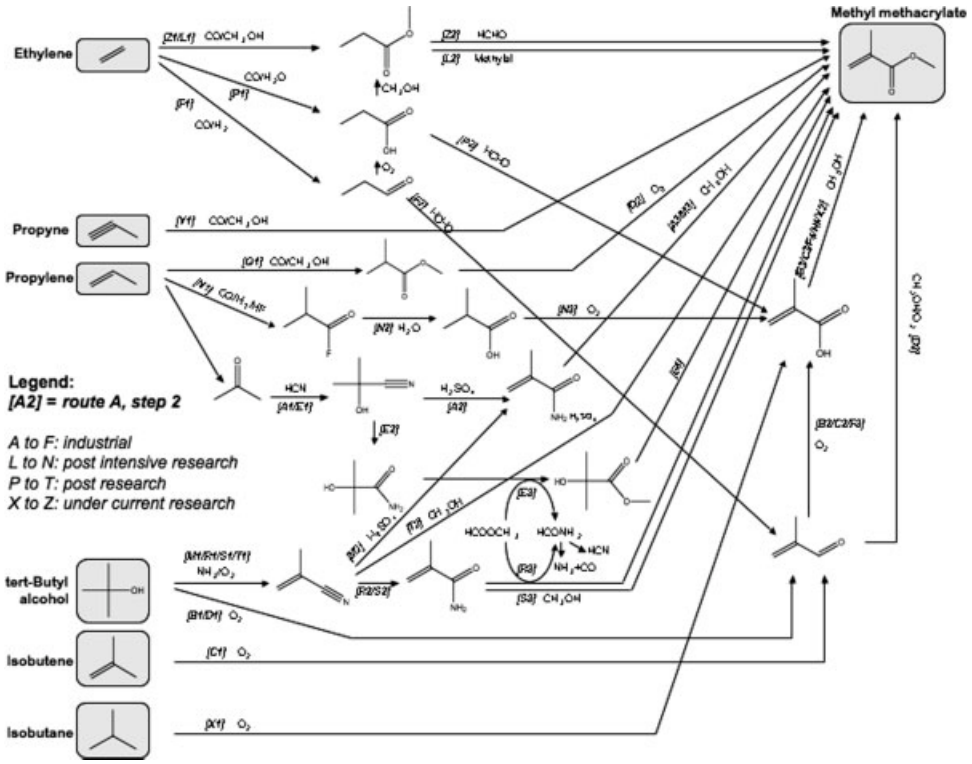

Figure 5. Reaction scheme of 17 synthesis routes of methyl methacrylate (MMA); adapted from Nagai.[44]

is heuristic. In aggregation step 1, weighting factors within cost category as presented in Figure 4 are based on industrial statistics on the ratio of raw material and separation cost. The same weighting factors are applied in CED category, for which such empirical values were not available. The adopted values are from commodity industry and in other processes weights can be different, e.g., in fine or specialty chemicals raw material costs are typically more relevant. Within the hazard category, indicated values are chosen so that each category (4 in safety, 2 in health, and 4 in environment) has equal importance. Factors in aggregation step 2 reflect company's culture to rank cost, CED, and hazard. We have specified, as a default set values of 0.5, 0.2, and 0.3 for each of them, thus reflecting an equal weighting of monetary and nonmonetary aspects.

Case Study

We performed a case study on the design of a MMA process starting from 17 different synthesis routes. The proposed framework is mimicked step-by-step in order to demonstrate decision-makings at each stage. As a validation of the framework, reaction routes that were evaluated inferior were modeled up to the level of the last stage and were compared to the results obtained at earlier stages.

Settings of the case study

There are various reaction routes to synthesize MMA. Nagai[44] reported 17 possible routes of MMA synthesis as shown in Figure 5, and we consider all these routes in this case study. Routes can be differentiated by four types, which are indicated by route labels (see inset in Figure 5). The design situation is assumed as a grassroot design of a MMA production process at 100 (kt/year) which is projected to run for 15 years. Open data for prices (e.g., chemical market reporter[45]) and CED (e.g., ecoinvent[36]) are used thus assuming that all materials are supplied on the market basis and not from dedicated processes within the company. For EHS assessment, all categories are included except for bioaccumulation where all substances involved showed almost no effect.

Application of the framework

Process Chemistry I. All synthesis routes in Figure 5 are considered at this stage. Evaluation results in four considered aspects are shown in Figure 6. Results in (Figure 6a) raw material cost, (Figure 6b) raw material CED, and (Figure 6c) MLI represent the theoretical minimum. This first characterization of all routes can serve as a basis for a first feasibility analysis at this stage, e.g., comparison to a certain threshold value such as market price of MMA (e.g., 2 $/kg which is higher than the raw material cost in Figure 6c of all routes). Or results in Figure 6 can function as a target of process development in later stages, i.e., as the potential best performance. In (Figure 6d) EHS hazard of hydrogen cyanide (HCN) which is used in route A is shown as an example. With this substance-level assessment, various hazard properties of a substance can be visualized as 0 (low) to 1 (high hazard) index value. For categories with high hazard values, use of protection measures (see Koller[46] and Shah et al.[47]) is necessitated: in HCN example, fire and irritation must be considered at first.

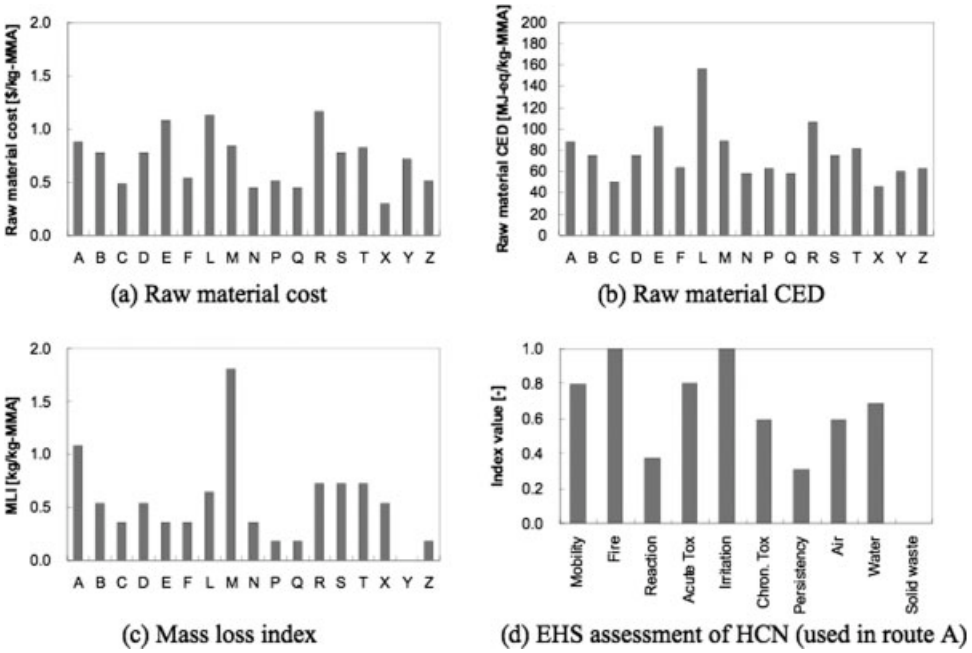

Figure 6. Evaluation results of MMA synthesis routes A to Z at Process Chemistry I.

Technical aspects can rather be a reason to eliminate a route here. For example, when raw material availability is considered, route *Y* starting from propyne, a rather rare alkyne, can be discarded regardless of its excellent potential performance in, e.g., MLI. In this case study, we selected only routes A, B, C, D, F, and X for further evaluation because only for these sufficient information is available in the open literature; this decision to eliminate routes is not based on the evaluation results shown in Figure 6.

Process Chemistry II. For the six selected routes process modeling was carried out as indicated in Figure 2a and based on information obtained from literature, e.g., Ullmann's encyclopedia,[48] technology reviews,[49,50] articles or patents from MMA producers (for route A,[51] B,[52] C,[53] D,[54] F,[55] and X[56]) or industrial interviews.

Figure 7 shows the total score T^r_{PCII} for the investigated six routes. Each section within a bar for a route corresponds to the normalized score $\overline{X}^r_{\mathrm{PCII},i}$ (in Figure 4: Level 1) multiplied by weighting factors in both aggregation step 1 and 2, e.g., $w_{2,\mathrm{Cost}} w_{1,\mathrm{RMCost}} \overline{E}^r_{\mathrm{PCII}}$ is the area of raw material cost. According to the total score T^r_{PCII}, route C is the best choice here. Within individual aspects, some differences can be highlighted, for instance, route X is most lucrative when only economic aspects, i.e., raw material and gate-to-gate cost are considered. High raw material cost and CED can be seen in route B and D which both have *tert*-butyl alcohol as a starting material. ELI scores are highest in route D, and within this route, step D2 has a high ELI score because (a) methyl isobutylate which has a boiling point close to the one of MMA ($\Delta = 8^\circ$C) is produced as a byproduct, and (b) this oxidation (and thus exothermic) reaction takes place at exceptionally low temperature, i.e., 60°C, while all other oxidation reactions in MMA reaction systems are conducted at high temperatures over 300°C and thus provide the possibility for steam cogeneration. Environmental hazard is highest in route A. Among two types of environmental hazard considered in Eq. 8, i.e., accidental hazard and steady-state hazard, the former is significant in route A, mainly because of dangerous substances such as, e.g., hydrogen cyanide. Route X has a high hazard score in safety, because of the low conversion of isobutane (10%) in step X1 causing large isobutane throughput by recycling unreacted educts, and thus high hazard-index results in mobility and fire/explosion categories.

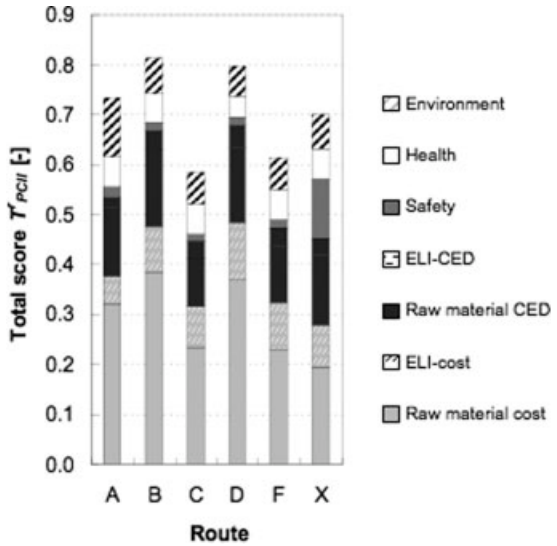

Figure 7. Total scores T^r_s for MMA synthesis routes at Process Chemistry II.

The height of the bars represents total score T^r_{PCII}; each section within a bar corresponds to normalized evaluation score $\overline{X}^r_{\mathrm{PCII},i}$ multiplied by weighting factors $w_{1,i}$ and $w_{2,j}$ (see Figure 5).

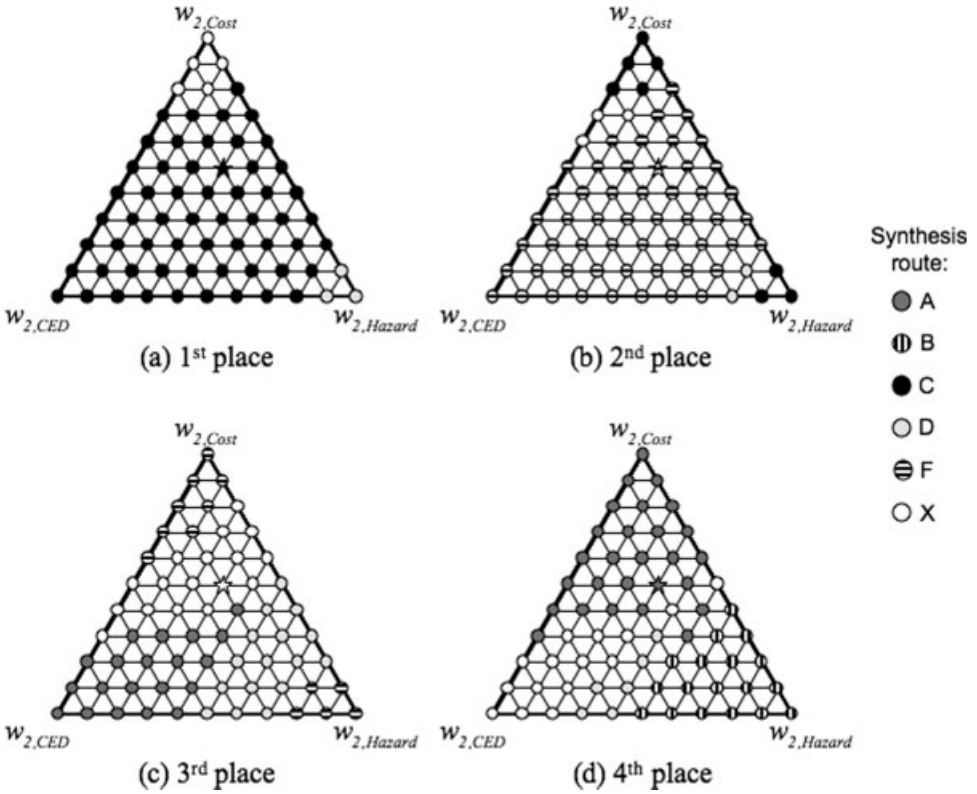

Figure 8. Effect of weighting factor $w_{2,i}$ choice on the ranking of process routes according to total score T_s^r at Process Chemistry II.

The default set of weighting factors used in calculating the total score in Figure 7: {0.5, 0.2, 0.3} for {$w_{2,Cost}$, $w_{2,CED}$, $w_{2,Hazard}$} is indicated by a star.

The aggregated result can be sensitive to the weighting factors used. Sensitivity analysis was performed to measure the impact of choosing various weighting factors at aggregation step 2 in Figure 4, i.e., {$w_{2,Cost}$, $w_{2,CED}$, $w_{2,Hazard}$} in Eq. 14. Weighting factors at aggregation step 1, $w_{1,i}$, are kept constant in this sensitivity analysis. In Figure 8, each ternary diagram corresponds to the rank of the route according to the aggregated score, and each node within a diagram is a set of weighting factors with 0.1 as interval. The default set of factors, i.e., {0.5, 0.2, 0.3} for {$w_{2,Cost}$, $w_{2,CED}$, $w_{2,Hazard}$}, is indicated by a star. In the diagram (Figure 8a) it can be seen that route X or D would be the best choice when economy or hazard had a strong weight, respectively, but basically route C is almost always the best over the whole range of possible weighting sets. Performance of a specific route can be analyzed by looking at one route in different diagrams. For example, route X is good in economy as can be seen in plot (Figure 8a), and slowly reduces its rank with weighting factors approaching an emphasis on CED, and at the same time becomes worst in hazard (not shown in Figure 8). Stability of the decision can also be checked by focusing on nodes around the star: route A would be at the third place instead of the fourth when using weighting set {0.4, 0.2, 0.4}. If the number of routes to be selected is set as three at this stage, the weighting factor set, especially on the axis between cost and hazard, is sensitive to the corresponding choice, and thus it should be well examined and agreed among designers. In this study, route A, C, F, and X that are within 30% range of route C's total score are selected for the next stage.

Conceptual Design I. For the routes selected in the previous stage, mass and energy balances of the whole process were calculated using short-cut models in Aspen Plus®[57] such as DSTWU models for distillation columns. Individual evaluation results were aggregated to the total score by the procedure presented in Section Evaluation Indicators with corresponding weighting factors presented in Figure 4. Figure 9 shows total scores T^r_{CDI} obtained for four routes. Each section of a bar for a route is, as in Figure 7, the normalized evaluation score $\bar{X}^r_{CDI,i}$ multiplied by weighting factors, e.g., $w_{2,Hazard}w_{1,S}\overline{SH}^r_{CDI}$ for safety. According to the total score T^r_{CDI}, route C is still the best choice at this stage. Route X appears promising only with respect to economy and performs extremely badly in safety and environmental hazard aspects. The latter result is due to the amount of tetradecane, used to absorb unreacted isobutane at a molar ratio of 10 to isobutane. Considering low conversion of isobutane (10%) and its relatively high molecular weight, the amount of tetradecane in the process is quite large, and this causes higher values in all safety categories and accidental environmental hazard. Cost of route F has become significantly worse as compared to other routes in Figure 9, and also as compared to the previous stage (Figure 7). Major reason is that loss of valuable materials, i.e., raw materials and catalysts, are rather high in route F because of its difficulty in separation part. This aspect was not apparently covered by the ELI proxy

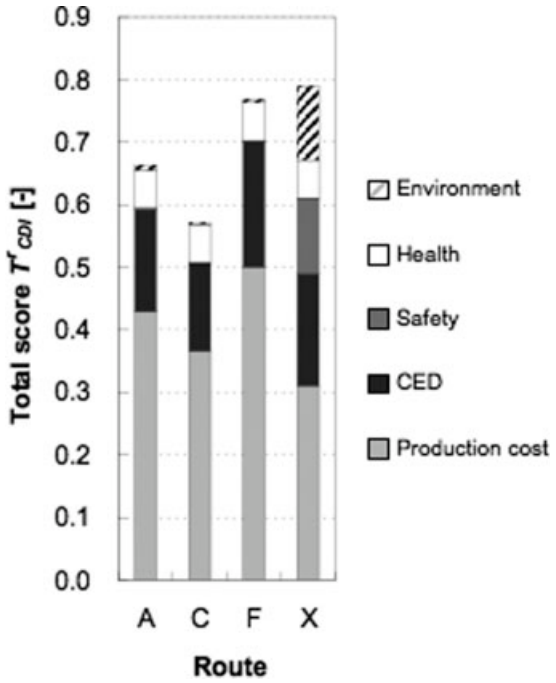

Figure 9. Total scores T_s^r for MMA synthesis routes at Conceptual Design I.

The height of the bars represents total score T^r_{CDI}; each section within a bar corresponds to normalized evaluation score $\overline{X}^r_{\mathrm{CDI},i}$ multiplied by weighting factors $w_{1,i}$ and $w_{2,j}$.

indicator in Process Chemistry II stage. In both routes X and F there are updates which were not foreseen in the previous stage, i.e., large-scale use of separation agents and loss of valuable materials, respectively, and these updates reduced the rank of these two routes. Now route A is the second best in Figures 9 and 10 where sensitivity to the weighting-factor choice is analyzed as in the previous stage. In this study, route C is selected for further investigation; if sufficient engineering capacity would be available, the second best route A might be included in a more detailed analysis at the next stage as well.

Conceptual Design II. At this stage a rigorous process model is created, and a detailed analysis and evaluation are performed on the selected route. Figure 11a shows the process flowsheet of route C. Short-cut models in the previous stage are replaced by rigorous ones, e.g., RadFrac models of Aspen Plus® for columns, and each reactor includes reaction kinetics, e.g., the model by Morita et al.[58] for RC1 reactor of step C1. For calculating NPV, which is the economic indicator at this stage, investment cost was estimated based on the created model and reported values in the literature.[59] As basic settings, 15 years of projected plant-lifetime and a discount rate of 12% were assumed.

Figure 11b shows an example of parameter optimization in the reactor temperature of step C1. Here a trade-off with respect to economy exists: by increasing reaction temperature, yield of the product (methacrolein in this step) increases, enlarging the profit. At the same time, the energy required to heating the reactor inlet increases as well, and at some point elevation of this cost takes over the profit given by the increased yield. On the CED side, there is no trade-off observed: temperature increase simply worsens environmental performance. Through this analysis, a temperature range between 325 and 350°C is identified Pareto-optimal as a reaction temperature of C1.

Figure 11c shows safety hazard analysis in each process section. In this detailed analysis, section S2 is identified as most hazardous, where methacrylic acid (MAA) is isolated from water/acetic acid mixture. The hazard here is mainly due to xylene, an extractive agent, which is used at large amounts and has high volatility and flammability under the respective process conditions. Methacrolein has large contributions in reaction/decomposition and acute toxicity categories. Such analysis prioritizes the installation of safety technology within a process, which is input information to the next development stages, e.g., piloting and detailed engineering.

Validation of decision-makings along the framework

So far six routes considered in the case study at Process Chemistry II have been screened out step-by-step resulting in the investigation of only route C at CD II. As a validation of the framework, these six routes were modeled and evaluated

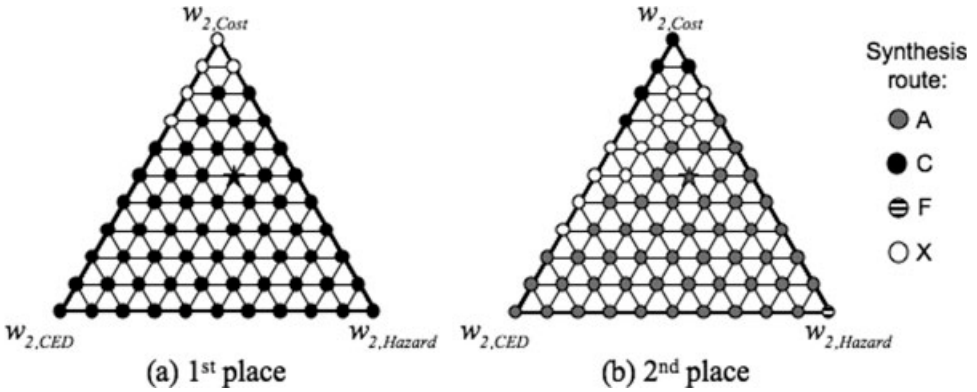

Figure 10. Effect of weighting factor choice $w_{2,j}$ on the ranking of process routes according to total score T_s^r at Conceptual Design I.

The default set of weighting factors used in calculating the total score in Figure 9: {0.5, 0.2, 0.3} for {$w_{2,\mathrm{Cost}}$, $w_{2,\mathrm{CED}}$, $w_{2,\mathrm{Hazard}}$} is indicated by a star.

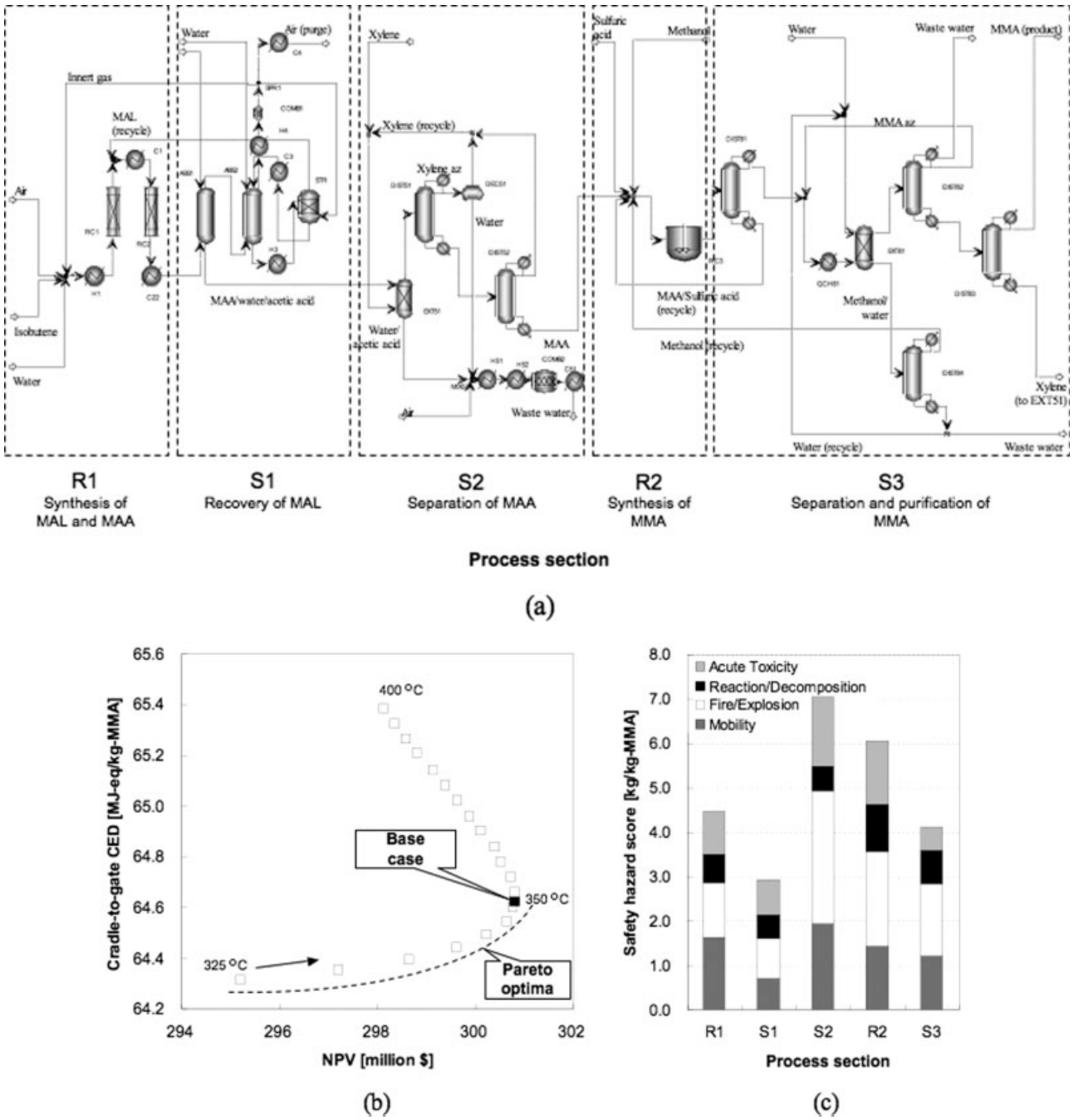

Figure 11. Process model and evaluation results for route C at Conceptual Design II: (a) flowsheet, (b) sensitivity analysis of the temperature in isobutene oxidation reaction (reaction step C1), and (c) safety hazard evaluation in different process sections as indicated in subplot (a).

up to the level of the last stage, and the resulting evaluation profiles are compared. Details of the process models of all six routes can be found elsewhere.[39]

Comparison of Individual Evaluation Results for MMA Routes Over Design Stages. The profile of economic, safety, and environmental hazard evaluations are shown in Figures 12a–c. In (a) economic evaluation, only raw material cost is calculated at Process Chemistry II, and at CD I, all the remaining costs are added to the production cost. In this step, raw material cost is updated by more precise yield and introduction of loss term in the separation processes. On the average, its increase is 6%, and it is especially high (16%) in route F which has a difficulty in the separation part. Utility costs of energy and separation agents that are added at CD I are estimated by ELI at Process Chemistry II, and its preciseness is discussed later in this section. Negative values indicate benefits from steam production within the process. The overall production costs, the balance of all costs and benefits are indicated as triangles in the figure. Toward CD II the use of rigorous models refines each fraction of the production

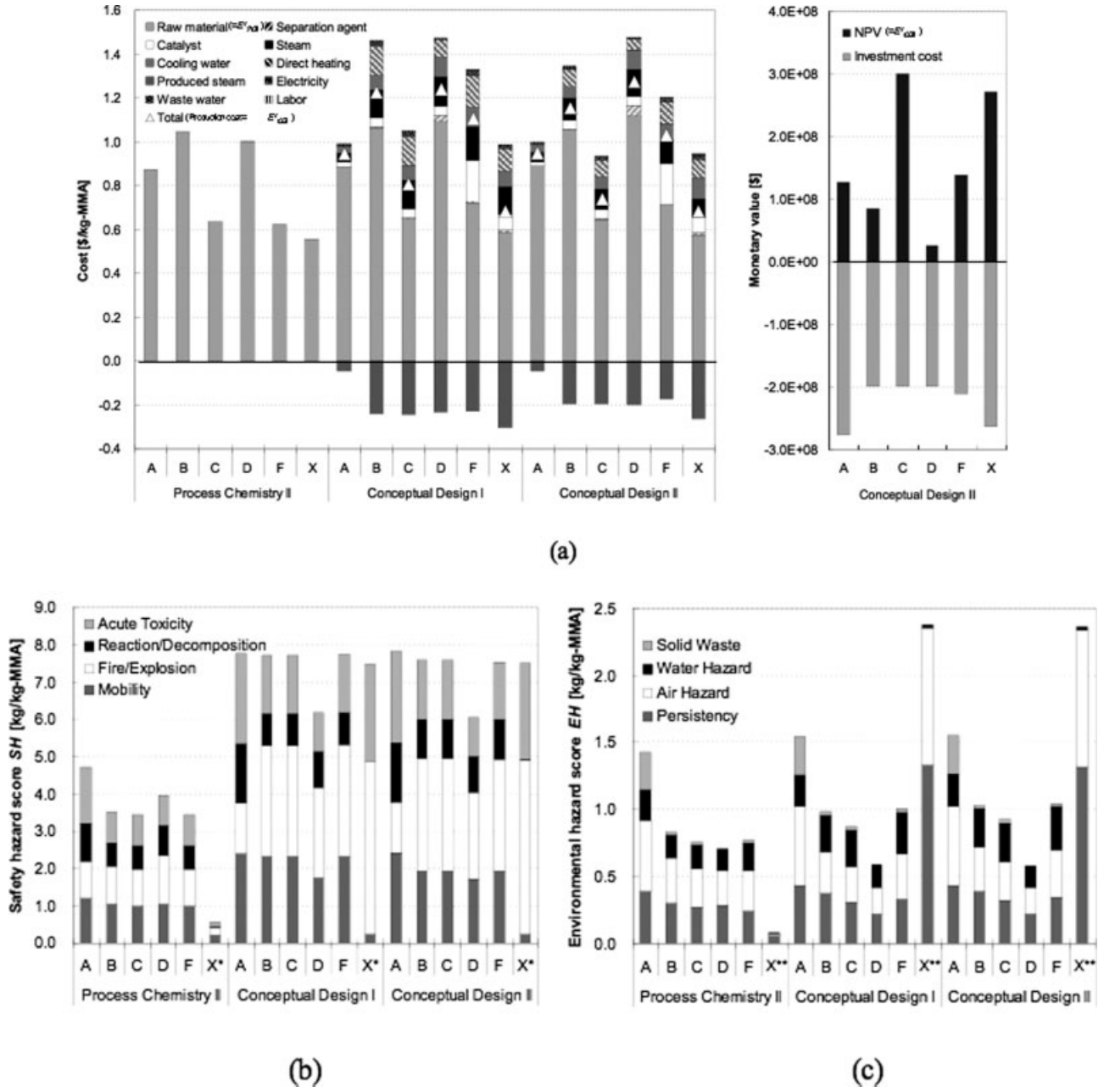

Figure 12. Profile of evaluation results of MMA synthesis routes A to X from Process Chemistry II to Conceptual Design II: (a) economic performance with production cost on the left and NPV at Conceptual Design II on the right, (b) safety hazard, and (c) environmental hazard.

Note: * and ** indicate that results of synthesis route X are divided by a factor of 50 in (b) and by a factor of 10 in (c), respectively.

cost. The update in the total production cost is, compared to CD I, −3% on the average, and the largest change (+3%) is observed in route D, which has azeotropic distillation systems. At this stage, NPV is used as an indicator for decision-making. In this study, investment costs for all processes were calculated based on reported values in the literature.[59] Together with the production cost, NPV was calculated for all processes shown in the right part of Figure 12a. The calculation settings, e.g., 15 years as projected life time, 12% as discount rate are common for all routes. The scale of NPV is inversely related to the cost, i.e., a higher NPV indicates better economic performance, and the investment cost, i.e., NPV at year zero is shown as negative value in the same graph. By comparing results of routes B, C, and D, the effect of integration over years can be seen in NPV: these three routes have the same investment costs but different production costs (10% and 42% smaller for routes B and C, respectively), and by summation over 15 years the NPV shows a very large difference (3 times better for route B, 12 times for route C). Use of NPV magnifies the difference of production cost by integrating the difference over years. Another point is that the rank in production cost is not necessarily the same one

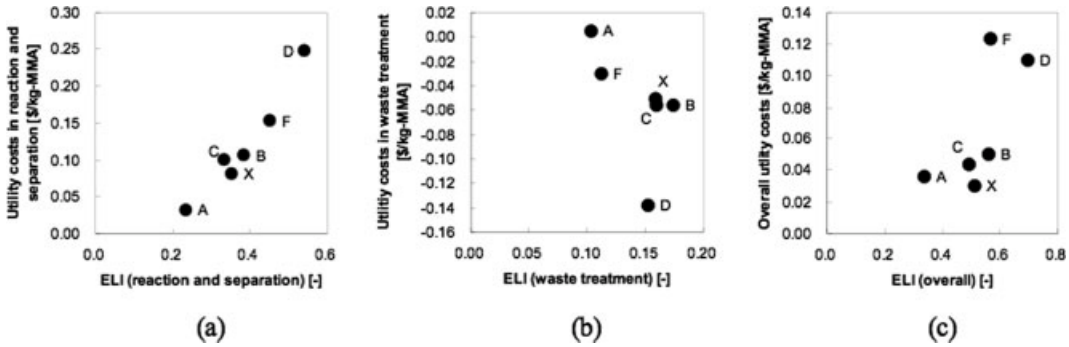

Figure 13. Comparison of ELI as obtained at Process Chemistry II and utility costs calculated at Conceptual Design II for MMA synthesis routes A to X in different process sections: (a) reaction and separation, (b) waste treatment, and (c) overall.

as in NPV because of the investment cost. For instance, route X has lower production cost than route C, however, due to higher investment cost the resulting NPV is lower in route X than in route C. The same phenomenon can be observed between routes A and F. Inclusion of investment cost, the new information available at this stage, has important effect on the evaluation result.

The evaluation profiles of safety hazards over design stages are shown in Figure 12b. The scale of route X is reduced by a factor of 50 to fit into the same graph. With respect to safety hazards, the evaluation perspective changes: at Process Chemistry II, hazard of one substance in a step represented the whole route while from CD I on hazard of a flow, or a set of substances, is considered in the assessment. This broadened evaluation scope increases the safety evaluation score in CD I as compared to Process Chemistry II. Introduction of new substances such as separation agents is another source of the increased evaluation score. This effect is most significant in route X where use of tetradecane as a separation agent at large scale shoots up the safety hazard. In route D on the contrary, no new substance is added as compared to the previous stage, and the evaluation score becomes smaller relatively to the other routes. In the last stage, CD II, changes introduced by the application of rigorous process models are rather low.

Profiles of environmental hazard evaluation are shown in Figure 12c, where the result of route X is reduced by a factor of 10. Introduction of new substances at CD I is the major factor in the increase of score as compared to Process Chemistry II. Application of rigorous models updates and refines the score toward CD II, but again with rather low magnitude. As compared to the safety hazard there are fewer changes in the ranking in the environmental hazard assessment.

The profile of CED is quite similar to the one of production cost, and similar arguments can be made on the updating factors. In health evaluation where the most hazardous substance represents the whole route or process, evaluation scores are almost identical in all stages. This is because quite hazardous substances in MMA processes were already considered in the first design stage, and thus scores were not updated later on.

In Process Chemistry II, ELI was used as a proxy indicator to estimate gate-to-gate costs and environmental impacts, and was applied for route screening. For judging precision of this proxy measurement ELI results are compared to the utility costs of six routes calculated in CD II. As shown in Figure 13, comparison was performed at different sections of the process: (a) reaction and separation, (b) waste treatment, and (c) overall. As utility costs energy-related utilities and separation agents were considered. In Figure 13a the ELI for reaction and separation parts are combined and compared to the utility costs in this process part. A rather good correlation is obtained (R^2=0.95), and thus, in this case study the estimation by ELI for this process section was successful. On the contrary in Figure 13b where ELI for waste treatment is compared to waste treatment costs, no correlation is found. In this case study most of the processes comprise steam generation in waste treatment, which gives an economic bonus in waste treatment. Generated amount of steam is proportional to the throughput of the waste treatment, which was dominated by separation agents or water in routes B, C, F, and X. In route D, methanol was used in addition, which gives highest profit in the steam generation. Such benefits of waste treatment processes that stem mainly from separation agents introduced only at CD I are not well predicted by the current version of ELI. This bad estimation in waste treatment aspects leads to the rather weak correlation in overall result as shown in Figure 13c.

Comparison of Overall Evaluation Results for MMA Routes Over Design Stages. In the previous section, profiles of individual evaluation categories were discussed and factors that cause significant changes in single indicator results were identified. In this section, the evolution of the overall score, which is the basis of decision-making, is analyzed for the same purpose.

Figure 14 shows profiles of evaluation results in (Figure 14a) economy, (Figure 14b) CED, (Figure 14c) EHS hazard, and (Figure 14d) total score over three stages. Scores in subplots (Figures 14a–c) correspond to mid-point scores $M^r_{s,j}$ multiplied by weighting factors {0.5, 0.2, 0.3} for {$w_{2,\mathrm{Cost}}$, $w_{2,\mathrm{CED}}$, $w_{2,\mathrm{Hazard}}$}; the sum of these products gives (d), the total score T^r_s. For CD I the inverse of NPV (1/NPV) was used in normalization and used as the economic mid-point score. The theoretical maximum at each subplot is as high as the corresponding weighting factors $w_{2,j}$, which can be achieved by a route with the worst score, i.e., a value of one in all sub categories of a mid-point score. In this figure, the effect of including new information by exchanging the evaluation indicator over stages is visualized.

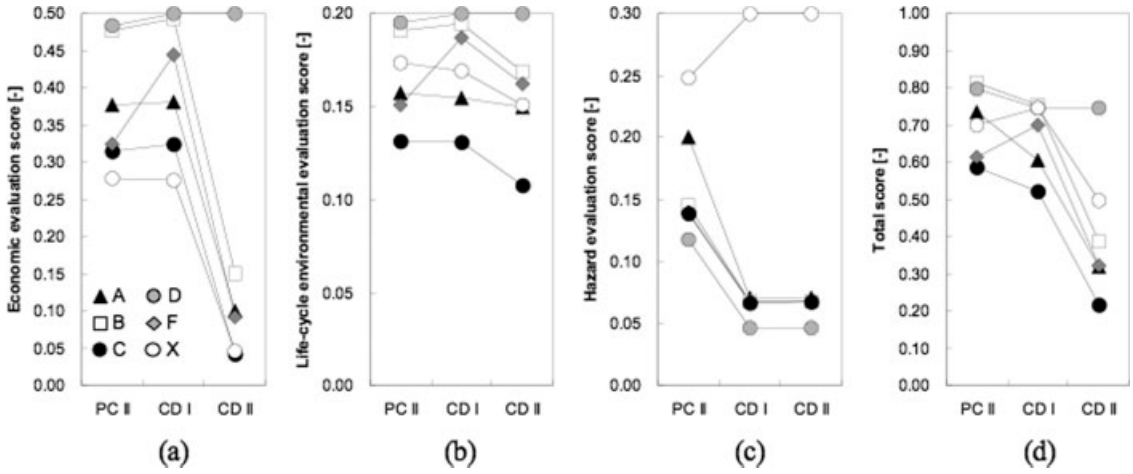

Figure 14. Profile of evaluation results of MMA synthesis routes A to X from Process Chemistry II (PC II) to Conceptual Design II (CD II).

Scores in plots (a–c) correspond to the mid-point score $M^r_{s,j}$ multiplied by $w_{2,j}$ (see Figure 5 for Process Chemistry II), and direct summation is the total score T^r_s in (d).

In Figure 14a, the economic evaluation score at Process Chemistry II is the combination of raw material cost and ELI. In CD I, where production cost is used, only route F becomes significantly worse because of the loss of valuable materials including raw materials and catalysts in the separation processes. This aspect, i.e., loss of valuables, was not part of the estimation by ELI, and thus the rank of F decreased so much that it becomes worse than route A. Ranks of other routes, which do not have too much difficulty in separation, remained the same, which indicates that the estimation by ELI had a reasonable accuracy. In the last stage, CD II, the economic scores for all routes decrease significantly except for route D, which is the worst at both stages CD I and II. As discussed in the previous section, use of NPV tends to magnify differences in production cost by its integration for the plant life time, i.e., 15 years in this case. This nature of NPV leads to the large difference of the score at this stage. Compared to CD I, changes in rank between routes C and X, A, and F can be observed due to the inclusion of investment cost as new information at CD II.

In Figure 14b where CED results are displayed, again route F becomes much worse from Process Chemistry II to CD I because of the same reason as in the economic evaluation. Otherwise, though some difference can be seen, these two stages show the same ranking of routes, which again indicates that estimation by ELI was reasonable. Toward CD II all results get more precise by the use of rigorous models in calculating mass and energy balances. With this refinement the CED in route D increases while this value stays almost the same for the other routes. This change reduces other routes' scores relatively; however, it does not change the ranking of routes.

In Figure 14c where EHS hazard is displayed, the score of route X shoots up in CD I, which now becomes worst in all subcategories of E, H, and S. This is due to the large-scale use of a separation agent, which is the new information added at this stage. This significant increase in route X reduces the score of all other routes. In the last stage, almost no change is observed, i.e., updates by application of rigorous models are negligible here.

Total scores T^r_s are displayed in Figure 14d which shows the addition of all subplots (a–c) and thus summarizes all the updating factors over stages. From Process Chemistry II to CD I, there are two crossings in the ranking. The first one concerns route A and F and is due to increased scores of route F in (a) cost and (b) CED, which stems from the incompleteness of the proxy indicator used at Process Chemistry II. In the second case, route X becomes worse than route A, which results from route X's significant increase in (c) hazard score caused by the large-scale inclusion of a new substance in the separation. In the last stage, CD II, the change in the results is dominated by the nature of NPV as discussed earlier, because of the highest weighting factor $w_{2,\mathrm{Cost}} = 0.5$ in (a) economic score as well as small and almost no changes observed in (b) CED, and (c) hazard. From route B and X, which had close scores at CD I, route B turns out better at CD II because the decrease of route B in (a) economic score is higher than the one of route X. The results for route A and F become closer which is the effect of including investment cost at this stage.

Conclusions

In this article, we presented a novel framework of chemical process design including four stages of decision-making considering economy, life-cycle environmental impacts, and EHS hazard. The four stages in early design phases, Process Chemistry I/II and Conceptual Design I/II, are defined according to the available information and characteristics of decision-making. At each defined stage, an appropriate modeling approach and evaluation indicators are selected. Here, ELI was proposed as a novel proxy indicator of energy-related efforts in a process based on the reaction information alone. Decision-making based on multiobjective evaluation results at each design stage is supported by the aggregation procedure using weighting method.

The proposed framework was demonstrated on the case study of MMA process design: starting with 17 possible synthesis routes, inferior routes were eliminated step-by-step and

at the last stage an optimized flowsheet of the route with the best multiobjective performance was produced; modeling, evaluation, and decision-making at each stage were illustrated. Another part of the case study was to validate the framework by observing the evaluation profile of six routes over different stages. In particular, impacts of acquiring new information and changes in the evaluation indicators over design stages were discussed.

The validation part revealed that extension of the design scope from process chemistry to process flowsheeting brought several significant updates in the evaluation results. In the aspects of economy and life-cycle environmental impacts, important factors were inclusion of energy-related utilities and losses of valuable materials into the process model. With respect to EHS hazards, introduction of new substances, especially separation agents, into the process models was observed as an important updating factor. With regard to the health hazard, almost all routes in this case study employed hazardous substances but these were already considered in the earlier design stages and thus the results were not updated significantly in later stages. Further refinement of the process flowsheet by replacing short-cut models with rigorous ones results in several updating factors as well. However, in the presented case study, these updates did not change the evaluation ranking in the nonmonetary aspects, that is, life-cycle environmental impacts and EHS hazard. As to the economic aspect, however, investment cost, which is covered by the indicators only at the last stage of the framework, had a rather large impact on the result.

Thus, there is a need for a good estimation of the aforementioned factors that are available only at later stages but cause significant updates on the results. For this purpose, ELI has been proposed in this work, to estimate required amount of energy-related utilities based only on reaction information. It showed a reasonable accuracy as far as observed in the case study; however, continuous refinement is needed through application in other cases. For other key factors such as loss of valuable materials, introduction of new substances and investment cost, development of proxy indicators for earlier stages would be an important issue.

Process development also includes iterations. In principle any combination of repeating single steps or sequences once or more is possible. We did not depict these possible combinations in the framework but obviously any step of the framework or sequences of these can be repeated with updated information and/or a different combination of process alternatives.

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Notation

cE = category in environmental hazard, e.g., air hazard
cH = category in health hazard, e.g., chronic toxicity
cS = category in safety hazard, e.g., fire/explosion
cX = category in energy loss index, e.g., reaction energy
C_i = cost or price of material i ($/kg)
C_L = labor cost [$/(kg product)]
CED_i = cumulative energy demand of material i [(MJ equiv)/kg]
CF_t = annual cash flow at year t ($/year)
d = discount rate (0,1)
E = economic indicator [$/(kg product)] or ($)
I_i = Index value in EHS hazard of substance i [0,1]
EH = environmental hazard indicator [kg/(kg product)]
$ELI_{cX,n}$ = calculated energy loss index in category cX at nth reaction step
F = Flow of mass or energy in reaction/process system, e.g., reactor inlet (kg/h) or (MJ/h)
HH = health hazard indicator [kg/(kg product)]
INV = investment cost ($)
L = indicator of life-cycle environmental impacts [(MJ equiv)/kg product)]
m_i^F = mass flow of material i in flow F per amount of product; referred to as specific mass flow [kg/(kg product)]
$M_{s,j}^r$ = mid-point score of route r in category j at stage s
$MLI_{i,n}$ = calculated mass loss index of reaction outlet type i, e.g., coupled product (CP), byproduct (BP), at nth reaction step
n = number of steps of a reaction route
N = projected plant lifetime (year)
P = proxy indicator for gate-to-gate costs/environmental impacts in Process Chemistry stages
r = reaction route or process
s = design stage of the framework
SH = safety hazard indicator [kg/(kg product)]
T_s^r = total score of route/process r at stage s
$w_{1,i}$ = weighting factor of evaluation category i in aggregation step 1 [0,1]
$w_{2,j}$ = Weighting factor of mid-point category j in aggregation step 2 [0,1]
w_{cX} = Weighting factor of energy loss index category cX [0,1]
$X_{s,i}^r$ = evaluation indicator of route/process r at design stage s in evaluation category i. X is a place holder of E, P, L, SH, HH, and EH.
$\overline{X}_{s,i}^r$ = normalized evaluation indicator of route/process r at design stage s in evaluation category i
z = fraction of mass emitted by accident from the maximum mass within the reaction/process system

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