**Early stage assessment to accelerate the development of sustainable chemical manufacturing processes**

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**Introduction**

Sustainability is a key challenge for the twenty-first century. Over the past couple of centuries, we have significantly improved our standard of living through increased use of fossil resources. However, our reliance on fossil resources poses critical questions in view of finite resources and environmental impacts. These concerns become even more crucial in the wake of increasingly resource-intensive consumption patterns across the world and have to be balanced against the growing needs of the world population. It is hence imperative to strike a balance among our economic, environmental and societal interests to achieve sustainability.

In recent years, an increasing awareness of sustainability issues has led to an impetus for efficiency improvement, hazard minimization and utilization of renewable resources such as biomass. As we develop novel chemical conversions, it is important to analyze these processes within a broader economic, environmental and social context. Such an assessment helps us to identify promising alternatives and channel capital accordingly. The flexibility of early-stage process development offers unique opportunities for chemists and engineers to use this assessment and make new pathways inherently sustainable.

A critical challenge while performing an early-stage assessment is to work with the limited information available. Green chemistry principles laid down by P. Anastas 1 have pioneered sustainability thinking in process development. Although useful, these principles are qualitative in nature and fail to consider trade-offs between the economic feasibility, environmental impacts, risks and benefits associated with the chemical process. There have been other quantitative and qualitative assessment techniques based on specific product and process attributes, such as E-factor 2, GME3, EcoScale 4 and ProSuite 5. More comprehensive methods such as BASF eco-efficiency 6 and the Sustainability Consortium Open IO 7 rely primarily on data from existing processes or rigorous process and supply chain modeling efforts. The comprehensive methods incorporate features such as techno-economic analysis, environmental and social life cycle assessment, and so forth. Most of these methods are either qualitative and very broad (based on brand image or final product characteristics) or extremely information intensive, which demands significant investment of time and resources. Hence there is a need for a tool that provides a rather quick but informative assessment that can aid key decision-making at the laboratory stage of a process. For such an assessment, it is important to utilize as much quantitative and qualitative information as is available at an early stage in process development. The work by H. Sugiyama 8 represents an important step in this direction. His approach takes into consideration factors such as raw material costs, environmental impacts and hazards and is primarily targeted toward petrochemical processes. In this paper we continue in the direction of H. Sugiyama’s work. We modify his approach by incorporating more practical aspects and propose a comparative assessment method for chemical processes at the laboratory stage. Figure 1 shows the stage in the process development pipeline at which the proposed methodology could be applied. In its current form it is primarily targeted at processes for fuels and bulk chemicals. However, the flexibility of the proposed method could enable additional applications with some minor modifications.

The proposed assessment incorporates basic reaction mass balance information along with data such as raw material prices, greenhouse gas (GHG) emissions and qualitative indicators. This information is integrated by means of weighting factors. In this article we use the method to analyze a biobased process and a comparable fossil-based process. This comparison gives us an important indication of the potential benefits that a proposed new process can offer over a conventional process in terms of sustainability. We also assess the robustness of this outcome in light of uncertainties in the input information.

This method has been developed and applied within the CatchBio program in the Netherlands, which focuses on the development of catalytic processes for conversion of biomass to fuels and chemicals. In this paper we apply this method to a catalytic process for the production of but-1,3-diene from ethanol, which is being developed within the CatchBio program. This process is compared with the dominant conventional method for production of but-1,3-diene from naphtha in a steam cracker. Using the results of this assessment, we analyze the plausibility of the results and explore various details regarding application of the methodology. This method has already been tested for approximately a dozen different processes and the results will be published in the near future.

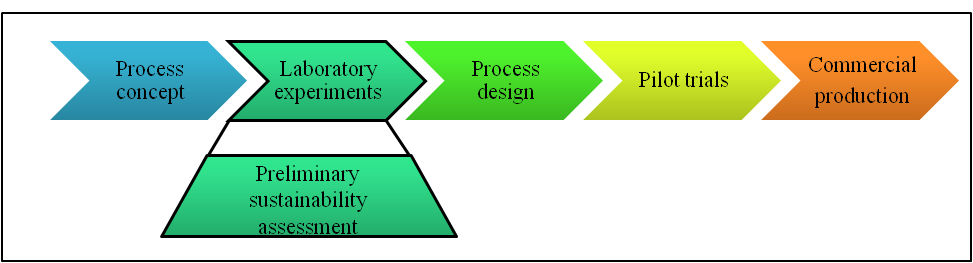


Figure 1: Process development pipeline and methodology application

# Methodology description

The method evaluates an innovative new chemical process and a comparable conventional process based on selected parameters that are used as proxies for economic feasibility, environmental impact, human health, and risks and opportunities. This method combines quantitative information about the raw materials and the process with qualitative indicators that reflect the sustainability of the process. The system considered by the assessment method includes the reaction and a separation process that is assumed to be ideal due to the lack of real process data (see figure 2). Figure 2 shows the level of process detail, where S represents the mass flow of various streams. S1 is the mixed input stream while S5 and S6 represent the product and co-product streams. S4 is the recycle stream and S7 is the waste stream. For this analysis, the parameters that contribute to the final score are as follows:

1. Economic constraint
2. Environmental impact of raw materials
3. Process costs and environmental impact
4. EHS index
5. Risk aspects

This method uses basic reaction data in conjunction with other information such as the physical and chemical properties of the chemicals, prices, the cumulative energy demand (CED), greenhouse gas (GHG) emissions, market availability and so forth. The first parameter, economic constraint, provides information about the raw material costs relative to the market value of the products. The second parameter combines proxies for the environmental impacts associated with the raw material consumption for the process. While the first two parameters concern raw material requirements, the third parameter represents an indication of the expected costs and environmental impacts associated with the processing of raw materials into final products. The fourth parameter provides information about the hazards associated with the process and can help in the development of inherently safer chemical processes. The final indicator incorporates information about the external market risks and potential technical aspects associated with the process. The first four mid-point parameters are based on the work of H. Sugiyama 8 and have been modified for our assessment method. The fifth parameter is an addition to the basic framework proposed by H. Sugiyama. Based on input from these five parameters, this method enables analyses of a conversion process in terms of its raw material costs and environmental impacts, processing costs, impacts and hazards, risk aspects. In this assessment scheme, lower values are desirable for each parameter. Figure 3 provides an overview of the proposed methodology. The following sections explain each of these parameters in detail.



Figure 2: Scope and level of detail

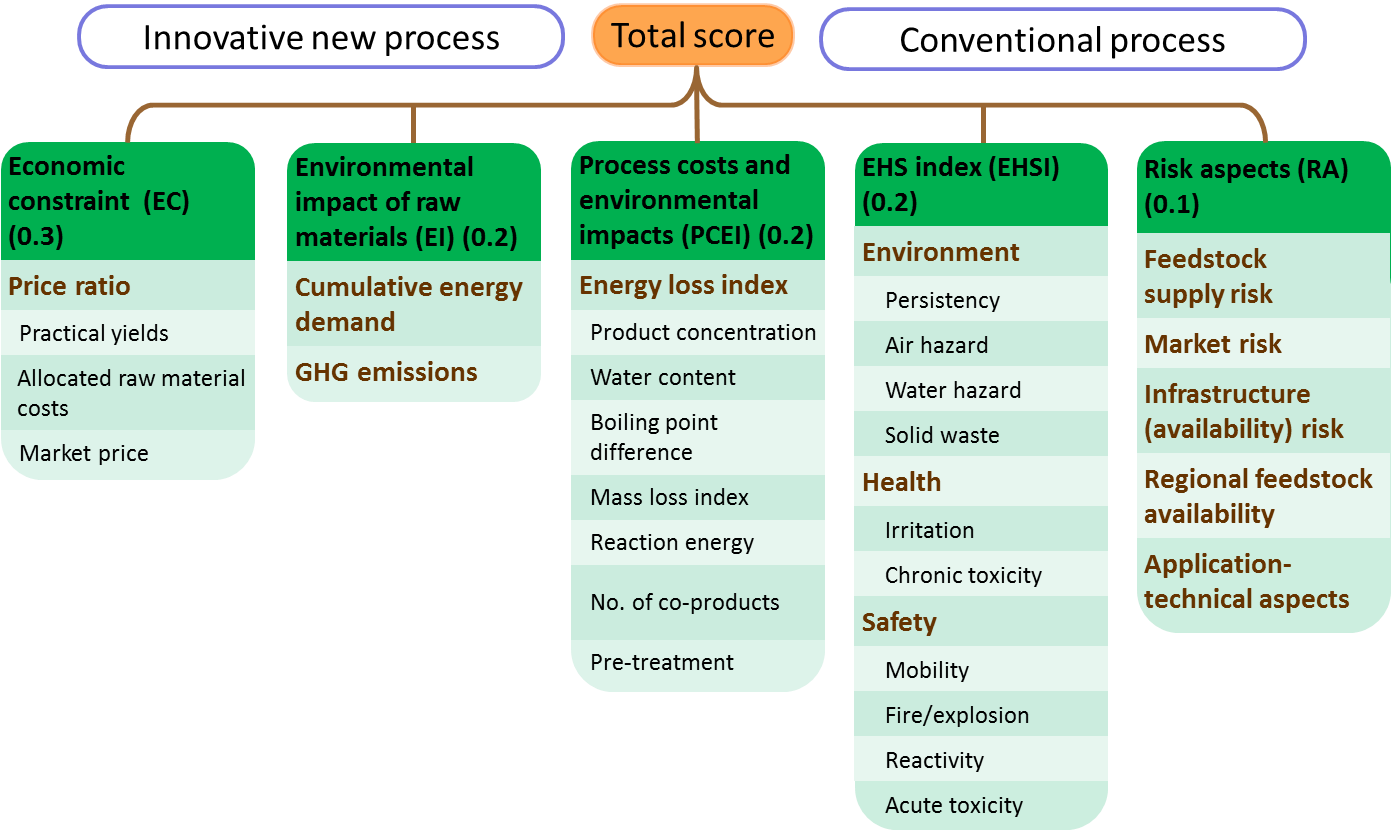


Figure 3: Overview of the assessment methodology

## Parameters

**Economic constraint (EC)**

Economic feasibility is critical for the practical implementation and economic sustainability of a chemical process. It is essential that the market price of a product covers the raw material costs and leaves room for processing costs. Economic constraint as defined here represents the raw material costs as a fraction of the value of the products and co-products. This parameter, which is based on quantitative information, is a function of the market prices of the products and co-products, raw material prices and practical yields. The yields are based on complete conversion of raw materials assuming recycle. It is calculated as a ratio of the economic value (market price × mass flow) of raw material inputs to the combined economic value of the products and co-products. The mathematical formulation can be described as follows:

In equation 1, *am* and *bm* are the respective prices and mass flows of the *mth* raw material and *xn* and *yn* are the respective prices and mass flows of the *nth* product. In the case of multiple reaction steps, the raw materials and products across all the steps are taken into account. This formula for EC also includes economic allocation for analyzing the main product without co-products. Please refer to supplementary information for details regarding the derivation of equation 1.

For economic constraint, a lower ratio (<1) indicates higher opportunity in the form of lower feedstock costs relative to the market value of the products. A ratio higher than 1 indicates that the market value of the products and co-products does not cover the raw materials costs. A process with a lower ratio allows more room to accommodate other capital and processing costs.

*Challenges and solutions*

Fluctuations in prices can lead to variations in the parameter value. To reduce uncertainty and ensure a consistent assessment, prices at a similar point in time or for a similar time period should be used for calculations. Also, historical prices if available should be used as an input for uncertainty analysis. A cut-off criterion could be applied to leave out lower-value co-products that may be difficult to recover. However, implementation of a cut-off criterion is based on the decision to recover lower-value co-products with additional capital investment, which will be dictated by the size of the plant. It is difficult to take the size of the plant into consideration at this stage, in view of offering a fair comparison between processes as well as higher data requirements.

In this method, the cost of a heterogeneous catalyst is assumed based on catalyst specifications provided by J.P. Lange 9. Based on this reference, it has been assumed that catalyst consumption is below 1 kg catalyst/ton of product, above which catalyst costs can be critical for process feasibility. For homogenous catalysts, if the data indicates that catalyst is lost through side reactions or with the product, then that is accordingly taken into account. Based on further catalyst studies, more accurate information about the consumption of catalysts can be incorporated.

**Environmental impact of raw materials (EI)**

This parameter represents the environmental impacts of the raw materials required for the production of a unit mass of product. H. Sugiyama proposes the cumulative energy demand (CED) of all raw materials as an indicator of this impact. The raw material CED represents the total energy requirements from cradle to the relevant system boundary. In the context of this assessment this system boundary is the inlet factory gate (i.e., the gate to which raw materials are delivered). It represents the total of renewable and fossil energy inputs along with the feedstock energy content. The CED can be a good representative first indicator for a wide range of environmental impacts 10. In this assessment method, we have also included (with weight equal to the CED) the GHG (eqv. CO2) emissions associated with all the raw materials. GHG emissions function as an indicator of non-renewable resource use and climate change, which is an increasingly important long-term sustainability issue 11. Only the fossil GHG emissions have been taken into account, thereby also including fossil carbon embedded in the product, i.e. following a cradle-to-grave approach. This choice represents the conservative assumption that the embedded carbon will be released at a later point in time, through utilization in the case of fuels and either waste incineration or the action of micro-organisms in the case of chemicals. The reasoning is that fossil-based carbon will only be recycled after a long time span of millions of years, while contributing to global warming and depleted useful carbon resources in the meantime. Biobased carbon, on the contrary, is recycled rather quickly (on a perennial or biennial basis) and causes a significantly lower global warming effect if it is sustainably harvested and converted. The global warming potential is estimated based on a 100-year timeframe using the IPCC 2007 GWP 100 method. 12

Economic allocation is used to distribute process impacts over all the products and co-products. Allocation enables comparison on the basis of one unit of main product, which in essence is the functional unit for the assessment. Given the nature of this calculation, the assessment can be applied to any product from the process, regardless of its mass or economic value. Economic allocation has been used as opposed to mass or energy allocation because it accounts for the fact that the process is being operated primarily for economic reasons. This is because the target of a chemical conversion process is usually to achieve a certain functionality in the product which is reflected in the price of the product. It avoids assigning a substantial share of the overall process impacts to low-value by-products (especially relevant if these are produced in large quantities). The relevant equations for this parameter are as follows:

*Calculation of the allocation factor*

In equation 2, *fn* stands for the main product, which is the functional unit for our calculations. *xfn* and *yfn* are the price and mass flow, respectively, of the main product, while *xn* and *yn* are the respective price and mass flow of the *nth* product. The product mass flows are based on complete conversion of raw materials. *Afn* is the allocation factor for allocating the impacts to the main product.

*Calculation of CED (P) and GHG (Q)*

To estimate the CED of raw materials, the following two steps are taken: first the feedstock energy component of the raw material CED is removed by subtracting the calorific value of the raw material from the CED. The remaining part then represents the total renewable and non-renewable *process energy* for raw material production from cradle to factory gate. Economic allocation is applied to this value in the second step. In contrast, the part representing the feedstock energy content flows through the process and ends up in the energy content (calorific value) of the products from the process. Thus, the CED of raw materials for the main product is estimated by adding the *process energy* allocated to the main product and the energy content (calorific value, Efn) of the main product.

By analogy with CED, the GHG emissions of the raw materials refer to the system cradle-to-factory gate. However, contrary to CED, the cradle-to-factory GHG emissions do not include the portion originating from the feedstock. Hence,no subtraction is required, i.e. the raw material GHG emissions are allocated directly using economic allocation. These allocated GHG emissions and the potential GHG emissions from the fossil carbon embedded in the main product (e.g. petrochemical product) are added, to estimate the raw material based GHG emissions for the main product.

In equation 3 and 4, *ym* is the mass flow of the *mth* raw material. *Pm*, *Em* and *Qm* are the CED, calorific value and the GHG emissions, respectively, associated with the *mth* raw material. *yfn* is the mass flow of the main product and *Afn* is the allocation factor. *Efn* and *FCfn* are the calorific value and embedded fossil carbon, respectively, for the main product. *Pfn* and *Qfn* are the estimated CED and GHG emission values for the main product.

*Estimation of process environmental impact*

Both the CED and the GHG emission values of the new process are normalized against the respective values for the comparable conventional process. The normalized scores are then added using an equal weighting factor of 0.5.

*Challenges and solutions*

For calculation of CED and GHG emissions, allocation (here: economic allocation) can be applied in various ways. The most straightforward way is to apply alloction to the *total* CED and GHG emissions of the raw materials. However, a low allocation factor (reflecting a product with a low price and mass flow) can, however, lead to violation of the mass and energy balance principles, e.g. by resulting in a lower allocated energy requirement than the raw material’s calorific value. To avoid this effect, economic allocation is applied in the specific way as described above.

The CED and GHG emissions are good first proxies for environmental impacts, but there are certain limitations for factors such as toxicity. If the required data is available, other factors such as water use and land use can also be incorporated into the method.

**Process costs and environmental impact (PCEI)**

Given the early stage in process development, it is difficult to obtain quantitative information regarding the costs and environmental impacts involved in conversion of raw materials to products and subsequent downstream processing. Hence this parameter serves as a proxy to give an indication of costs and impacts based on quantitative data inherent to the reaction and products. This index builds upon the energy loss index (ELI) suggested by H. Sugiyama 8 and is based on the notion that energy loss in the reaction and separation section of the processing sequence can be used as an indicator for the expected costs and environmental impacts.13

The PCEI parameter aggregates seven different indicators, the scores for which are based on the data from the reaction. The individual scores vary from 0 to 1 or from -1 to 0, based on the value of the underlying parameter. The description for the first five parameters follows from H. Sugiyama 8. The last two indicators are our proposed additions to the ELI, due to their relevance for new processes (esp. biobased) and in line with other modifications to the method.

*Presence of water at the reactor outlet*

The presence of water at the reactor outlet has been considered because water can cause difficulties in the separation process and has a high heat of vaporization. Water that is distilled to the top of the distillation column is given a higher index value. This is determined based on the difference in the boiling points of water and the product (Scheme 1). 8



Scheme 1

*Product concentration (molar concentration of the main product at the reactor outlet)*

The second indicator is the molar concentration of the product at the reactor outlet, and is based on the inverse relationship between product concentration and the efforts required in separation (Scheme 2). 8



Scheme 2

*Boiling point (minimum difference between the main product and the substances at the reactor outlet)*

The third indicator is the difference in boiling point between the main product and other substances at the reactor outlet. These other substances may be co-products, auxiliary inputs or water. The boiling point of each substance at the reactor outlet is compared with that of the product, and the minimum difference is used for index calculation. The index value increases as the difference in boiling points decreases because that increases the difficulty of separation (Scheme 3). 8



Scheme 3

*Inherent reaction mass loss (measured by mass loss index)*

As a fourth indicator, the mass loss index 14 (MLI) for a reaction step is determined. This index serves as a proxy for mass loss related to the formation of waste and unconverted reactants in the reaction 8. This index is a ratio of the total mass of all components at the reactor outlet other than the main and co-products to the mass of the main and co-products from the reaction. The unwanted outputs from a reaction inherently end up in the waste treatment process. This index quantifies the efforts required in waste treatment and additional separation requirements (Scheme 4).



Scheme 4

*Reaction enthalpy (heating or cooling duty)*

Typically, a higher heat of reaction requires more utilities (e.g., steam, fuel) in an endothermic reaction, or cooling water in an exothermic reaction. When the exothermic reaction occurs above 200 °C, the generation of useful process energy (e.g., steam) becomes possible. In this case, a negative value is applied using the secondary scale, to credit the energy recovered (Scheme 5). 8



Scheme 5

*Number of co-products*

Extending the approach proposed by H. Sugiyama, we also consider the value of the co-products generated in the reaction. These co-products will need additional separation and purification if they are to be recovered. This indicator serves as a proxy for the increased processing requirements for co-products which will need to be separated from the main product and purified to achieve economic potential (Scheme 6).



Scheme 6

*Pre-treatment of feedstock*

This indicator is a further addition to the ELI as proposed by H. Sugiyama. In many processes, especially ones that start from biomass, additional pre-treatment of feedstock is necessary to either enable the reaction or to increase conversion efficiency. This indicator is used as a proxy for the additional efforts (ex. cutting, grinding, washing etc.) required in the pre-treatment of feedstock. It assumes discrete values of 0 (no pre-treatment) or 1 (pre-treatment required) (Scheme 7).



Scheme 7

As a default, equal weights are assigned to each of these indicators contributing to the ELI. The scores of all the indicators are added up to derive the ELI of the process. For processes with multiple reaction steps, a separate ELI is calculated for each reaction and separation step, and the scores of all steps are added to arrive at a single ELI for the whole process.

*Challenges and solutions*

As an alternative to the use of equal weights, another approach would be to vary the weights based on the relative contribution of each parameter to the intensity of the processing requirements. Since the determination of specific weighting factors would require a separate in-depth study, we have chosen to apply equal weighting as the default, which could be complemented by a sensitivity analysis using different weighting sets based on expert judgment.

The use of the mass loss index might seem to penalize low conversions without consideration of selectivity. However, low conversions inevitably lead to additional processing which needs to be considered. Other parameters in the method, such as the EC and the EI, take into account the yield of the product based on complete conversions and selectivity, thus justifying the use of the MLI.

Depending on the availability of data, in addition to the above indicators, catalyst performance could also be included. This could be based on either of the catalyst characteristics, such as turnover frequency, weight hourly space velocity, on-stream time and regeneration time. These characteristics of a catalyst can potentially play a crucial role in the capital and operating costs associated with a project. However, further work is required to develop an operational indicator for catalyst performance.

As an alternative to reaction enthalpy, exergy change in the reaction can also be a useful indicator regarding the energy use and the impacts of processing. The challenge with its use as an indicator is that the calculation involves more steps and certain assumptions have to be made regarding the process heat flows. This can lead to an increase in the difficulty of calculation for this indicator. Hence, considering ease of implementation, reaction enthalpy is used instead of exergy change.

The total energy loss in the process [LHV(feed + fuel) - LHV(product)] can also provide an indication of the capital costs 15. This has not been included because the fuel input for the process is not yet known at the laboratory stage.

**EHS index (EHSI)**

Hazards are an integral part of chemical processing. It is essential to develop inherently safer chemical processes to minimize hazards and try to prevent incidents such as the Bhopal tragedy 16. Inherently safe processes allow for the reduction of hazard control costs. This index proposed by H. Sugiyama 17 and based on G. Koller et al. 18 considers the safety, health and environmental (ecological toxicity) aspects of a chemical process and is suitable for an early stage assessment19. The individual categories and contributing indicators that are aggregated to the EHS index are shown below. The weights for the environment, health and safety categories are 0.4, 0.2 and 0.4, respectively. The calculation of this index is based on the indicator value for each chemical present within the process. Refer to the supplementary information for this article and H. Sugiyama 17,8 for a detailed explanation of the calculation.

1. Environment (E) (0.4)
   * persistency (half-life in water)
   * air hazard (index value of chronic toxicity)
   * water hazard (L(E)C50 aquatic, R-codes)
   * solid waste (based on substance class)
2. Health (H) (0.2)
   * irritation (EU-class, R-codes, LD50dermal)
   * chronic toxicity (EU-class, GK, R-codes)
3. Safety (S) (0.4)
   * mobility (partial pressure, boiling point)
   * fire/explosion (flash point, R-codes)
   * reaction/decomposition (NFPA reactivity, R-codes)
   * acute toxicity (IDLH, EU-class, GK, R-codes)

The property parameters and hazard classifications of each chemical compound are taken into account to assign index values to each of the parameters. The weights are assigned in such a way that each category within environment, health and safety has equal importance. As originally proposed, the hazards in a process are calculated on the basis of mass flows and indicator values for the chemicals present in the system. In the case of multiple products, we modify the approach suggested by H. Sugiyama by implementing economic allocation to distribute the burden of process hazards over the main product and co-products. Consequently, in the calculation of the category values, the mass flows represented in figure 2 should be used instead of the ones used by H. Sugiyama.

In equation 5, *E*, *H*, *S* and *wE*, *wH*, *wS* are the scores and weights for each category, respectively, while *Af* is the allocation factor derived in equation 2 and EHSI is the score for the EHS index.

In the case of a process with multiple reaction steps, the methodology to determine the hazard potential can be applied in two different ways: the first approach is to apply the methodology separately for each of the process steps. This results in a higher value for the EHS index because the hazard potential of the intermediate product is considered twice—once as the output from one conversion step and once more as the input to the subsequent step. This seems an adequate approach for a non-integrated facility requiring separate storage, transportation and handling of intermediate raw materials and products. In contrast, twofold consideration of the hazard potential seems inadequate in the case of an integrated facility combining the multiple steps. Thus in the second approach for integrated operation, the EHS methodology is applied jointly over all the conversion steps.

*Challenges and solutions*

The calculation of the EHS index is rather data intensive and can be the most time-consuming aspect of the methodology. It requires information on certain hazard parameters for each of the chemical compounds present in the process. However, not all the required information may be available for all the compounds. To address this issue, we recommend using indicator values for compounds with similar functional groups or molecular structure. In the case of product streams with a mixture of chemicals (e.g., bio-oil), representative chemical compounds can be used for preliminary hazard assessment. As more processes are analyzed using this method, more chemicals will be added to the database with the required hazard information, thereby significantly reducing time requirements.

**Risk aspects (RA)**

This parameter is based on the external economic aspects and technical aspects of the product molecule or reaction pathway, which can play a crucial role in the practical implementation of a new process. It takes into account factors that are not covered explicitly by prices. This parameter has been developed in the context of the CatchBio project framework. The time frame envisioned for the first large-scale implementation of new lab-scale processes is 10-15 years. The indicators have been chosen accordingly and are targeted at processes for commodity chemicals and fuels. The indicators considered are shown below. The respective weights (the numbers after each indicator) are based on expert opinion within the CatchBio project team (socio-economic assessment). Each process is assessed based on scoring statements (qualitative phrases) for each indicator. The overall parameter score is obtained by weighted addition of indicator scores.

Feedstock supply risk – 0.25

Regional feedstock availability – 0.15

Market risk – 0.25

Infrastructure (availability) risk – 0.2

Application-technical aspects – 0.15

Chemicals: functional groups – 0.5

Chemicals: retention of raw material functionality – 0.5

Fuels: high energy content – 0.5

Fuels: engine compatibility – 0.5

Inherent functional and pathway (application-technical) aspects can play an important role in unwrapping future potential for the molecule or pathway. These aspects can open up new markets with greater added value or can act as critical potential barriers. Moreover, the sustained availability of feedstock and a larger market will definitely play a major role in the practical implementation of the process. A process compatible with current infrastructure generally implies a lower risk and investment associated with it. Regional feedstock availability represents local growth opportunities and the avoidance of strategic risks that arise from wars or resource protectionism.

The details of the scoring scheme and qualitative phrases are as follows:

*Feedstock supply risk*

**0.0**: Large-scale availability (commodity chemical or fuel) and the major current application is of a lower value than the one targeted.

**0.5**: Potential for near-term bulk availability. Multiple equivalent or lower-value applications in sight. Feedstock under development.

**1.0**: Conceptual feedstock (needs fundamental development). Potential applications have a higher value than the one proposed.

This indicator takes into account the global feedstock availability. Technically speaking, a bulk of the available feedstock is only “available” if the proposed application is of a higher value than the current application. For a lower-value proposed application, additional feedstock needs to be produced, since the currently available feedstock will not be diverted from a higher-value application. Hence it is important to take into account the value of the proposed application when feedstock availability is considered.

*Regional feedstock availability*

**0**: Feedstock available in bulk quantities within a trade region (e.g., the European Union).

**0.5**: Feedstock available in other parts of the world in free and open markets.

**1**: Feedstock primarily available in regulated markets with limited global market access.

This indicator is used to incorporate feedstock security issues and local growth opportunities.

*Market risk*

**0.0**: Existing bulk chemical/fuel market.

**0.33**: Existing commodity (e.g., lactic acid).

**0.66**: Near-term bulk chemical/fuel market potential.

**1.0**: Long-term market potential, possibly accelerated by interesting properties.

*Infrastructure (availability) risk*

**0.0**: The process can be integrated or retrofitted into existing processing infrastructure. Also, the existing target product is part of existing processing and supply chains.

**0.33**: New processing plants are required based on known technologies. Also, the existing target product is part of existing processing and supply chains.

**0.66**: New processing plants are required based on known technologies. Also, the target product is new and would need new processing and supply chains.

**1.0:** New greenfield process plants built with new technologies. Also, the target product is new and would need new processing and supply chains.

*Application-technical aspects*

Chemicals

**Functional groups** (defined as the number of same or different functional groups on the hydrocarbon backbone)

**0**: Between 2 and 4 functional groups. Platform molecule. Wider potential applications.

**0.5**: More than 4 functional groups. Difficult platform molecule to work with, which can narrow down potential applications.

**1**: One functional group. Limited potential for platform chemical.

**Retention of raw material functionality**

**0**: Complete functionality is preserved. Fundamentally efficient approach, that can offer future improvement potential.

**0.5**: Limited modification of functionality.

**1**: All functionality stripped off. Lower theoretical improvement potential.

Fuels

**Energy density**

**0**: High energy density. Greater than or equivalent to gasoline/diesel(as applicable)

**0.5**: Energy density 80-90% that of gasoline/diesel.

**1**: Energy density below 80% that of gasoline/diesel.

**Engine compatibility**

**0**: Perfectly compatible. Gasoline/diesel equivalent. No engine modification required for use.

**0.5**: Potential for use in existing engines when mixed with gasoline/diesel.

**1**: Engine modification necessary for use. Will be a critical application barrier.

*Challenges and solutions*

In the case of functional groups, exceptions can be found wherein fewer functional groups are desirable or more functional groups create problems. However, it is impossible to know this about a compound when the applications are unknown. Hence, even though a bit vague, the indicator is useful to ensure consideration of new molecules. For some different contexts (e.g. when the process does not target a bulk chemical) the scoring statements (e.g. for market risk) might not be exactly applicable. In such cases the scoring statements can be appropriately modified to reflect the circumstances.

## Normalization and weighting

The parameters considered in this assessment fall into different categories and as such their scores cannot be added together directly. For this reason, the scores for the new process are normalized against the respective scores for the comparable conventional process. The scores are normalized to 1, meaning that each score is divided by the maximum of the two. Thus the process with a higher raw score gets a 1 and the other process gets an accordingly lower score. Table 1 explains this using the economic constraint (EC) score as an example.

Table 1: Normalization of scores

|  |  |  |
| --- | --- | --- |
|  | New process | Conventional process |
| Raw EC score | *B* | *P* |
| Normalized EC score |  |  |

The normalized scores for each parameter are added together using their respective weighting factors. The proposed weights for the five different parameters are as shown in table 2.

Table 2: Parameter weights

|  |  |
| --- | --- |
| Parameter | Weight |
| Economic constraint (EC) | 0.3 |
| Process costs and environmental impact (PCEI) | 0.2 |
| Environmental impact of raw materials (EI) | 0.2 |
| EHS index (EHSI) | 0.2 |
| Risk aspects (RA) | 0.1 |

The reasoning leading to these weights is as follows:

In today’s market-economy-driven and competitive world, a process will not be implemented on a commercial scale unless it is economically feasible. Therefore economic constraint is assigned a relatively high weight. The next parameter, the process costs and environmental impact, can play a significant role in the economic feasibility of the process while also contributing to the environmental life-cycle impacts of the process. We assume that the PCEI parameter contributes equally to the cost and the environmental impact parameters (i.e., 0.1 each), effectively increasing the weight of cost-related aspects to 0.4.[[1]](#footnote-1) If the process makes economic sense, then—with the goal of long-term sustainability and the minimization of environmental impact—life-cycle environmental impacts have to be taken into account. Hence the environmental impact of raw materials has an effective overall weight of 0.3,[[2]](#footnote-2) which is lower than the weight for costs. The EHS index represents relatively short-term or immediate hazards associated with the process. Even though these are extremely important, especially in a social context, these hazards can be controlled, albeit at an increased cost. Hence the EHS index has a relatively lower weight of 0.2 and this argument also supports the higher weight for costs. The risk aspects can potentially be crucial; however, the uncertainty in quantifying the effects of these parameters is quite high. Hence this factor has the lowest weight of 0.1 based on the uncertainty coupled with the lack of definite information regarding the importance of these factors at an early stage of development.

## Total score and index ratio

Following the multi-criteria approach, a total score is estimated based on the normalized scores for the process for each parameter and the corresponding weighting factors. The following equations detail the calculation.

In equations 6 and 7, *NB/P, j*is the normalized score of each parameter for the new (B) or conventional (P) process. *j* represents each of the five individual parameters used as proxies for the estimation of economic feasibility, environmental impact, hazards, risks and opportunities. *TB* and *TP* are the total scores for the new and the conventional process, respectively, while *wj* is the weight for parameter *j* (table 2) in contribution to the total score.

The index ratio *IB,P*, calculated using equation 8, is a ratio of the total score for the new process to that for the conventional process. This is the final outcome for the model and gives an indication of the potential benefits associate with proposed novel process. As such, a lower index ratio (< 1) indicates that the new process can provide certain benefits compared with the conventional process.

## Uncertainty and sensitivity analysis

The index ratio that we calculate is based on a model with a variety of data inputs and assumptions. There is always uncertainty associated with the data inputs (e.g., the yields can change in practice, and market prices change all the time). Subjectivity is involved, especially in the weighting, and hence different people in diverse situations can have different opinions about them and may change them accordingly. In light of these uncertainties it is important to analyze the variation in outcome and its robustness. This is a crucial step in the utilization of any model outcome for decision-making purposes. For this method, we analyze the effect of these uncertainties using the Monte Carlo analysis technique. This provides us with the distribution of results for a wide range of possible scenarios. A quick analysis of this distribution can give us a good indication of the robustness of the outcome and its usefulness for decision-making. We consider the effect of variations in factors such as prices, yields, the CED and GHG emissions. For this purpose we take into account historical variations in prices and price correlations for key raw materials and products. For information about uncertainties in the CED and GHG emissions, alternative datasets and values from the Ecoinvent database 12 have been used. The software @RISK 20 has been used to examine the effect of random variations in these inputs on the index ratio. Given the semi-quantitative proxy nature of other parameters (e.g., PCEI) it is difficult to objectively include the uncertainty in such parameters for Monte Carlo analysis. Hence only the aforementioned parameters and inputs are taken into account for the uncertainty assessment.

In a multi-criteria assessment such as the one conducted here, the use of weights for different categories can have a profound effect on the outcome and the conclusions that are subsequently drawn. Thus we analyze the effect of variations in the weighting factors for the five different parameters on the outcome. To this end, 1000 different randomly generated weighting sets within the ranges specified in table 3 are used. Given the selection and nature of the parameters (e.g., cost aspect covered by two parameters) under consideration, these ranges enable us to generate plausible as well as varied weighting sets. These random weighting sets, in which the sum of weights is always ‘1’, are generated using an excel based algorithm that we developed specifically for this purpose. While generating these weighting sets, the environmental impact parameter is broken down into the CED and the GHG emissions. Separately varying the weights for the CED and GHG emissions enables us to incorporate viewpoints that place higher importance on some environmental impacts than others.

In future, a scheme of weights based on parameter or specific indicator scores can also be envisioned to better incorporate and reflect the assessment context and different viewpoints (e.g. the importance of cumulative energy demand compared to GHG emissions within the parameter EI).

Apart from uncertainty analysis, to incorporate the focus on yields, the sensitivity of the outcome to different yield scenarios is also considered. This gives an indication of the change in outcome with changes in yields of the main product under consideration. Two scenarios, one positing a 20% decrease in yields and one positing theoretical yields, are considered in this assessment.

Table 3: Range for variation in weights of individual parameters

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Default weights | Weight ranges  Min Max | |
| Economic constraint (EC) | 0.3 | 0.25 | 0.60 |
| Process costs and environmental impact (PCEI) | 0.2 | 0.15 | 0.35 |
| Cumulative energy demand (CED) | 0.1 | 0.05 | 0.30 |
| Greenhouse gas emissions (GHG) | 0.1 | 0.05 | 0.30 |
| EHS index (EHSI) | 0.2 | 0.05 | 0.30 |
| Risk aspects (RA) | 0.1 | 0.05 | 0.25 |

## Laboratory decision-making

The primary goal of this work is to provide an assessment tool for processes that are in an early development stage. It should be used carefully so as to avoid stifling innovation. Rather, it should be used to guide innovation toward sustainability. At an early stage it can be used to pinpoint bottlenecks and set research targets in process development. It can aid in analyzing potential alternatives being considered in the laboratory, within a broader context. As an example, the tool can provide a basis to evaluate the costs and benefits of using a certain toxic solvent that leads to higher yields against those of using a greener solvent with lower yields and potentially useful by-products. Thus, using such an assessment, key decisions that are made as the process is being developed can result in a sustainable process.

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1. 0.1 (from the parameter “Process costs and environmental impact”) + 0.3 (from the parameter “Economic constraint”) = 0.4. [↑](#footnote-ref-1)
2. 0.1 (from the parameter “Process costs and environmental impact”) + 0.2 (from the parameter “Environmental impact of raw materials”) = 0.3. [↑](#footnote-ref-2)