Metrics Of Green Chemical Technology

Alexei A. Lapkin

Department of Chemical Engineering
University of Bath, Bath BA2 7AY, UK
E-mail: A.Lapkin@bath.ac.uk

Department of Chemical Engineering
University of Bath
July 2002.

Abstract

State-of-the-art in the indicators for assessment of the environmental impacts of new and existing chemical technologies is discussed. Current best practice in metrics is overviewed and the applicability of various existing metrics to the aims of the CRYSTAL† Faraday partnership is discussed.

Keywords: green chemistry, green chemical technology, sustainable chemistry, sustainability, metrics, environmental performance indicators

Introduction

This paper was written for the *CRYSTAL* Faraday partnership – a UK virtual centre of excellence in green chemical technology (GCT). The partnership was set-up jointly by the Royal Society of Chemistry (RSC), the Institution of Chemical Engineers (IChemE) and Chemical Industries Association (CIA) with start-up government funding. Its main objective is to demonstrate the existing opportunities for economically viable "green" chemical processes. This is to be achieved via a number of projects with demonstrable improvements in the environmental performance of processes, while retaining their economic viability. It is envisaged that in order to achieve this objective, *CRYSTAL* will have to effect a step-change in business and environmental performance of GCTs. The success of the demonstration projects should encourage the uptake of best available and emerging "green" technologies by chemical industries and in particular small and medium size enterprises. The aims of the partnership are summarised in Table 1.

Table 1. Aims of CRYSTAL Faraday partnership

1	To audit current and potential future industry needs, as well as available best practice and potential future solutions
2	To develop a mechanism for the transfer of green chemical technology into practice
3	To identify strategic research directions that are likely to form the backbone of chemical industry of the future, and to prime research projects in these areas
4	To develop a system of metrics that will be (i) used by CRYSTAL to identify and evaluate progress of the strategic research projects, (ii) evaluate the results of projects used for the transfer of best practice and (iii) generally accepted across chemical industry
5	To provide a single point of contact for the UK for information on green chemical technology

† CRYSTAL web site: www.crystalfaraday.org

Let us first define green chemistry and green chemical technology. There exist a number of definitions of green chemistry. For example, Anastas defined green chemistry as *"an approach to addressing the environmental consequences of* (chemical) *products or processes at the design stage"* [1,2], and consequently devised a list of *twelve principles of green chemistry* (see Appendix A, p.25) [3]. These principles relate not only to the synthesis and chemical hazards of the chemical products themselves, but also to the minimisation of energy use, switch from depleting to renewable raw materials and the end-of-life eventuality of chemical products. Thus, although the vast majority of publications on green chemistry are dedicated to either new syntheses or use of renewable feedstocks, the remit of green chemistry is broader and may include:

- application of innovative technology to established industrial processes;
- development of environmentally improved routes to important products;
- design of new *green chemicals* and materials;
- use of sustainable resources;
- use of biotechnology alternatives [4].

Graedel [5] suggested an assignment of the different aspects of green chemistry to four structural levels: from products and processes (selectivity, use of solvents, operating conditions), to companies (energy efficiency, site decommissioning, etc), infrastructure (availability of feedstocks and energy) and society (availability of clean water, sustainable agriculture, atmospheric pollution, global warming). Any new process or an improvement made to the established process would have an impact at every level of the hierarchy. For example, an increase in reaction selectivity may result in better product quality (level of products), improved energy efficiency (company level), decreased energy and raw-materials use (level of infrastructure) and decreased atmospheric and/or other emissions (level of society). Such a distinction is helpful for (i) simplifying the problem of assessment of "greenness" by considering it within each structural level and, hence, within a defined system boundary, and (ii) understanding what issues and their associated metrics should be used in communicating process improvements to the stakeholders. Continuing the same example, reaction selectivity by itself may be used as an indicator of process improvement and be used by the R&D team. However, to the general public (i.e., society) the per cent reduction in emissions, into which an increase in selectivity translates (directly, and via energy conservation), would be a more appropriate, understandable and resonant measure.

Considering different aspects of green chemistry at appropriate scales allows also to correlate the concepts of *green* and *sustainable* chemistry. Sustainability means continuity over time, where continuity is problem-specific. Continuity over time makes sense for large generic problems that can be considered on the levels of infrastructure and/or society. Thus, "sustainable agriculture", "sustainable fresh water supply", "sustainable electricity generation", *etc* are all valid problems: food, water and energy (≡electricity) are essential for supporting life and the quality of life. The latter includes *eg* medicine, education and culture. At the same time "sustainable manufacture of polyethylene", as an example, is not a valid problem.

Specific products should be viewed as means of delivering required functions and, as such, will vary with the advances in science and technology, availability of required feedstocks and changes in public perception. Therefore, any specific product cannot be sustainable. What *sustainable chemistry* means is the manufacture of chemical products delivering socially required functions by using technology and resources that do not compromise long-term availability of depleting feedstocks and clean water, and have little or no influence on the environment and human health.

Considering products as functions is an increasingly popular approach. It is directly applicable to e.g., functional foods and most of the consumer products (adhesives, paints, etc). Understanding of required product functionalities and discovering the relations between the nature of molecules, structure of materials and their bulk functional attributes, has become a vital part of these businesses. However, this is a generic approach and can be applied to any product. In fact, the chemical industries awoke to the functional approach considerably later than mechanical, electrical and electronic, software design and social sciences.

One of the first descriptions of the functional approach to product and process design is given by G.Altshuller and other developers of Russian directed innovation techniques with a common name TRIZ [6]. According to this methodology, every product or process has its *main useful function* (as well as auxiliary functions originating from resources imbedded in the product/process i.e., *emerging* functions in systems-science jargon). The best way of delivering this function is by ideal solution, when a function is delivered without incurring any *harms*. Harm could include used energy, spent capital, depleted resources, damage to the environment, etc. In principle, ideal product is such that delivers its function without physically existing.

To identify what might be an ideal solution it is necessary to clearly understand what is the actual function which is required. As an abstraction, ideal solution does not relate to any particular technology and as technology evolves – provided that the function remains in demand – different solutions will appear. Every next step will be bringing processes/products closer to the ideal solution. Understanding of this process is a key to long-term *business sustainability.* At the same time, requirement for the ideal solution to deliver a function without any harm also satisfies the current requirements to sustain depleting natural resources and a clean environment.

There is a direct link between the concept of ideality and chemistry. Thus, Gladysz [7] listed criteria for an ideal synthesis, which include 100 per cent reaction selectivity, ambient temperature and pressure, no need for inert atmosphere or any activators (or use of catalysts with high Turn Over Numbers‡), no use of solvents, no need of work-up steps, fast reaction, high atom efficiency. These factors clearly lead to accumulation of 'harm' or 'cost' at which the required chemical product could be synthesised. Similar logic applies to a process. Thus, ideality provides a universal indictor of how good a product/process is, compared to what it is supposed to do. It will be shown below that nearly all indicators developed so far are derivatives of this generic concept. However, in order to obtain a useful and meaningful indicator, it should be evaluated and applied within a certain structural hierarchy level [5].

A large number of indicators of environmental performance and various metrics have already been developed and several high-profile organisations (e.g. AIChemE, IChemE, European Environment Agency, UN) are involved in the work on metrics. The following sections provide an overview of methodologies, measures, complete metrics and individual indicators proposed to aid in the assessment of the environmental performance of processes and products, and the development of future sustainable technologies. A comparative discussion of the reviewed metrics completes this paper.

Indicators, metrics and indices

An *indicator* is a tool for simplifying, quantifying and communicating information [8, 9, 10]. The main role of indicators is to reveal phenomena not immediately apparent. For example, the population (concentration) of certain microorganisms in rivers is an indicator of water quality,

‡ Definitions of some terms are given in Glossary

which in turn may reveal the influences of the discharges of the upstream factories. A number of desired properties of indicators have been identified, based on the fulfilment of the three main functions of an indicator: simplification of the phenomenon, its quantification and communication of the actual or potential implications of the phenomenon [8-10, 11].

An indicator is only useful if it correctly represents the phenomenon. For example, the use of gross national (or domestic) product (GNP and GDP) as an indicator of welfare has been questioned for a long time [9]. Slesser, amongst others, stressed that GNP is a good measure of economic activity but a very poor measure of welfare [12]. An illustration given in [12] is the loss of profit by energy companies after a warm winter. The impact on GNP will be negative. However, it will also increase individual spending and decrease environmental impact, thus indirectly having a positive impact on welfare. The link between the phenomenon and its numerical indicator must be justified scientifically.

The indicators must be based on readily available data of known and verifiable quality. The availability of data has implications towards the cost of computing the indicator, sustainability of its use over prolonged period of time, and the period of time between the variations in the phenomenon and the understanding of their implications.

The implications of a phenomenon are communicated via the numerical values of indicators. This communication function may sometimes conflict with the technical accuracy of an indicator, which largely depends on the target audience and the specific application of the indicator. In the case of environmental indicators, scientists and engineers are likely to prefer indicators with well-characterised causal links and significant levels of confidence in the accuracy of data. For example, the already mentioned indicator of water quality – the concentration of particular microorganisms in rivers – is scientifically valid and easily measurable. However, it would not necessarily mean much to a person with limited knowledge of populational ecology. Such indicators are sometimes called "cold" – technically accurate and only meaningful to specialists. However, many cold indicators can be converted into the more meaningful to the layperson by normalising to a justified standard. For example, some indicators can be presented in per cent of background level (e.g. for magnetic field, noise or radiation) or as per cent of set exposure limits. This allows rapid qualitative judgement of the state of a local environment but the technical accuracy of some "warm" indicators might be compromised by the need to set certain standards which are often

difficult to justify scientifically. Even more so for "hot" indicators whose main function is to achieve a resonance with the public.

An example of the list of users of a particular set of indicators, namely indicators of environmental performance of firms is shown in Table 2. A list of desired properties of indicators is given in Table 3.

Table 2. Users of indicators of environmental performance of companies [13].

Stakeholder category	Use of indicators
Business managers	Management tool, external communication
Banks and insurers	Assessment of economic risks
Fund managers	Response to environmental and ethical concerns via investment decisions
Policy makers	Evaluation of effectiveness of policy instruments
Environmental groups	Comparison of environmental profile of firms in order to put political pressure on poor performers
Neighbours	Information to what extent companies damage local environment
Researchers	Analysis of patterns and trends

Table 3. Summary of properties of a *good* indicator

• Scientifically valid	• Sensitive to changes it is meant to represent
• Based on readily available data of known quality	• Cost effective
• Integrative	• Showing trends over time
• Representative	• Anticipatory
• Easily interpretable	• Sustainable over time
• Giving fast response	• Has a standard for comparison
• Nationally or locally relevant	

In order to characterise various aspects of a complex phenomenon a number of indicators are selected into a *metric*. Usefulness of a metric would strongly depend on the number of indicators: too few may not provide an adequate description of a phenomenon, whereas too many would make the cost of completing the metric prohibitively high. For a comparatively simple case – environmental performance of an organisation (this may include the use of various resources e.g., paper, energy, water, as well as emissions), the total number of indicators of 7 has been recommended [11]. Such a small number of indicators could suffice if a metric is focused on a particular well-defined problem.

An example of a sub-set of indicators selected to fit a particular problem is the metric developed within GlaxoSmithKline (detailed description of this metric and the individual indicators is in the following sections) [14]. The selected indicators provide information specific to the business employing multistage organic synthesis and using a broad range of solvents and some toxic intermediates. The focus of this metric is on "green chemistry" in its narrow sense – avoiding the generation of harmful wastes and decreasing the input material intensity via modification of synthetic routes to the desired chemical products. The same set of indicators would be largely inadequate for a bulk chemicals business or a fuel-cell manufacturer, where the amounts and types of emissions are quite different and the focus might be on energy integration and closed material cycles.

However, regardless of type of problem, each metric should be problem specific and should also reflect continuous improvement. The latter is essential if a metric is being used to illustrate compliance with regulatory requirements.

Krotscheck and Narodoslawsky [15] suggested to distinguish between *indicators*, as tools for the characterisation of a certain phenomenon, and *measures* (or *indices*), as cumulative numerical parameters suitable for strategic planning. The advantage of a single index rather than the collection of indicators is the ease of communication [9]. However, there are many disadvantages, such as loss of detail, loss of accuracy due to the combination of parameters with varied accuracy and magnitude, and the need to provide conversion coefficients to express all variables in the same units. Three types of cumulative indices have been proposed based on the area of land, cost and energy. These are described in detail below. The following sections describe individual indicators, measures, the life cycle assessment method and several proposed sets of metrics.

Life Cycle Assessment

The concept of Life Cycle Analysis (LSA) is central to green chemistry. "Greenness" of a product or a process is characterised not only by the amount of waste and harmful materials released during the manufacturing process, but also by the consumption of energy and depleting raw materials, and the afterlife eventuality of chemical products. Evaluation of the range and scope of environmental impacts at all stages of a process or within a life-cycle of a product is the underlying principle of environmental LCA [16,17]. The main idea of LCA is to collect and evaluate the data on the emissions and their environmental impacts at every step in a process of production of a

given product or provision of a service, starting from acquiring raw materials (including energy), and finishing with the end-of-life disposition and/or elimination of incurred emissions/wastes (so called "cradle to grave" approach). Thus, two alternative technologies providing a similar service (service here understood in a broad sense and includes manufacture of products that are then used to provide a service, e.g. manufacture of cars), can be compared on the basis of a) their overall environmental performance and b) of the environmental performance of individual stages in their life-cycles. LCA is a holistic approach, ensuring that no potential environmental problems within a given system of service provision are overlooked. The literature on LCA is extensive; therefore, only the major limitations of the methodology will be discussed here.

Analysis of environmental impacts of products and processes from *cradle to grave* aims to avoid the false impression of the environmental friendliness of processes which can arise from considering only part of the life cycle. A good example from recent history is the case of methyl-tert-butylketone (MTBE). MTBE can be produced using an efficient catalytic distillation process and performs well as a fuel additive. However, the combination of three facts - carcinogenic potency, significant solubility in water and the difficulty of avoiding the leakage of MTBE into the ground water table at the point-of-use - make use of this fuel additive highly undesirable. In order to identify such problems a broad system boundary is necessary. On the other hand, considering the overall environmental impact of a system within broad system boundary often gives inconclusive results.

In [18] a comparison of bio- and chemical catalytic reductions using LCA was performed. Two reactions were considered with a bio- and chemical catalyst in each. The study showed that neither bio- nor chemical catalytic technology is a clear winner based on their overall LCA score. However, in both cases the largest environmental contribution is not from the reaction but from the work-up procedures, such as solvent recycle, distillation and rectification. A comparison of the environmental impacts of water-based and organic solvent-based automotive base coatings showed that neither type of product could be distinguished on the basis of their overall environmental performance [19]. Despite the lower level of emissions from water-based coatings, application of these coatings require more energy (even including VOC abatement for solvent-based processes) due to the slow evaporation of water.

This problem of distinguishing alternatives is partly due to the agglomeration of many numbers of varied magnitude, accuracy and reliability into a single parameter. Accessibility to data and accuracy of the data are of particular importance. Undoubtedly, the problems relating to data collection and verification will very soon be resolved via standardisation in data presentation and the development of new databases and search software. However, there remains the problem that the larger is the scale of consideration, the lesser there will be the difference between *mature* competing technologies.

However, besides definition of the system boundary, by far the most difficult issue of LCA, as well as all other environmental indicators, is the evaluation and comparison of individual environmental impacts. The large number of chemicals in use, the uncertainty about the exact nature of their effects on the environment and human health, the complexity of interactions of chemicals in natural ecosystems and uncertainty over their long-term effects makes impact analysis very difficult and ambiguous. However, for the effective use of LCA methodology it is necessary to evaluate environmental impacts in terms of a single normalising parameter. Such a normalising parameter could be cost, energy or area of land. In order to use these normalisation parameters it is necessary to define the corresponding conversion coefficients, e.g. units of energy required for abatement of given quantity of a certain pollutant. The main advantage of using a single normalising factor for all stages of product/process life-cycle and all environmental impacts, is that it enables direct comparison between different technologies. At the same time it simplifies calculations in the case of complex processes: complex processes can be divided into a series of smaller systems, while calculations across system boundaries require parameters to be presented in the same units. Several approaches are described in the following subsections.

MIPS: Material inputs per unit service

The MIPS parameter of a process is defined in [20] as weighted material inputs over the entire life-cycle per units of service obtainable. It includes all direct and indirect raw material inputs such as energy. The inverse of MIPS has a meaning of resource productivity – the amount of service obtained per spent amount of resources. In general terms, if resource use is considered as a penalty for delivering a service or performing a function, the inverse of MIPS is the ideality parameter described in the Introduction. The use of the MIPS parameter for assessment of process/product greenness is warranted by the fact that availability of raw materials is one of several constraints of the production process. The drive towards more sustainable processes requires a need to decrease

the dependence on the depleting raw materials, including energy sources. Thus, a decrease in the resource dependency of delivery of required service/function is a step in the right direction. This can be directly translated to the manufacture of chemical products. One of the most efficient ways of decreasing the resource dependence of the chemical industry is by improving the conversion of resources into useful products.

This can be illustrated by the concept of atom efficiency. A reaction is atom efficient if the product incorporates all of the atoms of the reactants [21]. Such a reaction is inherently waste-free and resource efficient. Reactions with the highest atom efficiency are, for example, reactions of addition, polymerisation and hydrophormylation. Reactions employing protective groups and stoichiometric reagents have the lowest atom efficiency. The principle of atom efficiency is, therefore, directing developments in synthetic chemistry towards highly selective reactions not requiring stoichiometric reagents/activators [22]. However, atom economy is not a very good measure of reaction efficiency. In calculating atom efficiency one has to assume 100 per cent conversion and selectivity. Furthermore, the requirements for auxiliary resources, such as solvents, work-up steps etc are not taken into account. Another potential limitation is the inability to account for useful by-products.

GlaxoSmithKline has developed the reaction mass efficiency (RME) indicator which takes into account reaction yields and the actual reactant molar quantities [14b]. It is calculated as a ratio of the mass of product (taking into account yield) to the sum of the mass of reactants (taking into account any required excess). However, in order to account for solvent use, a separate mass intensity indicator is suggested – kg(product) per kg (solvent use) (see Appendix B). The main differences between the RME and MIPS indicators are that the latter accounts for energy use by including the equivalent mass of fuel required, and would also include solvents. Solvent as material input may be excluded from MIPS calculations if solvent re-use is close to 100 per cent. In this case only the loss of solvents should be included in the overall mass-intensity indicator. However, the energy required for solvent recycle will still have to be accounted for.

The mass intensity indicators are certainly very useful for the selection of the most resource-efficient chemical routes to the products with desired functional properties. However, these indicators should not be used alone. The serious limitation of mass intensity indicators is the complete absence of any links with the environmental effects of the materials used. The RME

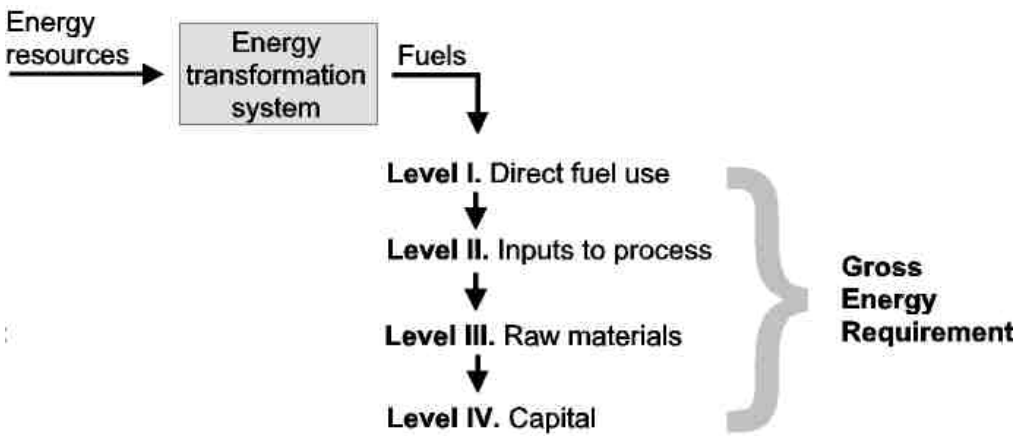
indicator also does not account for energy use. Resource-mass-intensity indicators also cannot account for the end-of-life eventuality of the products.

Using energy to normalise environmental impacts

Energy is one of the major constraints on the production process. Production can be defined as "anything that happens to an object or set of objects that increases its value… The basic physical condition necessary (to effect any such changes) is that energy must be applied…" [23]. Because most energy is currently produced from depleting resources, there is a natural limit to how much energy can be produced. Therefore, less energy-intensive processes are more sustainable. A comprehensive analysis of the contributions of energy to transport, the manufacturing process itself, support of labour, and production of energy is given in [24] and recent developments of the energy analysis method are described in [12]. However, in order for energy analysis methods to be applicable to chemical industries, contributions from end-of-life and complete emissions abatement should be considered as well.

The advantage of using energy as a common denominator is that every step in the process' life-cycle and all inputs (raw materials, etc) can be evaluated in the units of energy. This considerably simplifies calculations across the system boundaries. Figure 1 illustrates the procedure of calculating the gross energy requirements for the provision of a service or a product. The entire process is split into four levels. The biggest proportion of energy is required for levels 1 and 2 – direct use of fuel and provision of material inputs to processes. Use of fuel for transport may also be included into level 2. Level 3 is the provision of raw materials and capital equipment, whereas level 4 refers to the capital – machines for making machines. This level can often be ignored due to its low weighting in the overall energy balance.

Figure 1. Energy analysis procedure



The overall energy demand for the manufacture of a given product can be used for comparison between competing technologies. However, it cannot give an absolute measure of how "green" processes are. It fails to indicate whether it is worth spending a given amount of energy to produce the desired product, as such an analysis would require judgement on the non-monetary value of services/products.

Despite these limitations energy the intensity metric is very useful for the analysis of alternative chemical processes and process improvements. An example of the use of energy indicators developed by the Centre for Waste Reduction Technologies (see Metrics and Appendix B) in the chemical industry is presented in the pilot study undertaken by BRIDGES to Sustainability, a Houston based not-for-profit educational organisation [25]. The published report was commissioned by the US Department of Energy and compares the energy performance of five major chemical processes: manufacture of acetic acid, acetic anhydride, maleic anhydride, terephthalic acid and caprolactam. The adopted approach was to calculate five energy performance levels, providing benchmarks for the development of improved processes. The levels of energy performance are defined in Table 4.

The following energy requirements were calculated: net power and hot utility requirements, net fuel energy consumed by the process, total energy consumed by the process, and total energy consumed by the product chain. Energy and economic criteria were established for the selection of various options for heat integration and process re-design. On Level 2, the criterion for energy was the lowest net fuel energy used and the economic criteria – payback period of 3 years or less. On Level 3, the energy criteria were the lowest net fuel energy consumed, the lowest total energy consumed and the lowest total product chain energy consumed, whereas the economic criterion was that the product value is lower than that of base process.

Table 4. Levels of energy performance of chemical processes

Level 0	Base case	Energy requirement by an unimproved process; energy produced by a process and recovered is included.
Level 1	Benchmark heat integration	Minor improvements including heat exchange networks, improved solvents, incorporation of power generation
Level 2	Optimum heat integration	Optimised heat exchange flowsheet, chage in process conditions that enable further heat integration (the basic aspects of the process such as catalysts, feedstock etc are the same as in base case)
Level 3	Process redesign	The same reaction chemistry as in base case but can incorporate changes in feedstock, improved catalyst, different process configuration, alternative separation techniques.
Level 4	Theoretical energy requirement	Change of enthalpy of reaction at standard conditions assuming 100% yield.

This methodology is particularly relevant for process improvement projects when there is no possibility to change the main product. However, the methodology could be further improved. Firstly, use of standard enthalpy of reaction as a base theoretical energy requirement would rarely give a meaningful number. Theoretical energy requirements should be calculated for specific process conditions and product yield, and should also include separation stages specific to given reaction system. Selection of alternative process re-design strategies should, in most cases, also include change of reaction chemistry and go beyond scanning of available patent and journal literature. A systematic approach to process re-design is necessary.

Another example of the use of simplified energy-based LCA methodology is given in [26] for a "motor vehicle". The term "burden" was used to describe the environmental impacts of five generic stages (material production, manufacture and assembly, operation, service, maintenance, end-of-life) in the life-cycle of a motor vehicle. Ultimately, "burdens" were evaluated in energy units.

Although the overall energy consumed by a process cannot be used as an absolute measure of process efficiency, Dewulf et al [27] have developed an exergy based sustainability parameter which is supposed to do just that. Exergy can be defined as the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes [28]. Exergy is a more accurate measure of how much work could be obtained from a certain process in the open systems.

The sustainability parameter (S) proposed by Dewulf et al is a mean of the renewability and efficiency parameters for a given process: $\text{Sustainability} = \frac{1}{2} \times (\text{Renewability} + \text{Efficiency})$. Renewability is defined as a ratio of the rate of renewable exergy consumption to the total exergy consumption. Therefore, renewability varies between 0 and 1. Renewability is equal to 1 when only renewable exergy is used within the process life-cycle. This therefore accounts not only for the direct energy use as fuel, but also for the supply of raw materials. Thus, petrochemical based feedstocks would invariably result in very low renewability parameters. The efficiency parameter is calculated from various energy contributions to the manufacturing process: direct exergy use for manufacturing, emission abatement, product abatement at the end-of-life, exergy content of the useful product, and losses due to irreversible processes. A list of equations and details of all the parameters involved in computing the sustainability parameter is given in Appendix B. The efficiency parameter also varies between 0 and 1. Hence, a sustainable process (S=1) is one that only uses renewable exergy sources, has zero emissions, does not require product abatement and does not have energy losses due to irreversibilities.

A comparison of three different routes to ethanol manufacture (from petrochemicals, using fermentation and from hydrogen and CO_2 using solar power for hydrogen generation) showed that the latter two processes have very similar sustainability parameters around 0.5, whereas the petrochemicals based route has sustainability parameter of 0.18 [27a]. Perhaps, the most important conclusion from this example is that calculation of the exergy-based sustainability coefficient is not as difficult as it may seem. It requires similar data inputs that any other energy-based calculations do. It could be argued that using energy instead of exergy would be just as good, and would avoid the considerable lack of appreciation of the exergy concept by scientists and engineers.

The results of the ethanol production case study also clearly show that renewable chemical feedstocks have very low production efficiencies due to the low efficiency of agricultural production of raw materials, as well as low useful product yields [27a]. Another serious limitation of the agricultural route to chemical raw materials, which can not be accounted for by the sustainability coefficient (S), is the requirement for large areas of arable land and intensive agricultural methods, both of which have considerable environmental impact. It was also

demonstrated in [24] that the area of land is often a more serious constraint to the manufacturing process than the availability of feedstocks or energy.

Using area of land to normalise environmental impacts

The use of land area as a normalisation factor is warranted by the constraint the availability of land places onto various processes [15]. Land is required for the generation of energy, production of food, human habitat (including municipal waste disposal), transport infrastructure, support of natural ecosystems, absorption of emissions, etc. Most of the parameters characterising a process can be normalised to the required land area. For example the amount of energy required for the manufacture of a product depends on the manufacturing process as well as on the energy generation technology and, therefore, sensible to variation between renewable and non-renewable energy sources. The main limitation of this approach is the availability of data enabling calculation of the conversion coefficients, e.g., the amount of waste-water generated and the area of land required to support waste-water treatment facilities. A maximum *sustainable* amount of given emissions that a natural ecosystem can tolerate may be defined. However, there will be significant geographical variations and large gaps in the knowledge of the tolerance of natural eco-systems to given pollutants. Also, the complexity of the network of interactions between the components of natural ecosystems and of the fate of chemicals in the environment is such that establishment of quantitative exposure limits (i.e. quantification of the area of land required to sustainably assimilate emissions) with any degree of accuracy would be problematic.

A sustainable process index (SPI) based on area of land was proposed in [15]. The index is calculated as a ratio of total land area required to *sustainably* provide a service or manufacture a product, to the average available land area for an individual. The total land area is calculated as the specific area per unit of product or service provided. Thus, in the case of energy generation the unit of total energy requirement is m^2 per kW in a given period of time (usually a year), whereas the SPI unit is capita per kW. Five contributions to the total land area are considered: area required to produce raw materials, area necessary to provide process energy, area for installations, area required for the staff and the land area required to accommodate the products and by-products. A more sustainable process/product/service is one that requires less area of land for its provision.

This approach may be particularly relevant for the assessment of technologies based on renewable raw materials and energy resources. Production of biomass for conversion into chemical products

and/or energy requires fertile arable land, thereby creating a competition between land for food production and land for energy and chemicals production, as well as increasing demand for fertilisers. A case study of ethanol production from sugar beet for energy generation is presented in [15]. The analysis of all contributions to the total required area of land showed that the two most important contributions are production of beet crop (20%) and sustainable dissipation of bi-products (63%). It is very likely that a much better SPI could be obtained if all bi-products are to be converted into benign emissions i.e., water and carbon dioxide.

Using cost to normalise environmental impacts

Using costs to evaluate environmental impacts is believed to be an inferior method compared with energy or area of land. The variability of costs with geographical location, currency, inflation and economic conditions makes cost-based calculations very time- and site specific. However, for specific purposes cost can be a very useful measure. Thus the costs of environmental legislation, implementation of environmental technologies, as well as of abatement technologies and emission charges within a company could be evaluated using environmental cost accounting methodology [29]. The study of environmental cost accounting procedures within several large chemical and oil companies [29] concluded that the biggest disadvantages of environmental cost accounting are that the potential benefits of pollution prevention activities (as opposed to pollution abatement) are difficult to demonstrate clearly, and that cost does not adequately represent the improvements in environmental performance. However, the method seems to be most useful for demonstrating the benefits of implementing environmentally sound process improvements to the upper company management.

Castells et al [30, 31] developed a method of assembling the life-cycle inventory data into a numerical matrix. First, a multidimensional "eco-vector" (e_v) is collected for each process stage. The elements of eco-vector represent various emissions e.g., mass of a particular pollutant (kg per functional unit). An example of the elements of eco-vector is: e_v={(air emissions), (liquid discharges), (radiation), …}. It often useful to select vector elements such that pollutants/emissions are categorised according to their main environmental impact, e.g. global warming potential, human health impact etc. Contributions of different pollutants within each category are than added up to a single number using weighting factors (or potency factors, see Appendix B). The collection of eco-vectors over the entire life-cycle produces a multidimensional numerical matrix. By using appropriate conversion coefficients the matrix can be transformed into a cost matrix.

Environmental Performance Indicators

The methodologies described above, in particular the mass input indicator, energy analysis and area of land analysis, allow simplification of life-cycle assessment by avoiding the issue of quantifying specific environmental influences of chemicals. One of the arguments for adopting these approaches is that it is virtually impossible to obtain complete knowledge of the fate and interactions of chemicals in the natural environment. However, there is a strong drive towards developing specific environmental performance indicators. Specific indicators allow identification and monitoring of a particular problem much more accurately than any complex indices. A widely adopted framework for developing indicators of environmental performance is described for example in [32]. Three sets of indicators are distinguished: indicators of state, of pressure and response. Human activities exert *pressures* onto the environment, which evoke changes in its *state* (quality of the environment and stocks of natural reserves). Society *responds* to these changes through policy-making mechanisms. For the purpose of this review only indicators of state are of interest.

The indicators of state are developed in the following categories: air, water, land, wildlife and natural resources. Within larger sets of indicators – sustainability metrics – state indicators also include economic and social factors i.e., wealth and welfare. Large sets of indicators have been published [32, 33, 34]. Some of the most common indicators are listed in Appendix B.

Metrics

A number of organisations have been actively involved in developing sustainability metrics. The most prominent efforts are by the Centre for Waste Reduction Technologies (CWRT) and the Institution of Chemical Engineers (IChemE). It is interesting to note that industry is playing a leading role in developing eco-efficiency indicators and various metrics. Not surprisingly, the main focus of industry-developed metrics is on economic profitability of products and processes, reflected by the wide acceptance of the value added as a normalising factor. The economic and social indicators are not included in this overview.

CWRT metrics of sustainability

The CWRT metrics are developed on the basis of the eco-efficiency concept and the indicators introduced by the World Business Council for Sustainable Development [35]. Eco-efficiency is

defined as a ratio of product (or service) value to its environmental influence, where value is understood to be capital creation, and the main environmental influences are due to consumed energy, materials and water, and released green house and ozone depleting gases. The important aspects of the CWRT metrics are (a) normalisation to dollar sales or value added, (b) consideration for relative environmental impacts of different pollutants and (c) use of national databases.

The main categories included in CWRT metrics are: energy, mass, water usage, pollutant, human health and eco-toxicity [36]. Indicators of human health and eco-toxicity are based on the parameters already widely used in the assessment of chemical hazards, i.e. permissible exposure limits and 50% of lethal concentration. The indicators also take into account the life-time of chemical pollutants in various media of the environment.

IChemE metrics of sustainability

The IChemE metrics of sustainability consist of 49 indicators classified into three main categories: economic, environmental and social [37]. The environmental indicators within the IChemE metrics are similar to those in the CWRT metrics. However there are some differences. The IChemE metrics include area of land as an environmental indicator. The actual indicators are (i) the sum of directly occupied and affected land per value added and (ii) the rate of land restoration. Other differences relate to the assessment of the relative impacts of pollutants on the environment and human health. The IChemE indicators do not take into account life-time of chemicals in various media of the environment. The human health indicator is limited to carcinogenic effects and is normalised to benzene.

European Environment Agency indicators

The European Environment Agency (EEA) considered four major areas of impacts of technology on the global scale: (1) consumption of mineral resources (excluding energy sources), (2) consumption of fossil fuels, (3) consumption and dispersion of chemicals hazardous to the environment and human health and (4) consumption of biological resources, including bioproduction, biodiversity and land use [38, 39].

An interesting comment regarding the third focus area – consumption and dispersion of hazardous chemicals – is given in the EEA documents: rigorous scientific proof of the effects of chemicals onto the environment and human health is not feasible due to the complexity of the

problem. EEA calls for the principle of caution, i.e. to assume that the damage of toxins to human health will increase in the future and effort should be made to cut down as much as possible on the use and dispersion of toxic chemicals. Additional factors relevant to cleaner technology are water, waste, occupational health and management indicators.

The EEA document states that it is impossible to define a universal normalisation, as normalisation is production dependent. However, any normalisation used must be agreed with an industry sector. Normalisation of indicators suggested by EEA include:

1 mPE (milli-person-equivalent) = $\dfrac{global\ annual\ emission\ or\ consumption\ of\ a\ resource}{world\ population \times 1{,}000}$

NEP(j) (normalised environmental impact potential)

$$NEP(j) = \frac{environmental\ impact\ potential\ (emission)\ per\ product}{duration\ of\ service\ (years) \times normalisation\ (e.g.\ mPE)}$$

WEP(j) (weighted environmental impact potential) = WF(j) x NEP (j), where

$$WF(j) = \frac{environmental\ impact\ potential\ of\ emissions\ in\ 1990}{environmental\ impact\ potential\ of\ 2000\ emission\ goal}$$

Resource weighting = $\dfrac{(normalised\ resource\ consumption) \times (annual\ production)}{(total\ reserve)}$

Standardisation

ISO 14001:1996	Environmental management systems – specification with guidance to use
ISO 14031:2000	Environmental management – Environmental performance evaluation – Guidelines
ISO 14040-14043	Life Cycle Assessment

ISO 14001 contains requirements that may be objectively audited for certification/registration purposes and/or self-declaration purposes. The following categories make-up the standard: Environmental Policy, Planning, Implementation and Operation, Checking and Corrective Action, Management Review.

ISO 14031 describes two classes of indicators: environmental performance indicators (EPIs) and environmental condition indicators (ECIs). Furthermore, EPIs are split into management performance indicators (MPIs) and operational performance indicators (OPIs). The standard does

not proscribe which indicators should be used but provides information on how an organisation might go about selecting the appropriate indicators. A long list of possible indicators is provided.

Discussion

The issues of sustainability and pollution clearly focus on few important aspects: energy, raw materials, land, state of the environment, climate change and risks to human health that processes/products may present. Long-term sustainability requires continuous availability of: arable land for agriculture and for human habitat, land for preservation of bio-diversity and as a climate regulator, fresh water and clean air, as well as resources for manufacturing products and generation of energy. Thus the key focus areas for green chemical technologies are:

- energy efficiency and use of energy produced from renewable resources
- use of renewable feedstocks; recycling, re-use or benign disposal of products e.g., biodegradation
- zero pollution strategy; sustainable level of emissions of greenhouse gases
- use of benign chemicals
- use of intensive processes with small footprint
- site regeneration

From the point of view of the hierarchy of industry, various issues should be considered on appropriate levels and matched with suitable indicators. An example of how indicators could be associated with the structural hierarchy levels is shown in Table 5. The indicators which are used on the level of society should be meaningful and interpretable by the layperson. These indicators should directly correspond to the issues of individual's welfare and to the issues of sustainability. Thus, for example, if environmental expenditure is accounted for, an indicator (kg product per value added) adequately describes efficiency of production process. But it is only meaningful to the company managers and possibly shareholders, and is irrelevant to the general public. Value added normalisation is most appropriate at the company level. Similarly, value added normalisation is not very useful on the product/process level.

Table 5. Example of indicators associated with structural hierarchy levels

Level	Issues	Issues for chemical industry	System boundary	Indicator
Society	Continuous availability of energy	Overall energy efficiency of processes	Complete life-cycle	*energy efficiency* = $\frac{\textit{energy spent on production}}{\textit{overall energy spent}}$
		Dependency on non-renewable energy		*renewability* = $\frac{\textit{rate of consumption of renewable energy}}{\textit{overall rate of energy consumption}}$
	State of air	Emissions		*production efficiency* = $\frac{\textit{volume of emissions}}{\textit{value added}}$, excluding green-house and ozone-depleting gases. Use specific substances, e.g. NOx, SOx, photochemical smog generating substances.
		VOC from solvents		$\frac{\textit{solvent recycled}}{\textit{total solvent use}}$
	Climate change	Emissions of green-house gases		*total annual release of GHGs* = $\Sigma(GHG_i \times P_i)$, where GHG_i is i-th green-house gas; P_i is global warming potential, relative to CO_2.
				per cent of annual sustainable release of CO_2 *- equivalent per capita (per area of land≡country)*
		Emissions of ozone depleting gases		*total annual release* = $\Sigma(ODG_i \times P_i)$, where ODG_i is I-th ozone-depleting gas; P_i is potency factor, relative to CFC-11.
	Continuous availability of fresh water	Closed water cycle	Individual Processes	$\frac{\textit{fresh water intake}}{\textit{overall water used}}$
		Water use		$\frac{\textit{amount of water used}}{\textit{unit of product}}$
	Availability of land	Footprint of production process	Complete life-cycle	*Sustainable technology index (STI)* [15]
		Land contamination	Site	*Concentration of specific harmful chemicals per unit area*
Infrastructure	Availability of resources	Dependence on depleting resources	Raw materials to end product	*MIPS = materials input per unit service* [20]
				$\frac{\textit{renewable materials input}}{\textit{overall materials input x product unit}}$

Table 5. Contd.

Level	Issues	Issues for chemical industry	System boundary	Indicator
Company	Availability of energy		Site	$\frac{\textit{amount of energy}}{\textit{product unit}}$ $\textit{production efficiency} = \frac{\textit{amount of product}}{\textit{value added}}$
	Process efficiency	Emissions	Complete product life-cycle	$\textit{production efficiency} = \frac{\Sigma(GHG_i x P_i)}{\textit{value added}}$, where GHG_i is i-th green-house gas; P_i is global warming potential, relative to CO_2.
				$\textit{production efficiency} = \frac{\Sigma(ODG_i x P_i)}{\textit{value added}}$, where ODG_i is I-th ozone-depleting gas; P_i is potency factor, relative to CFC-11.
		Water use		$\textit{production efficiency} = \frac{\textit{amount of water used}}{\textit{value added}}$
Products Process	Use of energy	Energy efficiency	Individual process	$\textit{energy efficiency} = \frac{\textit{theoretical energy requirement}}{\textit{actual energy spent}}$
	Use of raw materials	Dependence on depleting resources		*Reaction Mass Intensity* [14b]
				$\frac{\textit{renewable materials input}}{\textit{overall materials input x product unit}}$
			Reaction	*atom efficiency*
	Use of solvents		Process	$\frac{\textit{amount of solvent}}{\textit{amount of product}}$
				$\frac{\textit{amount of solvent lost}}{\textit{amount of product}}$
	End-of-life of product	Recyclability	Product	$\frac{\textit{number of different materials}}{\textit{unit product}}$
		Further use		*% material used as feedstock*
				% material used for energy generation
		Biodegradablility		*% biodegradable material*
				half life-time in medium

Glossary

Eco-efficiency	$\frac{\text{product (or service) value}}{\text{environmental influence}}$
Environmental load	The amount of chemical, radiation, noise, etc. released to the environment, causing actual or potential adverse effect onto environment and/or human health.
Environmental load factor (ELF)	Normalised amount of emission (chemical, radiation, etc). Typical normalisation factors: mass/area/volume of product (or raw material, intermediate), selling price, value added, etc.
Eutrophication	Excessive algae growth due to high concentration of nutrients, leading to long-term aquatic ecosystem disruption by oxygen depletion.
Exergy	Amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes.
Indicator	A numerical parameter corresponding to a certain, not apparent, phenomenon. An indicator has three main functions: to simplify the phenomena, to quantify, and to communicate information to the target audience.
Index (or measure)	A cumulative numerical parameter calculated as a sum of multidimensional contributions, normalised to a common unit such as energy, required area of land or cost.
Metric	A collection of indicators describing different facets of a complex phenomenon
Turn Over Number (TON)	Rate of reaction per number of active catalyst sites: $\frac{\text{number of product molecules}}{\text{number of active sites x time}}$

Appendix A. 12 principles of green chemistry, after [3]

1. It is better to prevent waste than to treat or clean up waste after it is formed
2. Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used
6. Energy requirements should be recognised for their environmental and economic impacts and should be minimised. Synthetic methods should be conducted at ambient temperature and pressure
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable
8. Unnecessary derivatisation (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimise the potential for chemical accidents, including releases, explosions, and fires

Appendix B Summary of indicators

Composite Sustainability Indicators					
Indicator	**Definition**	**Abbreviation**	**Description, comments**	**Metric**	**Ref.**
Sustainability coefficient	$\frac{\alpha+\eta_1\eta_2}{2}$; $\alpha=\frac{R_{cons,renewable}}{R_{cons}}$; $\eta=\eta_1\cdot\eta_2$; $\eta_1=\frac{R_2}{R_1+R_2+R_3}$; $R_2=E+P+I_P$; $\eta_2=\frac{P}{E+P+I_P}$	S	S is the average value between renewability parameter (α) and the production efficiency (η). Renewability (α) is calculated as the ratio of the rate of consumption of renewable exergy to the rate of consumption of non-renewable exergy. Production efficiency (η) depends on a number of exergetic flows. R_2 is exergy required for production. R_1 is exergy required for abatement of emissions. R_3 is exergy required for transforming the product after its use into harmless products. E represents non-useful exergy emissions. I_p is irreversibility of the process.		27
Sustainable process index	$\frac{a_{tot}}{a_{in}}$, where a_{tot} is the specific service area required to embed a give process sustainably; a_{in} is the mean theoretical area available per capita.	SPI	$A_{tot}=A_{raw\ mat}+A_{energy}+A_{inst}+A_{staff}+A_{prod}$ $A_{raw\ mat}=A_{renewable}+A_{nonren}$		15
Environmental Performance & Human Health Indicators					
Normalised environmental impact potential	$\frac{environmental\ impact\ potential\ (emission)\ per\ product}{duration\ of\ service\ (years)\times normalisation\ (e.g.\ mPE)}$	NEP(j)		EEA	38
Milli-person-equivalent	$\frac{global\ annual\ emission\ or\ consumption\ of\ a\ resource}{world\ population\times 1{,}000}$	mPE		EEA	
Weighted environmental impact potential	*WF(j) x NEP (j)*	WEP(j)		EEA	
	$\frac{environmental\ impact\ potential\ of\ emissions\ in\ 1990}{environmental\ impact\ potential\ of\ 2000\ emission\ goal}$	WF(j)		EEA	
Human health	$\sum(Y_i\times m_i)$, where m_i is the mass of an emission *i* in kg and Y_i is the effect of an emission *i*. Effect of an emission is calculated as $Y_i=\frac{P_i\times BCF_i}{PEL_i}$, where P_i is a multi-media weighted half-life (hr^{-1}), BCF_i is bioaccumulation factor and PEL_i is permissible exposure limit.			CWRT	36
Human health (carcinogenic)	$\frac{tonne\ per\ year\times potency\ factor}{value\ added}$; potency factor = ($OEL_{benzene}/OEL_{substance}$); OEL = Occupational Exposure Limit		Occupational Exposure Limits are set by UK Health and Safety Executive	IChemE	37

Ecotoxicity	$\sum(Y_i \times m_i)$, parameters as above; $Y_i = \frac{P_i \times BCF_i}{LC_{50i}}$, where LC_{50i} is the lowest LC_{50} value obtained for the species algae (green), daphnid (daphnia magna) and fish (rainbow trout or blue gill). Alternatively a EC_{50} can be used instead of LC_{50}.			CWRT	
Ecotoxicity to aquatic life, metals	$\frac{tonne\ per\ year\ Cu\ equivalent}{value\ added}$			IChemE	
Ecotoxicity to aquatic life, non metals	$\frac{tonne\ per\ year\ CH_2O\ equivalent}{value\ added}$			IChemE	
Eutrophication	$\frac{weight\ PO_4^{3-}\ equivalents}{value\ added}$			IChemE	
Eutrophication	nitrates in rivers and ground water; phosphorus in rivers and ground water		Unit: annual average concentration mg/L		32
Acidification	$\frac{\text{kg } SO_2 \text{ equivalent}}{\$ \text{ value of product sold}}$; $\frac{\text{weight } SO_2 \text{ equivalents}}{\text{value added}}$		All environmental burden indicators in the IChemE metrics are calculated in the units $\frac{tonne\ per\ year \times potency\ factor}{value\ added}$, where the potency factor defines weight equivalent of a certain pollutant, unless otherwise stated.	CWRT, IChemE	
Aquatic oxygen demand	$\frac{\text{weight x potency factor}}{\text{value added}}$		Potency factor is stoichiometric oxygen demand. Potency factors of ethylene and aqueous ammonia sulphate are 1.	IChemE	
Aquatic oxygen demand	biochemical oxygen demand	BOD	Unit: mg/L oxygen consumed in 5 days at constant temperature of 20°C.		33
Photochemical ozone creating potential	$\frac{\text{kg ethylene equivalent}}{\$ \text{ value of product sold}}$; $\frac{\text{weight ethyelen equivalent}}{\text{value added}}$			CWRT, IChemE	
Stratospheric ozone depletion	$\frac{\text{kg CFC-11 equivalent}}{\text{value added}}$			IChemE	
Global warming	$\frac{\text{kg } CO_2 \text{ equivalent}}{\$ \text{ value of product sold}}$; $\frac{\text{weight } CO_2 \text{ equivalents}}{\text{value added}}$			CWRT, IChemE	
Mass Intensity Indicators					
Atom utilisation	$\frac{molecular\ mass\ of\ desired\ product(s)}{molecular\ mass\ of\ all\ reagents}$, *per cent*		Atom utilisation is calculated assuming 100% conversion.		21
Reaction mass efficiency	$\frac{\text{product mass}}{\text{mass of all reactants}}$	RME	Product mass is calculated taking into account reaction yield; reactant mass includes required excess.	GSK	14
Solvent use	$\frac{\text{mass solvent}}{\text{mass product}}$			GSK	
Water use	weight per year; $\frac{mass\ water\ consumed}{mass\ product}$; $\frac{mass\ water\ consumed}{unit\ value\ added}$			IChemE	

Water use	([all water used]-[once-through cooling water]+[rain water treated]-[sea water used]) per (value added)			CWRT	
Mass intensity	$\frac{total\ mass\ in\ (raw\ materials,\ products,\ packaging,...)}{\$\ value\ of\ \ products\ sold}$			CWRT	
E-factor	$\frac{mass\ waste\ generated}{mass\ product}$				22
MIPS	Sum of mass of all input materials (including mass energy equivalent) per unit service obtainable	MIPS	Material Inputs Per unit Service		20
Energy Intensity Indicators					
Energy intensity	$\frac{total\ BTU's\ conversion\ energy\ consumed}{\$\ value\ of\ \ product\ output}$			CWRT	
Primary energy usage	$\frac{\text{kg fuel}}{\text{kg product}}$, $\frac{\text{kg fuel}}{\text{unit value added}}$			IChemE	
Resource Use Indicators					
Raw material use	$\frac{mass\ raw\ material}{mass\ product}$; $\frac{mass\ raw\ material}{unit\ value\ added}$; $\frac{hazardous\ raw\ material\ mass}{mass\ product}$			IChemE	
Raw materials recycle	Fraction of recycled raw materials from total raw materials use. Recycled within company and/or from customers			IChemE	
Water usage	$\frac{\text{kg net water consumed}}{\text{kg product}}$; $\frac{\text{kg net water consumed}}{\text{value added}}$			IChemE	

References

1. Anastas, T.T., and Warner, J.C. (1998). "Green Chemistry: Theory and Practice", Oxford University Press.

2. Anastas, P.T., & Lankey, R.L. (2000). Life cycle assessment and green chemistry: the yin and yang of industrial ecology. *Green Chemistry*, **2**, 289-295.

3. Anastas, P.T., Kirchhoff, M.M., & Williamson, T.C. (2001). Catalysis as a foundation pillar of green chemistry. *Applied Catalysis A: General*, **221**, 3-13.

4. Sanghi, R. (2000). Better living through 'sustainable green chemistry'. *Current Science*, **79:12**, 1662-1665.

5. Graedel, T.E. (2001). Green chemistry as systems science. *Pure Appl. Sci.*, **73:8**, 1243-1246.

6. a) Altshuller, G. (1984). Creativity as an exact science. Gordon & Breach Scientific Pub. b) Salamatov, Yu. (1999). TRIZ: the right solution at the right time. INSYTEC B.V. The Netherlands, c) http://www.triz-journal.com

7. Gladysz, J.A. (2001). Recoverable catalysts. Ultimate goals, criteria of evaluation, and the green chemistry interface. *Pure Appl. Chem*., **73:8**, 1319-1324.

8. Warhurst, A., et al (2001). Environmental and Social Performance Indicators. Methodology and Field Handbook. A report by Mining Environment Research Network. University of Bath.

9. MacGillivray, A. (1995). Indicators indicators everywhere. In Accounting for Change, papers from an international seminar, Toynbee Hall, October 1994, New Economics Foundation, London, p.11-14, and references therein.

10. Indicators of sustainable development for the United Kingdom, Department of the Environment, Government Statistical Services, 1996.

11. "Environmental Performance Indicators for the Financial Industry". *Report of an international project undertaken by financial institutions*. Available from: www.epifinance.com

12. Slesser, M., King, J., & Crane, D.C. (1999). The Management of Greed. Resource Use Institute, Edinburgh, Scotland.

13. Available from www.environmental-performance.org/approach/index.php

14. a) Constable, D.J.C., et al. (2001). Green chemistry measures for process research and development. *Green Chemistry*, **3**, 7-9; b) Curzons, A.D., Constable, D.J.C., Mortimer, D.N., & Cunnigham, V.L. (2001). So you think your process is green, how do you know? – Using principles of sustainability to determine what is green – a corporate perspective. *Green Chemistry*, **3**, 1-6; c) Smith, P. (2001). How green is my process? A practical guide to green metrics. In Clean technology for the manufacture of speciality chemicals, Eds. Hoyle, W., & Lawcastrer, M., Royal Society of Chemistry.

15. Krotscheck, C., & Narodoslawsky, M. (1996). The sustainable process index. A new dimension in ecological evaluation. *Ecological Engineering*, **6**, 241-258.

16. For literature on LCA see e.g. a) b) Anastas, P.T., & Lankey, R.L. (2000). Life cycle assessment and green chemistry: the yin and yang of industrial ecology. *Green Chemistry*, **2**, 289-295.

17. ISO 14040

18. Jodicke, G., Zenklusen, O., Weidenhaupt, A., & Hungerbuhler, K. (1999). Developing environmentally-sound processes in the chemical industry: a case study on pharmaceutical intermediates. *Journal of Cleaner Production*, **7**, 159-166.

19. Hazel, N.J., Walker, P., Bray, R. (1995). LCA based environmental evaluation of automotive OEM basecoat alternatives. Presented at International Body Engineering Conference, 2nd November 1995, Detroit, USA.

20. Schmidt-Bleek, F. (1993). MIPS re-visited. *Fresenius Envir. Bull.*, **2**, 407-412.

21. a) Trost, B.M. (1991). The atom economy – a search for synthetic efficiency. *Science*, **254**, 1471-1477; b) Trost, B.M. (1995). Atom economy – a challenge for organic synthesis: homogeneous catalysis leads the way. *Angew.Chem.Int.Ed.Engl.*, **34**, 259-281.

22. Sheldon, R.A. (2000). Atom utilisation, E factors and the catalytic solution. *C.R. Acad. Sci. Paris, Serie IIc, Chimie*, **3**, 541-551.

23. Ref. 19 as cited in [24].

24. Slesser, M. (1979). *Energy in the economy*. The Macmillan Press Ltd., London, p.164.

25. BRIDGES to Sustainability. (2001). A pilot study of energy performance levels for the U.S. chemical industry. Awailable at http://www.aiche.org/cwrt/practical.htm

26. Sullivan, J.L. (2001). Sustainability metrics for vehicles. *Pure Appl.Chem.*, **73:8**, 1273-1276.

27. a) Dewulf, J., Van Langenhove, H., Mulder, J., van den Berg, M.M.D., van der Kooi, H.J. & de Swaan Arons, J. (2000). Illustrations towards quantifying the sustainability of technology. *Green Chem.*, **2**, 108-114. b) Dewulf, J., Van Langenhove, H., Dirckx, J. (2001). Exergy analysis in the assessment of the sustainability of waste gas treatment systems. *The Science of the Total Environment*, **273**, 41-52; c) Dewulf, J. & Van Langenhove, H. (2001). Assessment of the sustainability of technology by means of a thermodynamically based life cycle analysis. *Environ. Sci. & Pollut. Res.*, **8**, 1-7.

28. Szargut, J., & Steward, F.R. (1988). Exergy analysis of thermal, chemical and metallurgical processes. Hemisphere Publ. Corp., N.Y./Springer Verlag, Berlin, 332 p.

29. Shields, D., Beloff, B., & Heller, M. (1996). Environmental cost accounting for chemical and oil companies: a benchmarking study. Downloaded from the Environmental Protection Agency web site http://www.epa.gov.opptintr/acctg/

30. Sonnemann, G.W., Schuhmacher, M & Castells, F. (2000). Framework for the environmental damage assessment of an industrial process chain. *Journal of Hazardous Materials*, **B77**, 91-106.

31. Castells, F., Aelion, V., Abeliotis, K.G., & Petrides, D.P. (1995). An algorithm for life cycle inventory. *AIChE Symposium Series on pollution prevention via process and product modifications*, **90:303**, 151-160.

32. Indicators of sustainable development for the United Kingdom. (1996). Government Statistical Service, Department of the Environment, London.

33. Indicators of sustainable development. Framework and methodologies. (1996). United Nations, New York.

34. ISO 14031.

35. Verfaillie, H.A., & Bidwell, R. (2000). Measuring eco-efficiency: a guide to reporting company performance. Web publication by the World Business Council for Sustainable Development.

36. See documents posted on www.aiche.org/cwrt/

37. The Sustainability Metrics. Sustainable development progress metrics. Institution of Chemical Engineers, 2002.

38. Available from http://service.eea.eu.int/envirowindows/41shtml

39. A first set of eco-efficiency indicators for industry: pilot study. Final Report 13.12.1999. Commissioned by the European Commission: Eurostat and DG Enterprise.