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Review

New trends for design towards sustainability in chemical engineering: Green engineering

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Abstract

A broad review of disciplines and technologies concerning the last-decade-advances and state-of-the-art in the understanding and application of sustainability from a Chemical Engineering viewpoint is presented. Up to now it was hard to find useful sustainability criteria and ready-to-use guidance tools for the design of products, processes and production systems. Fortunately, in the last decade a range of practices and disciplines have appeared transforming the way in which traditional disciplines were conceived. Firstly, a review of the concept of sustainability and its significance for the chemical and process industry is presented. Then, several inspiring philosophies and disciplines which are the basis of the new trends in design are briefly reviewed, namely, The Natural Step, Biomimicry, Cradle to Cradle, Getting to Zero Waste, Resilience Engineering, Inherently Safer Design, Ecological Design, Green Chemistry and Self-Assembly. The core of the manuscript is a deep review of what has been done in Green Engineering so far, including its main definitions and scope of application, different guiding principles, frameworks for design and legislative aspects. A range of illustrative industrial applications and several tools oriented to GE are analysed. Finally, some educational considerations and training opportunities are included, providing education at academic and university levels allows for the creation of a critical mass of engineers and scientists to foster green engineering and sustainable development in the future.

Keywords: Green engineering; Chemical engineering; Sustainable development; Ecoefficiency; Green chemistry

1. Introduction

Nearly twenty years away from the first definition of sustainable development and sustainability sentences like ‘much remain to be done in the areas of sustainability’ or ‘the underlying science is still far from exact and we all still need to make a big effort’ are common introducing and/or concluding phrases in both literature and scientific forums. Hopefully, in the last years underlying science has been promoted and clarified and as a result of this a coloured variety of successful industrial and academic examples of sustainable products, processes and production systems are now available.

The concept of sustainability was first mentioned in scientific literature by the German Miner Hans Carl von Carlowitz referring to sustainable forestry in *“Sylvicultura oeconomica”* in 1713. There, sustainability meant cutting only as much timber as was regrowing, with forestry having to ensure that soil fertility was maintained or even increased.

In the 1960s the emerging environmental philosophy was engendered among visionaries such as Rachel Carson who published her alert Silent Spring in 1962 [1]. Nevertheless, it was only after the publication of a report entitled ‘Our Common Future’ by the Brundtland commission in 1987 when the full idea of sustainable development settled down in the whole international scientific community [2,3].

The definition provided by the commission left space for various interpretations certainly on purpose. At the Rio Conference in 1992 and over the years which followed, the content of this concept was defined more precisely, and it has been confirmed since through a wide range of agreements, national programmes, action plans and scientific studies [4]. Today there are very few scientific, societal and political areas which have not been the subject of an examination based on sustainability criteria. It should be noted that sustainable development is a continuing process during which the definitions and activities

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it generates are in constant evolution. The evolutionary process which consists of reflecting on how we can ensure that our descendants have a decent future and assuming responsibility for our actions is in itself positive, although there is also the risk that theory will be put into practice in a number of different ways, creating a highly complex situation. It is for this reason that there are many different interpretations of what constitutes sustainability and sustainable development, a term which is often misused well-worn concept to serve particular interests. An analysis of the definition is presented in text trying to clarify the meaning of sustainability within the area of chemical engineering.

The hackneyed argument that the welfare state of modern society lies on a range of products that are produced in different chemical processes throughout the world and that 'unfortunately' this has caused severe damage to the environment is applicable once more [5,6]. As Albert Einstein observed we are facing these consequences now and as he pointed out the urgent problems that exist in the world 'today' cannot be solved by the level of thinking that created them. For us, our thinking (read here engineering disciplines) must evolve (be transformed) in such an innovative ways that can reconcieve the problems (starting from scratch?) providing the world with novel sustainable solutions.

A great variety of questions arise. What do and do not contribute to the sustainable development? What can a Chemical Engineer (CE) do to assure that a product, a process or a production system, PPS, is sustainable? What can a CE do to transform engineering disciplines in order to promote sustainability? Is Green Engineering (GE) the solution for CEs? Is it necessary to change minds at the industry, at professionals, at universities or users? How can we tackle the problem?

In the manuscript the state-of-the-art of Green Engineering and a range of novel disciplines that are basic inspiring philosophies are discussed in detail. First, a review of the concept of sustainable development and its significance for the chemical and process industry is presented. Then, several inspiring philosophies and disciplines which are or will be the basement of the future designs are briefly reviewed. These disciplines are the health spa to understand current and future design trend lines in Chemical Engineering. The core of the manuscript is a deep review of what has been done in GE so far, including its main definitions and scope of application, different frameworks for design and several legal aspects, specifically the European Directive. Several illustrative industrial applications and case studies are included to present the tangible side of the discipline. In order to help in the design process, different tools oriented to GE are listed and analysed. Finally, some educational considerations are included considering that green engineers must be formed at early stages of the training period ('from the cradle to the cradle').

2. The goal of sustainability in the chemical and process industry

Sustainability is achieved through the promotion of sustainable development, and sustainable development can be promoted from a very wide variety of disciplines, all of them necessary to achieve the final goal.

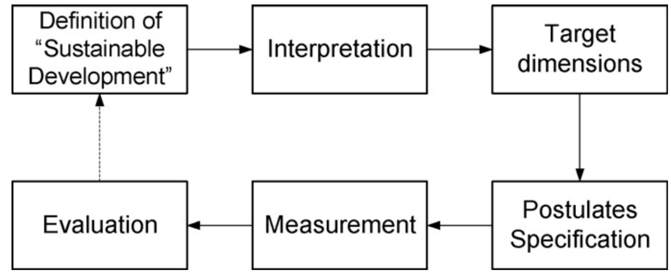

Fig. 1. Main stages of a sustainability analysis.

Fig. 1 illustrates the consecutive stages necessary for the implementation of a consistent framework for the achievement of sustainable development. Six main stages have been considered within this approach, definition of the term, interpretation, targeted dimensions, specification, measurement and finally evaluation [7]. This framework is crucial to understand how the indexes, principles and frameworks of design related to sustainable development are managed and implemented. It is necessary the clear definition of what 'sustainability' means in the different contexts from the individuals to the governmental policies and the entire Earth.

2.1. *Definition of the term*

The most widely known definition of sustainable development, which has been used as the basis for innumerable number of definitions because its openness and wide range of possible interpretations, is that given in the Brundtland Report in 1987: 'Sustainable development is development which meets the needs of the present without compromising the ability of future generations to meet their own needs' [2]. Liverman et al. went beyond this definition, and defined "... sustainability to be the indefinite survival of the human species (with a quality of life beyond mere biological survival) through the maintenance of basic life support systems (air, water, land, biota) and the existence of infrastructure and institutions which distribute and protect the components of these systems" [8].

In the present world, the goal of sustainability will not be attractive if it is not exceedingly advantageous. Fortunately (probably also intentionally), sustainability implies a three-fold added-value itself, economic, social and environmental profit, 'all in one'. Otherwise, only few companies had promoted sustainable PPSs if they do not visualise a clear benefit at the same time. "Green" is in some way "smart" and that is interesting; as the high-technology company Wilkinson S.L. suggested that "Green" could be even profitable provided that it becomes a central strategy for those firms in terms of policy, the so-called sustainability" [9].

This encrypted definition needs to be specifically reworded for each case, e.g. continent, country, century or decade and even industry or household if we want to feel the advantage [7].

2.2. Interpretation

Analyzing individually the terms ‘sustainable’ and ‘development’ one can find that:

- Sustainable means ‘capable of being sustained’, which links to the capacity of durability, stability, permanence or even eternalness. This adjective has a kind connotation of immobility or perpetuity.
- Development connotes the act of improving by expanding, enlarging or refining. This includes both qualitative and quantitative features. The word itself induces the thought of movement as the way of improving. So, dynamics is clearly included in the definition.
- ‘Present’ and ‘future’ are also non-static terms and must be revised and redefined for a precise characterization of the time in which were, are or will be analysed.
- ‘Ability’ has multiple connotations, including capability, because having the material means is not enough and also intellectual solutions are required.
- ‘Intra- and intergenerational’, the entitlement to having needs met is taken to extend over space and time. It applies to all human beings currently alive and to the future population of the Earth. It should be noted that one single generation might experiment different ‘definitions’ of ‘sustainable development’ during its existence. Again it is necessary the clear definition of system boundaries.
- ‘Compromising’ or ‘maintenance of options’, this phrase is crucial in the understanding of ‘meeting needs’. From the two theories about the Earth it can be concluded that, on the one hand actual needs may be replaced by different solutions in the future as soon as technical solutions were viable (mainstream sustainability). On the other hand, if the same options were to be maintained then Earth’s resources should be dosed in the right proportion to avoid depletion (environmental sustainability). The argument of maintaining the largest possible number of options entails comprehensive protection of the full diversity of the natural foundations of life; in other words: guarantee biodiversity.
- ‘Meeting needs’ joins essential biological, physiological and social needs, which ensure subsistence, at the same time as guaranteeing human rights, identity and dignity (concept of justice). Economical needs are also difficult to classify due to the requirement of including the concept of property within the definition.

Therefore, rewriting the definition ‘Sustainable development means continuous ensuring dignified living conditions with regard to human rights by creating, expanding, enlarging, refining and maintaining the widest possible range of options for freely defining life plans. The principle of fairness among and between present and future generations should be taken into account in the use of environmental, economic and social resources. Comprehensive protection of biodiversity is required in terms of ecosystem, species and genetic diversity and all of which the vital foundations of life are’.

2.3. Target dimensions

The next step is to define target dimensions for various issues, which will be observed using an indicator system for sustainable development. In most of the cases, environmental sustainability is the predominant approach to sustainable development for industrialised countries. However, recently a broader interpretation has now taken over, which relates sustainable development to the fields of society, economy and environment. These three dimensions are central to ‘Agenda 21’ adopted at Rio in 1992 [4], which is an important frame of reference for efforts in the field of sustainable development, and also in the ‘Bellagio Principles’ [10]. The integration of theses three dimensions is often represented a “magic triangle”. This three-dimension approach is a sensible way of setting out which areas may be subsumed under the concept “sustainable development”. Besides, the data sources which are required to construct the individual indicators are also often classified in a similar way. However, one criticism is that this approach divides more than unites and the division is artificial. It would be therefore sometimes difficult to assign indicators clearly to one of the three dimensions.

The three dimensions, i.e. environmental sustainability, social solidarity and economic efficiency must be satisfied, however, how much percentage of them is fulfilled will vary through the different continents, nations, governments and industries in order to obtain the maximum efficiency point at the least cost. This means, for instance that environmental protection measures have to be socially practicable and economically efficient, or that certain engineering solution must agree with social requirements and necessities besides being economically feasible and environmentally friendly.

The definition of sustainability goals from the chemical and process industry viewpoint encompass certain difficulties that are out of the scope of this paper, but that must be carefully taken into account. Traditionally economic criteria were the only criteria applied in the analysis of profitability of a chemical plant. Four decades ago, environmental criteria were pushed by more and more stringent legislative frameworks. Environmental concerns and solutions included within chemical engineering projects has been shown to give economic profits in most of the cases. Sustainable development seeks for the social equity as well. However, the implementation of social concerns within the chemical and process industry is not that evident and must be defined with care because it can be used to justify environmentally unsustainable situations.

According to the World Business Council for Sustainable Development (WBCSD) the six main topics that are shaping the sustainability agenda are: Ecoefficiency, Innovation & Technology, Corporate Social Responsibility, Ecosystems, Sustainability & Markets and Risk [11]. Other organizations are more human-oriented such as the United Nations Global Compact which focuses efforts in four ways, namely, human rights, anti-corruption, the environment and labour [12].

2.4. Postulates specification

A number of different postulates have been utilised within the different frameworks of sustainability. Publications by IDC Rio, the UVEK departmental strategy and the comments of the Council for Sustainable Development on the SFSO and SAEFL report entitled 'Indikatoren der Nachhaltigkeit'. Some of the have been compiled to prepare particular methods, such as MONET of the Swiss Federal Statistical Office [7].

2.5. Measurement and evaluation: indexes of sustainability

In the field of Environmental Sustainability, ES, several composite indicators have been proposed at different levels [13]. For this work, we will center our attention in two of these indexes because of their importance for the chemical industry.

The first one is the index of sustainability defined by The Institution of Chemical Engineers, IChemE. This index introduces a set of indicators that can be used to measure sustainability performance of an operating unit. The operating unit envisaged is a process plant, a group of plants, part of a supply chain, a whole supply chain, a utility or other process system. IChemE index assumes that most products in which the process industries are concerned will pass through many hands in the chain resource: extraction, transport, manufacture, distribution, sale, utilization, disposal, recycling and final disposal. It is essential in reporting the metrics to make clear where the boundaries have been drawn, because suppliers, customers and contractors all contribute to this chain and their viewpoints and necessities are different. Then, if comparable statistics are gathered from a number of operations, they can be aggregated to present a view of a larger operation, on a company, industry or regional basis for instance [14].

The second one and maybe the one with the most projection for the future is the Global Reporting Initiative (GRI). GRI spearheaded in 1997 by CERES (Coalition for Environmentally Responsible Economies) in partnership with the United Nations Environment Programme (UNEP). The GRI's Sustainability Reporting Guidelines first released in draft form in 1999, represented the first global framework for comprehensive sustainability reporting, encompassing the "triple bottom line" of economic, environmental and social issues. According to their statistics to-date, nearly 1000 organizations in over 60 countries have used the GRI Framework as the basis for their reporting. In October 2006 the new generation of guidelines, G3, will be launched. These guidelines are available for downloading from the website [15]. Fig. 2 illustrates a summary of these guidelines and the scope of use.

In order to respond to the European Union's strategy for sustainable development and to promote better law-making, the European Commission for Research, Scientific Support for Policies, has been committed to performing impact assessments for all policy proposals considering the economic, environmental and social dimensions of policy, and their interlinkages [16].

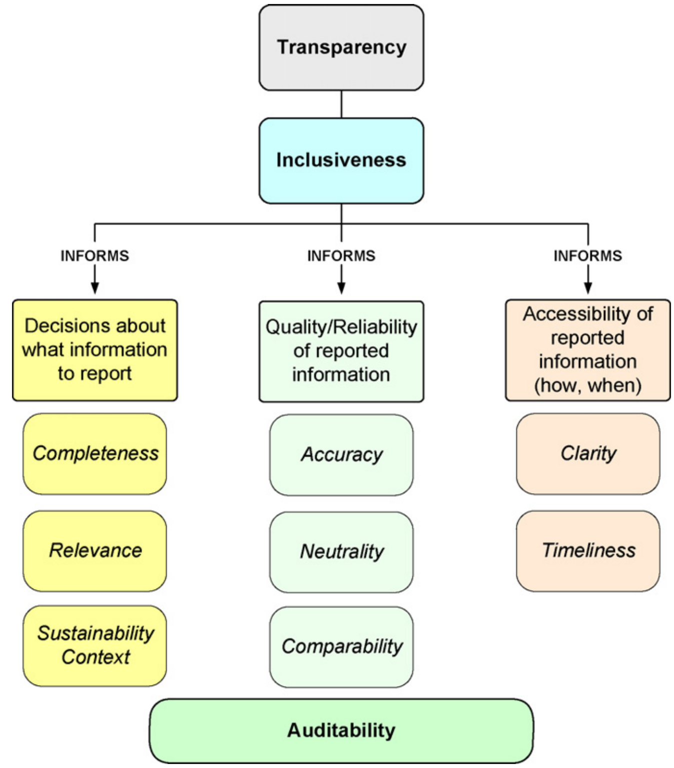

Fig. 2. GRI framework guidelines.

2.6. Resources

The Sustainability Experts panel represents all sectors: officials in multilateral organizations, government ministries, corporations, industry associations, sustainable development consultants, journalists, and academics, as well as leaders of major policy institutes and non-governmental organizations. From the last Survey of Sustainability Experts it can be extracted that the most cited websites about sustainability are, listed by importance: (1) World Business Council for Sustainable Development, WBCSD [11], (2) International Institute for Sustainable Development [17], (3) various United Nations websites, i.e. United Nations Framework Convention on Climate Change [18], United Nations Development Program (UNDP) [19] and GlobalCompact [12], (4) the World Resources Institute [20], (5) Worldwatch Institute [21] and (6) several EU sites.

Further sustainability sources can be found in web-library page maintained by the Center for Economic and Social Studies on the Environment located at Université Libre de Bruxelles [22].

3. Base inspiration philosophies and other related disciplines

Is GE a brand-new discipline created from scratch? Is or has to be GE different from what we understand of Chemical Engineering? If it does, which parts should be preserved and which devised? In the literature and in GE forums, what have been called the 'Principles of Green Engineering' and 'Principles Green Chemistry' are well accepted as the base of these disciplines. However, we consider that GE must be the natural continuation of traditional Chemical Engineering. If one asks the question: what are the 'Principles' of Chemical Engineering? Probably, the answer will be that Basic Unit Operations, Heat and Mass Transfer, Fluid Flow, Reactors and Kinetics and by extension, Maths, Chemistry, Physics, Thermodynamics and some others are the basic pillars of Chemical Engineering, which were well established during the 20th century. Therefore, we assume that what have been enounced as principles so far are really 'Design guidelines or new trends in design for chemical engineers'. Moreover, these guidelines respond to some novel disciplines and theories of sustainable designs that must be included within Chemical Engineering curriculum in the same way as Statistics, Economics and Materials Science were included at some point.

Novel designs must have the possibility of dynamically change and adapt to changes as a result of the inputs and boundary conditions with regards to be as sustainable as possible at short-, mid- and long-term.

To sum up, fundamental pillars of Chemical Engineering are well-established but moving towards sustainability in the design of products, processes and production systems entails to reinforce the foundations adding novel-fresh disciplines and design guidelines and theories and creating dynamic interconnectivity among them.

The disciplines and design philosophies that we consider are the inspiration for the future designs in Chemical Engineering are presented next. We have divided these disciplines in four categories attending to the matter of application. Innovation and creativity are two of the most important starting points to change and create novel solutions to lasting problems (see principle number 2 from the 12 Principles of Engineering for Sustainable Development, 'Innovate and be creative').

3.1. Design philosophy

3.1.1. The Natural Step

The Natural Step (TNS) was developed in 1989 and offers a framework of four System Conditions for sustainability underpinned by basic scientific principles [23]. The scientific principles and four System Conditions define what is required in order to move from a linear economy (where materials are extracted, used and disposed) to a cyclic economy (where waste equals food) allowing individuals and companies to create prosperous businesses and a sustainable relationship with nature. The Natural Step (TNS) is an international charity which operates under licence of Forum for the Future [24].

TNS framework assumes the triple bottom line for the achievement of sustainability where economic profitability and environmental and social accountability are weighted equally. This model conceives that sustainability rests on the preservation of the 'sustainable capital'. There are five types of sustainable capital from where we derive the goods and services we need to improve the quality of our lives, namely natural, human, social, manufactured and financial capital. We are currently facing the incessant decreasing of this capital and, joined to this, the continuous increasing of the demand of the capital in its different types. This has been represented by the metaphor of the funnel

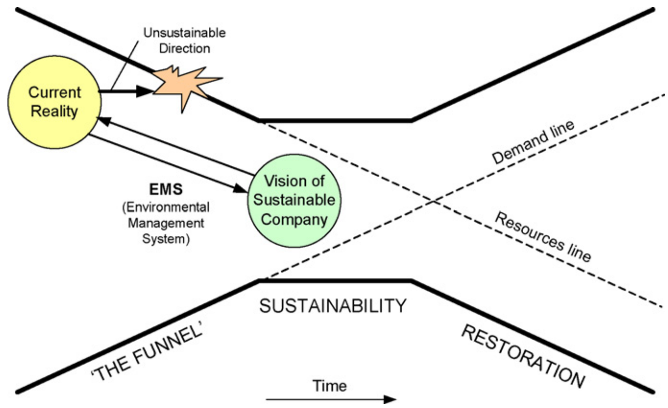

Fig. 3. The natural step metaphor of the funnel.

illustrated in Fig. 3. A company having a vision oriented to sustainability will manage the resource and demand lines in such a way that instead of converge will be kept constant or in the best scenario the lines will diverge (restoration of the system) [25].

The scientific principles are: (1) Matter and energy cannot be created or destroyed (first law of Thermodynamics), (2) Matter and energy tend to disperse (second law of Thermodynamics), (3) What society consumes is the quality, purity, or structure of matter, not its molecules and (4) Increases in order or net material quality on earth are produced almost entirely through sun-driven processes.

TNS System Conditions are four: (1) substances from the Earth's crust must not systematically increase in concentration in the ecosphere, (2) substances produced by society must not systematically increase in concentration in the ecosphere, (3) the physical basis for the productivity and diversity of nature must not be systematically deteriorated and (4) there must be a fair and efficient use of resources with respect to meeting basic human needs.

An appropriate capital investment strategy for sustainable development following the above principles and conditions will lead to a successfully developed sustainable society.

The ideas of TNS are also included in other inspiring philosophies such as Cradle to Cradle and Biomimicry, as seen next.

3.1.2. Biomimicry

Biomimicry is the science of innovation inspired by nature (from the Greek, *bios*, life and *mimesis*, imitation). Janine Benyus enounced her theory about what need to be the muse of inspiration in designing for the environment [26]. According to Dr. Benyus we need to consider:

- *Nature as a model*. Natural models are studied and then imitated or taken as a inspiration for the new designs.
- *Nature as a measure*. The ecological standard is always the best solution in terms of 'rightness' or efficiency, because after 3.8 billion years of evolution Natures knows what works, what is appropriate and what lasts.
- *Nature as a mentor*. Natural world is valued for what can teach to us not only for what can deliver to us. This means 'learn rather extract from'.

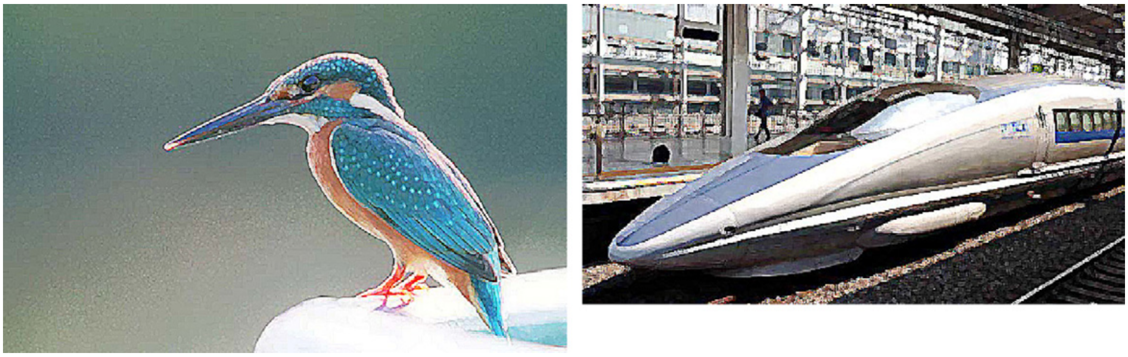

Fig. 4. King fisher and a Japanese high speed train (500 Series Shinkansen in Kyoto).

J. Benyus is certainly one of the most influent 'gurus' of the current 'green' sciences providing a useful answer to the emergency call that Rachel Carson foresaw in her book '*Silent Spring*' [1]. The main principles that resonate in her book chapter after chapter are listed next: (1) nature runs on sunlight; (2) nature uses only the energy it needs; (3) nature fits form to function; (4) natures recycles everything; (5) nature rewards cooperation; (6) nature banks on diversity; (7) nature demands local expertise; (8) nature curbs excesses from within; (9) nature taps the power of limits. A number of application examples where nature has been mimicked in order to solve an engineering problem are explained in detail in her book. Thus, for instance, severe noise problems because of a sudden shockwave may appear when a high-speed train enters a tunnel. The solution was found in the *King fisher*, a skilful bird that hunts diving from the air to the water at high velocity without making any noise and injuring itself (see Fig. 4). Added to the total elimination of the problem of shockwaves in tunnels an important energy reduction was achieved when the shape of the bird was adopted for the train.

3.1.3. Cradle-to-cradle. remaking the way we design things

The concept of Cradle to Cradle (C2C) was furthered by W. McDonough (architect) and M. Braungart (chemist) in 2002. C2C approach is a simple method of conceiving the way in which engineers must remake things [27,28]. The authors introduced this philosophy using some well-known Einstein words comparing the telegraph with the radio: *"Wire telegraph is a kind of a very, very long cat. You pull his tail in New York and his head is meowing in Los Angeles. Do you understand this? And radio operates exactly the same way: you send signals here, they receive them there. The only difference is that there is no cat."* So, the way of innovation goes through rethinking and re-conceiving from a different viewpoint.

The three tenets of C2C are:

- *Waste equals food*. In nature waste virtually does not exist because the output of one organism is used as a valuable input for other organism, closing the cycle within the whole ecosystem. To eliminate the concept of waste means to design things, products, and processes from the very beginning on the understanding that waste does not exist.
- *Use current solar income*. Considering the ecosystem as a whole, trees and plants lay at the bottom of the sustain pyramid. In fact, trees and plants use solar energy as their primary energy source at the minimum possible temperature (ambient temperature), producing complex organic carbon molecules and oxygen as the main products. This reaction is clearly controlled by mass transfer and kinetics, so high surface area is used (leaves).
- *Respect and celebrate biodiversity*. Diversity makes an ecosystem resilient and able to respond successful to change. Natural systems thrive on diversity where each living organism has its own essential function and expertiseness. Our designs must consider and protect biodiversity.

There are clear similarities between Cradle to Cradle and Biomimicry principles and tenets.

The use of energy at high efficiency levels (maximizing exergy) from renewable sources is what nature does [29]. Some of the accepted renewable sources of energy are: solar thermal energy, solar photovoltaics, bioenergy, hydroelectricity, tidal power, wind energy, wave energy and geothermal energy [30]. Some of these renewable sources are 'infinite' but others are 'limited', e.g. the number of waterfalls to produce hydroelectricity is limited so, it limits the production. All of the renewable sources are not enough to satisfy actual energy demand now. Detailed planning and management of renewable energy use and resources using precise energy models is essential to reach sustainability [31].

A good example is found in the development of pinch technology introduced by Linnhoff and Vredeveld in the late 1970s [32–34]. Pinch technology uses a set of thermodynamically based methods that guarantee minimum energy levels in the design of heat exchanger networks. Pinch technology is both a simple and precise methodology for systematically analysing chemical processes and the surrounding utility systems by tracking heat flow for all process streams in a system, from an entire plant to a unit operation. This methodology is aimed at achieve financial savings in the process industries by optimising the ways in which process utilities (particularly energy and water), are applied for a wide variety of purposes. Maximization of exergy, quality of energy, is also taken into account within the method.

3.1.4. Getting to zero waste

P. Palmer have analysed the current state of recycling and the system of garbage and finds it wanting. The author exposes in detail the problem of residues within the chemical industry and by extension to all society in his book [35]. The author enounces five laws for the achievement of universal recycling: (1) recycle function (recycling is sometimes understand as downcycling, reusing a product at a lower quality level, usually because of degradation or contamination by other materials, etc.); (2) design in recycling up front; (3) remove the garbage industry; (4) eliminate dump subsidies; (5) make it profitable. Getting to Zero Waste (G2ZW) finds that the principal problem is that 'residue' is accepted as a valid product or side product, and that its only function is to be disposed properly out of sight. As the author suggests insistently the main raw material of garbage companies is the garbage itself, their treatment method commonly is reduced to the burial underground of everything without consideration, and their products harmful dumps everywhere. Universal recycling seeks for the elimination of the terms residue and garbage by finding the value of everything within its life cycle. Therefore, if garbage does not exist then garbage companies do not necessarily need to exist, full stop. More information can be found in G2ZW website [36].

3.1.5. Resilience engineering

'Resilience' is a physical property of a material that can return to its original shape or position after deformation that does not exceed its elastic limits. Resilience Engineering stands for the view that failure is the flip side of the adaptations necessary to cope with the complexity of the real world rather than a breakdown or malfunctioning as such. As Jin et al. suggested engineering issues that involve ecology are complex because they depend on the notions of value and justice of each human being [37]. Complex systems are inherently dynamic, nonlinear and capable of self-organizing to sustain their existence. The performance of products, processes and systems must always adjust to the current conditions and boundaries and because resources and time are finite such adjustments are always approximate. This dynamic conception adds at least two new variables to the simple reductionist design: time and randomness. Design must be resilient rather than resistant; this way designs will inherently respond correctly to unpredictable changes in their inputs/outputs or even accept/emit new ones [38,39].

Therefore, sustainability acquires a new essential dimension and becomes a characteristic of a dynamic evolving system instead of being a static aspired goal.

For the case of the process and chemical industry, surely, more than 90% of the designs are based on static-stationary states, given by material and energy balances or in any handbook equipment design equation. Thus, for instance, the controllability of the system is an important quality which denotes the ability and reliability to keep or maintain the steady-state design values under acceptable limits. Rangeability indicates how far from the design value can the system operate under control. But, what if raw material scarcity obeys to change inputs? Can the process absorb this unpredicted failure from within? Resilience engineering stands for design for adaptation.

3.2. Safety

3.2.1. Inherently safer design, ISD

Early in 1978, Trevor Kletz suggested that the chemical industry should re-direct its efforts toward elimination of hazards where feasible – by minimization, material substitution, alternative reaction routes, modified storage arrangements ('what you don't have can't leak') and energy limitation – rather than devoting extensive resources on safety systems and procedures to manage the risks associated with the hazards [40]. This novel approach to design was called 'Inherently Safer Design'. ISD means that hazards are eliminated not controlled, and the means by which the hazards are eliminated are so fundamental to the design of the process that they cannot be changed or defeated without changing the process [41].

There are four different safety strategies in order of safety: (1) procedural (in operation 'controls'); (2) active (in design 'acts'); (3) passive (in design 'contains'); (4) inherent (in design 'eliminates the risk').

ISD proposes five design principles:

(1) Intensification: the use of minimal amounts of hazardous materials assures that a major emergency is not created even if all the plant contents are released. The change in the design procedure implies going from scale-up to scale-out (e.g. micro-reactors).
(2) Substitution: use of non-hazardous compounds.
(3) Alternative Reaction Routes: in addition to using safer chemicals it is possible to reduce the risks associated with manufacture by making changes in the reaction routes.
(4) Modify storage arrangements: it has been summarized by the sentence 'what you don't have can't leak'.
(5) Energy limitation: limiting the amount of energy available in the manufacturing process also limits the possibility of a run-away process in case of failure.

3.3. Facilities and buildings

3.3.1. Ecological design: buildings for the environment

Ian McHarg has suggested that non-ecological design is "either capricious, arbitrary, or idiosyncratic, and. . .certainly irrelevant" [42]. Van der Ryn and Cowan define Ecological Design as an integrative, ecologically responsible discipline [43]. It is aimed at designing minimizing environmentally destructive impacts by the integration with the living organisms and processes. This integration implies that the design respects species diversity, minimizes resource depletion, preserves nutrient and water cycles, maintains habitat quality and attends to all the other preconditions of human and ecosystem health. For Nancy and John Todd it is "design for human settlements that incorporates principles that are inherent in the natural world in order to sustain human populations over a long span of time" [44].

Attending to a broader definition of sustainability goals, the idea of van der Ryn and Cowan of minimizing impacts should be substituted by the initiative of improvement of the environment with the newer designs, this is the central standpoint of what is understood as 'design for the environment'.

Comparing the main characteristics of conventional and ecological design the main issues that arise are: energy and materials use, pollution, use of toxic substances, economics, design criteria, sociological and cultural context, diversity and biodiversity spatial scales, underlying metaphors (i.e. building units), level of participation of the agents, types of learning (how the design transmits knowledge-base) and the different response to a likely sustainability crisis (resilience).

3.4. The chemistry and the process

3.4.1. Green chemistry

Moving towards the ideal chemistry means designing chemistries in which the target molecule is made from readily available starting materials in one simple, safe, environmentally friend and resource-effective operation that proceeds quickly and in quantitatively yield (see Fig. 5). In addition to this, the product should separate from the reaction in 100% purity [45].

The Environmental Protection Agency (EPA) defines Green Chemistry (GC) as the use of chemistry for pollution prevention at molecular level [46]. The mission of GC is to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products [47].

Three are the main focus areas of GC: (1) the use of alternative synthetic pathways, (2) the use of alternative reaction conditions and (3) the design of safer chemicals that are less toxic than current alternatives or inherently safer with regards to accident potential.

In 1998, Paul Anastas and J.C. Warner announced a set of 12 principles as a useful guide to design environmentally benign products and processes or to evaluate the already existing processes [48]. The principles are listed below:

(1) *Prevention*. It is better to prevent waste than to treat or clean up waste after it has been created.

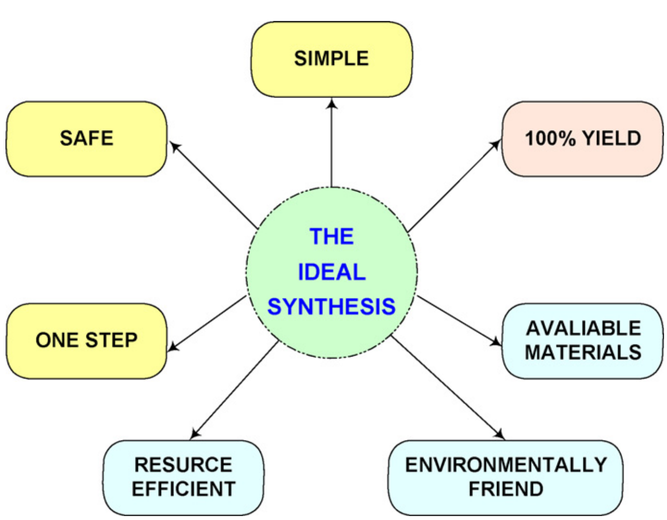

Fig. 5. Towards the ideal chemistry.

(2) *Atom economy*. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
(3) *Less hazardous chemical syntheses*. Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
(4) *Designing safer chemicals*. Chemical products should be designed to effect their desired function while minimizing their toxicity.
(5) *Safer solvents and auxiliaries*. the use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
(6) *Design for energy efficiency*. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
(7) *Use of renewable feedstocks*. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
(8) *Reduce derivatives*. Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
(9) *Catalysis*. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
(10) *Design for degradation*. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
(11) *Real-time analysis for pollution prevention*. 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) *Inherently safer chemistry for accident prevention*. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

The need for end-point engineering solutions to prevent pollution from being released into the environment is minimized when green chemistry principles are incorporated into feedstock and reagent selection, solvent use, and overall synthetic design [49]. As Kirchhoff indicated and illustrated with several examples, combining GC with GE at the earliest design stages is an effective strategy for maximizing efficiency, minimizing waste, and increasing profitability [50].

Important note: it must be remarked that several technologies such as supercritical fluids, ionic liquids, fluorous liquids, solventless technologies, microwaves, ultrasounds, catalysis and biological processes have been intimately associated with GC. In several forums and frequently in the literature these alternative technologies are considered directly GC with independence of the process or product handled. Here we want to emphasize that all these alternative techniques may be of use, but a deep analysis of each particular case study through the set of principles of GC should be carried out to clarify whether the chosen technique 'it is' or 'it is not' GC.

3.4.1.1. Example of GC in the pharmaceutical industry. A representative example of pharmaceutical green processes is ibuprofen production. The traditional industrial synthesis of ibuprofen was developed and patented by the Boots Company of England in the 1960s. This synthesis used a six-step process resulting in large quantities of unwanted waste chemical byproducts that must be disposed of or otherwise managed. The BHC Company has developed and implemented a new greener industrial synthesis of ibuprofen that used only three steps and that has a high level of atom efficiency. This lessens the need for disposal and mediation of waste products and increases the overall efficiency of the process considerably [51]. In mid-October 1992, the green synthesis was put into practice on an industrial scale at one of the largest ibuprofen manufacturing facilities in the world in Bishop, TX. This plant is operated by the Celanese Corporation for BASF and currently produces approximately 20–25% (more than 7 million lb) of the world's yearly supply of ibuprofen.

3.4.1.2. Examples of GC in the chemical industry. There are a number of examples of novel green chemistries that have been incorporated to industrial processes in the last years.

Davy Processes Technology has developed a new green route for ethyl acetate production. Consumption of ethyl acetate as industrial solvent has increased in recent years, mainly because it is replacing hazardous atmospheric pollutants such as methyl ethyl ketone and methyl isobutyl ketone. Davy Processes Technology offers a more environmentally friendly route to produce ethyl acetate from alcohol, without using acetic acid. A 100,000 tonnes/year plant is under construction in China. This is the second plant started-up for producing ethyl acetate using a green technology. This plant will use ethanol from fermentation as a sole feedstock. This new plant is a first example of a truly green process whereby atmospheric carbon dioxide is converted by photosynthesis to starch, harvest, fermented into ethanol which then is chemically converted to ethyl acetate. The completion of the CO_2 cycle adds guarantees in the production of a cleaner fuel; however, we must not forget that a responsible consumption is also required for sustainability [52].

BASF, for instance, is employing an ionic liquid in the manufacture of alkoxyphenylphosphines since 2003. *N*-Methylimidazole is used to scavenge acid that is formed in the process. The reaction results in the formation of the ionic liquid *N*-methylimidazolium chloride (Hmim-Cl), which has a melting point of 75 °C. The manufacture is carried out on a multiton scale in a batch reactor at elevated temperatures. During the process, which has the name BASIL (biphasic acid scavenging utilizing ionic liquids), the ionic liquid separates as a clear liquid phase from the pure product and is recycled. The separation takes place only by protonation or deprotonation of *N*-methylimidazole. Once protonated, it is miscible with the organic phase and it can be distilled like any other organic solvent. The compound is also a nucleophilic catalyst which accelerates the reaction rate tremendously. The deprotonated product is immiscible with the organic phase and decanted very easily (15 min residence time). Alkoxyphenylphosphines are precursors for the synthesis of photoinitiators that are used in the manufacture of printing inks as well as glass fiber and wood coatings. The phosphines are prepared by the reaction of phenyl-chlorophosphines with alcohols. In the conventional processes acid scavengers such as triethylamine are used, but they produce solids that are difficult to separate from product and require large amounts of organic solvents to keep in suspension and a post-filtration [53].

Some more examples of the application of GC can be found within the EPA Presidential Green Chemistry Challenge Program [46].

3.4.2. Self-assembly: building in a natural way

Self-assembly is the fundamental principle which generates structural organization at all scales from molecules to galaxies, from nanoscopic to macroscopic in Nature. Self-assembly in nature is older than life itself. It is defined as reversible processes in which pre-existing parts or disordered components of a pre-existing system form structures of patterns. Using other words self-assembly is the autonomous organization of components into patterns or structures without human intervention [54]. Protein folding, nucleic acid assembly and tertiary structures, phospholipid membranes, ribosomes, microtubules, and the nucleocapsides of viruses are representative examples of biological self-assembly in nature that are of critical importance to living organisms.

There are two types of self-assembly, intramolecular self-assembly (e.g. protein folding) and intermolecular self-assembly (e.g. supramolecular assemblies of a micelle with surfactant molecules in solution), both starting from a limited number of rather simple structural building blocks that hierarchically and spontaneously or assisted by other molecules (e.g. chaperones) organize from the atomic scale into mesoscopic structures [55]. One of the best examples is DNA chain where few molecules formed by one cyclic five-carbon sugar, one phosphate and one nitrogenous base are recognised and assembled in a number of ways preserving life characteristics.

Chemists and engineers have learned to design self-assembling systems with a modest degree of complexity. But the need for increased complexity is growing, driven by current necessities of miniaturized systems, e.g. circuitry or computers [56]. For instance, Warner, Woehrle and Hutchinson have developed methods of nanofabrication of nanoparticle arrays based upon the assembly of functionalized nanoparticles. One of these methods is biomolecular nanolithography that involves self-assembly of nanoparticles onto biopolymeric (DNA) scaffolds to form lines and more complex patterns. One potential application of these methods is the generation of molecularly integrated nanocircuits as a higher performance (and greener) approach in the microelectronics industry [57,58].

One of the recent advances in miniaturization results from the combination of engineering with the mathematical field of geometry. Fractals are mathematically generated patterns that

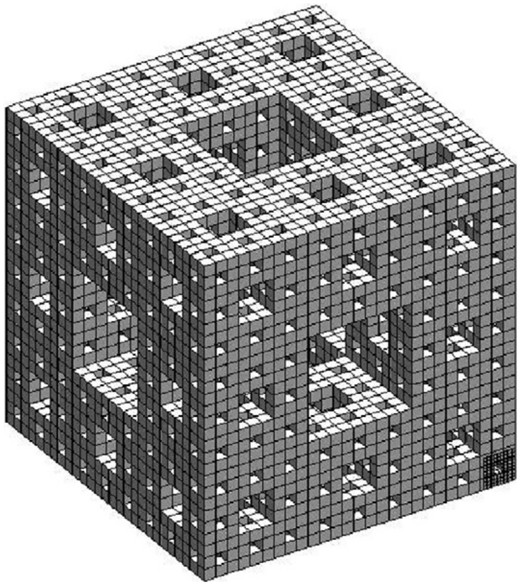

Fig. 6. Sierpinski Sponge fractal, level 3.

are reproducible at any magnification or reduction. Fractals are algorithms, or shapes, characterized by self-similarity and produced by recursive sub-division. For instance, fractals have been used with a great success for the design of smaller and more efficient antennas [59]. Such fractal antennas have multiple bands or are genuinely wideband. Fig. 6 illustrates an example of the Sierpinski Sponge fractal; one simple cube is sequentially repeated to construct the actual shape.

4. Green engineering

4.1. Definition and scope of application

Several adjectives have been used to qualify this branch of engineering, 'chemical', 'environmental', 'ecological', 'clean' and 'green'. Environmental Engineering refers to an actual sub-branch of engineering which is dedicated to the endpoint treatment of pollutants in gas, water and soil streams and it clearly does not fulfil the requirements and scope of application of the novel cradle-to-cradle analysis proposed. On the other hand, Ecological Engineering has been related to Ecological design, as discussed previously and has strong links to architecture and landscape management.

Amongst the different definitions of Chemical Engineering we have selected two. The first one is related to its occupational tasks: "Chemical Engineering is a broad discipline dealing with processes (industrial and natural) involving the transformation (chemical, biological, or physical) of matter or energy into forms useful for mankind, economically and without compromising environment, safety, or finite resources" [60]. The second one, which is the latest definition given from IChemE, is: "In its simplest form, chemical engineering is the design, development and management of a wide and varied spectrum of industrial processes" [61]. Chemical Engineer is a well-established professional career and discipline; nonetheless, it seems that the adjective 'chemical' causes some kind of contempt in the common people, as sounded in several non-professional forums.

Singh and Falkenburg considered that 'the primary objective of GE is to eliminate the waste or scrap generated as a result of design and manufacturing decisions if possible, otherwise reduce it to the best possible limits' [62]. Later, GE has been defined as "the design, commercialization, and use of processes and products that are feasible and economical while minimizing pollution at the source and risk to human health and the environment" by Allen and Shonnard [63]. The definition prepared during the Sandestin Conference was: "Green Engineering transforms existing engineering disciplines and practices to those that promote sustainability. GE incorporates development and implementation of technologically and economically viable products, processes and systems that promote human welfare while protecting human health and elevating the protection of the biosphere as a criterion in engineering solutions" [64].

IChemE's definition for Chemical Engineering considers formally the activities related to a range of industrial processes widening the definition as much as possible. In the first definition the authors add a significant tail to the traditional activities done by a chemical engineer "...without compromising environment, safety, or finite resources". In this way GE could be considered as the natural transformation of traditional Chemical Eng. practices, the same argument that comes out from the Sandestin definition. However, it must be noted that some people is sensitive to the adjective "green" because of its political connotations world-wide ('green parties').

Recently, the Royal Academy of Engineering (UK) has presented the Principles of Engineering for Sustainable Development, where the main challenges for Sustainable Development are covered but there is no adjective is used before the noun [65].

In this work we have chosen the name 'Green Engineering' mainly because we consider that currently this name carries the meaning through the different definitions given in the literature. Nevertheless, we would like to remark the all the disciplines and ideas for design compiled in the work show new trends and aids for design in Chemical Engineering to promote Sustainability through Sustainable Development.

4.2. Approaching sustainability through principles

Several institutions and individuals have defined sets of principles and guidelines which have been used as a reference in order to evaluate and design strategic plans to achieve sustainability. Some of these principles overlap and some others are not specifically technical. We have brought together all the sets that we considered are fundamental to understand the idea of Chemical Engineering promoting Sustainable Development.

(i) The Precautionary Principle, which guides human activities to prevent harm to the environment and to human health, it says: "When an activity raises threats of harm to human health or the environment, precautionary measures should be taken even if some cause-and-effect relationships are not fully established scientifically" [66].
(ii) The Earth Charter Principles, which promote respect and care for the community of life, ecological integrity, social

and economic justice, and democracy, non-violence, and peace [67].

(iii) The Natural Step System Conditions, which define basic principles for maintaining essential ecological processes and recognizing the importance of meeting human needs worldwide as integral and essential elements of sustainability [23,24].

(iv) The Coalition for Environmentally Responsible Economies (CERES) Principles, which provide a code of environmental conduct for environmental, investor, and advocacy groups working together for a sustainable future [68].

(v) The Bellagio Principles, which serve as guidelines for starting and improving the sustainability assessment process and activities of community groups, non governmental organizations (NGOs), corporations, national governments, and international institutions including the choice and design of indicators, their interpretation and communication of the result [10]. These principles deal with four aspects of assessing progress toward sustainable development: (1) establishing a vision of sustainable development and clear goals that provide a practical definition of that vision in terms that are meaningful for the decision-making unit in question, (2) the content of any assessment and the need to merge a sense of the overall system with a practical focus on current priority issues, (3) key issues of the process of assessment and (4) with the necessity for establishing a continuing capacity for assessment.

(vi) The Ahwahnee Principles, which guide the planning and development of urban and suburban communities in a way that they will more successfully serve the needs of those who live and work within them [69].

(vii) The Interface Steps to Sustainability, which were created to guide the Interface company in addressing the needs of society and the environment by developing a system of industrial production that decreases their costs and dramatically reduces the burdens placed upon living systems [70].

(viii) Twelve Principles of Green Chemistry [48], aimed at promoting innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products.

(ix) The Hannover Principles, which assist planners, government officials, designers, and all involved in setting priorities for the built environment and promoting an approach to design that may meet the needs and aspirations of the present without compromising the ability of the planet to sustain an equally supportive future [71].

(x) Design for Environment (DfE) Key Strategies produced by the National Resource Council of Canada [72,73]. DfE is a systematic way of incorporating environmental attributes into the design of a product. The three unique characteristics of DfE are that the entire life-cycle of a product is considered, it is applied early in the product realization process and that decisions are made using a set of values consistent with industrial ecology, integrative systems thinking or another framework of sustainability. DeMendonça and Baxter propose the adoption of DfE Principles by the US companies as measure to comply with international standardisation ISO 14000 [74].

(xi) Design through the 12 Principles of Green Engineering, which provide a framework for scientists and engineers to engage in when designing new materials, products, processes, and systems that are benign to human health and the environment [75–77].

(xii) Draft Principles of Green Engineering resulted from the Sandestin Conference, where a significant group of engineers and designers reviewed some of the previous principles and collecting them into several common thematic areas, i.e. (1) embody a holistic, systems approach to risk reduction, (2) minimize the use of non-renewable resources, (3) minimize complexity, (4) account for all wastes and dispose of them appropriately and (5) utilize life cycle concepts [64].

(xiii) The 12 Principles of Engineering for Sustainable Development endorsed by the Royal Academy of Engineering is one of the most recent approaches. The 12 guidelines are: (1) look beyond your own locality and the immediate future; (2) innovate and be creative; (3) seek a balanced solution; (4) seek engagement from all stakeholders; (5) make sure you know the needs and wants; (6) plan and manage effectively; (7) give sustainability the benefit of any doubt; (8) if polluters must pollute... then they must pay as well; (9) adopt a holistic, '*cradle-to-grave*' approach; (10) do things right, having decided on the right thing to do; (11) beware cost reductions that masquerade as value engineering; (12) practice what you preach. Some of these principles contain previous approaches, for instance, Principle (7) includes the precautionary principle, and Principle (3) includes most of the 12 Principles of Green Engineering. Several cases studies are included within the manual given. These cases studies are analysed applying the principles at five different stages of the process design, namely: (1) framing the requirements, (2) scoping the decision, (3) planning and detailed design, (4) implementation, delivery and operation and (5) end of usable life ('*the grave*') [65].

A categorised classification of the sets above considering the stage of implementation, the group of people involved, the main disciplines covered and the content is presented in Table 1. This table intends to be a quick selection guide to help the reader in the selection among the different set of principles according to their needs. Some of the sets are applicable to one design stage but no for another one, however, during the selection process, we strongly recommend using all of them as a fountain of ideas. Then, one or two of the sets can be chosen as a model for the analysis.

The principles themselves are too broad and qualitative in general. Vanegas suggested for the Architecture, Engineering and Construction (AEC) industry that every principle, from any source such as these, can be made operational by expressing it in terms of (1) specific objectives, (2) associated measurable goals, and (3) a detailed execution plan to achieve them [78].

Table 1
Quick selection guide for the sets of principles

Sets of principles	Stages of relevance						Group					Disciplines				Guide	
	Framing	Scoping	Design	Implement/ Oper.	End-of-use	Auto	Managers	Designers	Architecture	NGOs	Government	Chemical Eng.	Electrical Eng.	Civil Eng.	Politics	Technical	Ethical
1. Precautionary principle	*	*	*				*	*				*	*	*			*
2. Earth Charter principles	*	*	*				**					*			**		*
3. Natural step	*		*	*	*		*	*							**		*
4. CERES	*	*	*	*	*	*	**	**	*			*	*	*		**	*
5. Bellagio principles						*			**	*	**				*		*
6. Ahwahnee principles	*	*	*	*				*		*				***	*		*
7. Interface steps to sustainability	*	*	*	**	*		*	*				*				**	*
8. Twelve principles of GC	**	*	*					*				**				**	
9. Hannover principles	*	*	*	*	*			*				*		**		*	*
10. DfE key strategies	**	**	**	**	**			**				***	*			**	
11. Twelve principles of GE	*	*	*	*	*			**				**				**	
12. Sandestin principles of GE	*	*	*	*	*		*	*				**	*	*		**	*
13. Principles of engineering for sustainable development	**	**	*	*	*		*	*				***	**	**		*	*

* Adequate; ** Very adequate; *** Excellent.

In general, all these principles are intimately related with different aspects of the design, operation and implementation of the products, processes and systems. For instance, the well-known "12 Principles of GE" can be classified into six main areas, i.e. raw materials (principles 6, 9 and 12), energy use (principles 3, 4 and 10), production system (principles 5 and 8), prevention (principle 2), design (principle 1) and product use (principles 7 and 11). As Segars et al. indicated the 12 Principles demonstrate a move beyond the traditional paradigms of quality, safety, and performance to consider environmental, economic, and social factors [79]. However, we consider that their authors offered them as recommendations rather than statement principles, because these principles have been inferred from actual designs from organic biological and chemical systems on a molecular level large-scale industrial technical systems that are considered to be sustainable. Therefore, the 'principles' alone are not enough for the creation of the right framework of design towards sustainability and they need to be accompanied with base philosophy and a range of specific indicators and tools.

4.3. Green engineering frameworks for design

Many of the frameworks currently proposed for achieving sustainability in the chemical and process industry have been enounced based on the sets of principles listed above some of them have been created as a response to an urgent need or to a disaster. These frameworks are explained as follows.

Singh and Falkenburg presented, early in 1993, one of the first GE frameworks for the integrated design of products and processes [62]. The approach was strongly limited by the handled definition of GE only based on waste reduction. The authors presented a framework based on linear programming to find maximums and minimums of steady-state material and energy balances. Besides the approach given by the authors stands quite distant from what now is understood as GE, it set up the basis of the current approaches using multiple-objective programming (MOP).

Thomas and Graedel defined important research issues in sustainable consumption aimed at stimulating the creation of analytical frameworks for materials use and the environment [80]. Although important questions are formulated in this work, the paper is too focussed on technical aspects and major topics such environment (e.g. land use) and society (i.e. human development) are only schematically mentioned.

Diwekar proposes a structure where GE principles are introduced as early as possible at all levels of engineering decision-making [81]. The author establishes a framework for design based almost completely in process simulation models and multi-objective optimization tools. The 12 Principles of GE are categorized in those that have qualitative objective (i.e. principles 1, 2, 7, 9, 11 and 12) and those that declare design directions (i.e. principles 3, 4, 5, 6, 8 and 10). Five levels of implementation are considered. Level 1, innermost level corresponding to models for process simulation, steady-state process simulators are employed for this task. Level 2, a sampling loop, aimed at obtaining real data from the system to cope with the uncertainty of predictions. Probabilistic models are used for these simulations. Level 3 accounts for a continuous optimizer for decision-making for design and operating conditions. The gradient method (e.g. Jacobian) is used to approximate the way in which the maximum or minimum is obtained. Level 4, is a discrete optimizer for discrete decisions. Finally, Level 5 is a MOP that optimizes the algorithm numerically. Although this kind of framework can be of use in specific design problems, the solution relies in having a valid model too much, and it does not consider dynamics of the system. The way in which the principles are included in the design process is not clear and not easy of implementation. Moreover, the concept of sustainability is not fully present, not considering social dimension at any level.

Lapkin et al. proposed a methodology based on hierarchical approach for the evaluation of what they call the 'greenness' of chemical processes [82]. Existing environmental indicators are combined into a hierarchical multi-objective evaluation of the greenness of different chemical technologies to enable the comparison between alternative technologies. Four vertical hierarchy levels with their own stakeholders, system boundaries and possible indicators are considered: product and processes, company, infrastructure and society. This work is a useful approach for the comparison of technologies but again does not consider the dynamics of the system. The selection of the indicators for each level conditions the final result. The authors illustrate the methodology presenting a concise case study for the recovery of volatile organic chemicals (VOCs) using monolithic adsorbents.

Chen and Shonnard incorporated environmental considerations into all stages of chemical process design using a traditional hierarchical approach [83], similar to the 'onion's approach' given by Smith [84]. Their framework for design divides the design process in two parts: early design and detailed design. The goal of early design task is to screen a large number of reaction pathways and raw materials, to simulate a base-case flowsheet and then to create an improved flowsheet. In detailed design, the objective is to optimize a small number of flowsheets starting with the improved base-case flowsheet for each remaining process. MOP includes economic and environmental assessment is the heart of this approach. Detailed case study comparing benzene and n-butane routes for the production of maleic anhydride is included. As for all the previous cases, only steady-state simulations are included. Hierarchical approach is limited to process, economical and environmental dimensions, no social considerations are included within the algorithm.

Batterham proposed a hierarchical framework of sustainability based on the existing metrics that consist of five minimum levels connecting global and individual goals [85,3]. Level 1 refers to global objectives, level 2 to industry strategies, level 3 to enterprise targets, level 4 to specific projects and finally level 5 to individual actions and measured outcomes. The author advices of the risks associated with becoming too concentrated on one level of the sustainability hierarchy and losing sight of the big picture. Thus, a certain grade of interaction in both vertical and horizontal dimensions is required for a maximum efficiency.

Level 1 is mentioned in the next section, where sustainable development is briefly reviewed, nevertheless, more specific literature is recommended for detailed information. Level 2 refers to broad industrial strategies and it is related to what the basic green philosophies have stated, i.e. Cradle-to-Cradle, Zero Waste, Biomimicry and Ecological Design, introduced in Section 3. In this paper we want to focus our attention in the mid-level of the hierarchy. Green Engineering and Green Chemistry are presented and discussed in detail as the main tool to tackle levels 3 and 4, mainly concentrated in proper process design.

Dr. Vanegas offers an excellent road map and an initial set of guidelines for implementation of built environment sustainability [78]. The work is presented under an architectural view, but its deepness in the design satisfies many of the requirements of the design for the chemical and process industry. Five essential elements, the built environment (residential, non-residential, industrial and civil facilities), the natural environment (air, water, soil and biota), the resource base (built environment, industrial base, natural capital, economic capital and social capital), the industrial base (production systems for goods, products and services) and people (individuals, families, communities and organizations), the trinomial [environment and ecological] + [economic and financial] + [social, cultural, political and regulatory] systems and both spatial and temporal scales constitute the basis of sustainability. The system under study is complex and several characteristics are key for achieving the goal of sustainability:

(i) The system is enveloped by the combination of social, economical and environmental systems.
(ii) Intra- and intergenerational satisfaction of human needs and aspirations are an integral part of the outcomes of the development process.
(iii) Natural resources use has to be managed, monitored and controlled ensuring the satisfaction of actual demands but preventing total depletion.
(iv) Sustainable strategies and technologies are used proactively within every element of the system to promote development by using of environmentally conscious alternatives and substitutes to current resources and energy sources used, to prevent or mitigate environmental impacts and to correct environmental impacts when some damage to the environment already has been done.
(v) Direct reuse of reusable components, remanufacture of reusable elements, reprocessing of recycled materials, and monomer/raw material generation is actively promoted.
(vi) The system is resilient; the achievement of sustainability means a continuous movement towards the right goal.

The author proposes a three-level action to tackle the problem; firstly, strategic level (what, with what and how), secondly, tactical level and finally operational level (project definition and integrated project design). Operational level considers all fundamental aspects and phases of engineering designs including sustainability at all levels. This level is exhaustively explained in the cited work.

Other authors have developed specific indexes that clarify the use of the principles. Sheldon, for instance, have expanded the concept of atom efficiency as a key to waste minimization in the chemical and process industry, putting special attention to the fine chemical and pharmaceutical industry [86]. The E

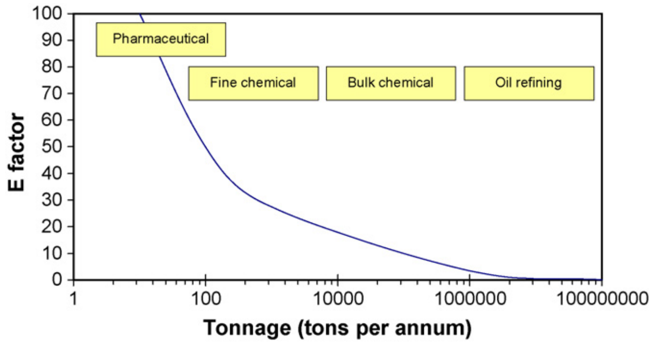

Fig. 7. Typical industrial E factors (adapted from [86]).

factors, defined as kg of waste per kg of desired product (defining waste as everything except the desired product), have become a widely used index for the quick evaluation of performance and environmental harm in the industry (see Fig. 7).

The concept of atom efficiency is used for the rapid evaluation of the amount of waste generated; however, more precise calculation must consider mass balances of the entire plant, taking into account other non-stoichiometric material streams such as utility consumption, purges, etc. In order to evaluate the environmental impact, the author introduced the term Environmental Quotient, EQ, which is the product of E factor times and arbitrarily assigned unfriendliness quotient, Q, which is function of the toxicity and easiness of recycling among others of the product. Advances in heterogeneous catalysis are the central example to demonstrate how E factor can be reduced by hundreds of times in comparison to traditional non-catalytic routes. Gronnow et al. presented the criterion of "Golden atom economy" to help in deciding whether a reaction is 'green' or not [87]. According to this criterion a green simple reaction should produce at least 0.618 mass units of target product per mass unit of all reactants used (E-factor > 0.618). The authors analysed thoroughly ca. 250 reactions discovered between 1828 and 1999 using this criterion. Moreover, Gronnow et al. include energetic consideration in their discussion what completes the analysis very well.

The Wuppertal Institute has developed, the MIPS unit, a measure which serves as an indicator of precautionary environmental protection [88]. MIPS stands for Material Input Per Service unit. MIPS can be applied on several levels e.g. for products and services, enterprises, households, regions and national economies. The environmental impact potential of a product is assessed on the basis of the life-cycle-wide material input, in other words: the fewer raw materials used, the less environmental impact ensues.

The calculation of the MIPS requires the estimation of the use of resources from the point of their extraction from nature: all data corresponds to the amount of moved tons in nature, thus to the categories of biotic or renewable raw material, abiotic or non renewable raw material, water, air and earth movement in agriculture and silviculture (incl. erosion). All material consumption during manufacture, use and recycling or disposal is calculated back to resource consumption.

There are three indicators to consider during the analysis. First, the Material Input (MI) which indicates the material input for the manufacture of one ton. MI initially gives adequate information if one wishes, for example, to compare various material alternatives. Second, Material Intensity (MIT) is the material input in relation to weight unit. Finally, when these material intensities are applied to a specific service unit, the index is called MIPS.

In the MIPS concept, the material inputs are divided into five different input categories. These five categories are: abiotic raw materials, biotic raw materials, earth movements in agriculture and silviculture (mechanical earth movement or erosion), water and air. A range of MI factors are periodically published and verified by the Wuppertal Institute [89]. The calculation of MIPS proceeds in seven steps: (1) definition of aim, object and service unit, (2) representation of process chain, (3) compiling of data, (4) MI "From cradle to product", (5) MI "From cradle to grave", (6) from MI to MIPS and (7) interpretation of results. These steps are basically independent of whether the calculations are made manually or with the help of an appropriate computer programme.

A detailed example based on the pig iron (raw iron, 4–5% carbon content) production is presented within the documentation of the index.

Life Cycle Assessment (LCA), as defined by SETAC, is 'a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to effect environmental improvements' [90–93]. It follows the life cycle of a product, process or activity from extraction of raw materials to final disposal, including manufacturing, transport, use, re-use, maintenance and recycling, i.e. from 'cradle to grave'.

LCA has been incorporated as a convincing environmental management aid within the ISO 14000 Environmental Management Systems (EMS) [94], EU Eco-Management and Audit Schemes (EMAS) [95], and EU Directive on Integrated Pollution Prevention and Control (IPPC) [96,97] requiring companies to have a full knowledge of the environmental consequences of their actions, both on- and off-site.

LCA applicability is two-fold. Firstly, LCA can be used for the quantification and evaluation of the environmental performance of a product or a process helping decision makers on choosing among alternatives. Secondly, it provides an excellent knowledge-base for engineers and environmental managers in the assessment of potential improvements in the environmental performance of the system.

The importance of LCA for process selection within EU Directive on IPPC [96], lays in the requirement of the consideration of the environment as a whole, including indirect releases, consumption of raw materials and waste disposal when choosing the Best Available Technique (BAT) to carry out an industrial activity.

Azapagic have reviewed exceptionally most of the important applications of LCA in different regulatory and environmental frameworks [98].

On the other hand are placed ecolabels. An ecolabel can be defined as 'a seal or logo indicating that a product has met a set of environmental or social standards' [99] ecolabelling systems exists for both food and consumer products. Both systems were started by NGO's but nowadays the EU has legislation for the rules of ecolabelling and also has their own ecolabels for food and for consumer products. EU ecolabel started to encourage the promotion of environmentally friendly products. The scheme came into operation in late 1992 and was designed to identify products which are less harmful to the environment than equivalent brands. The labels are awarded on environmental criteria set by the EU. They cover the whole life cycle of a product, from the extraction of raw materials, through manufacture, distribution, use and disposal of the product. The first products to carry the EU eco-labels were washing machines, paper towels, writing paper, light bulbs and hairsprays.

The achievement of an ecolabel endows companies with an emblem that differentiates their product from other products [63,5]. It is a recognition of environmental quality. The last intention of an ecolabel is to convince the consumer of such quality, and thus in some way to sell the product. However, as for the LCA to obtain and maintain an ecolabel involve a continuous process of improvement.

4.3.1. Renewed European policy for chemicals, REACH

REACH (Registration, Evaluation and Authorisation of Chemicals) is the current reform of the EU previous chemical policy. On 27 February 2001 the EU Commission issued a White Paper on a Strategy for a future Chemicals Policy [100]. This has subsequently been developed and extensively discussed with major stakeholders, resulting in the release on 29th October 2003 of the Commission's proposal (REACH). The REACH Regulation was formally adopted on 18 December 2006 by the Council of Environment Ministers following the vote in second reading of the European Parliament on 13 December 2006. REACH will enter into force on 1 June 2007 [101]. Under REACH enterprises that manufacture or import more than one tonne of a chemical substance per year would be required to register it in a central database. This legislation is based in the substitution of hazardous substances with safer alternatives whenever available, the so-called 'Substitution Principle'.

The previous EU legislative framework for chemical substances was a patchwork of many different Directives and Regulations which has developed historically. There are different rules for "existing" (before 1981) and "new" chemicals (after the 1981 cut-off date). While new chemicals have to be tested before they are placed on the market, there are no such provisions for "existing" chemicals. Thus, although some information exists on the properties and uses of existing substances, there is generally a lack of sufficient information publicly available in order to assess and control these substances effectively. Currently, the European Chemicals Bureau (ECB) provides scientific and technical support to the conception, development, implementation and monitoring of EU policies on dangerous chemicals [102]. There will be a period of 11 years and 3 months to register all the substances after REACH entry into force.

This reform has become one of the most intensely discussed pieces of legislation in EU history because of the importance of the matter and the economical side-effects in the chemical industry. The global production of chemicals has increased from 1 million tonnes in 1930 to 400 million tonnes today. We have about 100,000 different substances registered in the EU market of which 10,000 are marketed in volumes of more than 10 tonnes, and a further 20,000 are marketed at 1–10 tonnes. The chemical industry is also Europe's third largest manufacturing industry.

REACH forces the study and knowledge of the toxicological effects of chemical substances. Nevertheless, for low volume chemicals, which constitute two-thirds of the substances covered by REACH, the system is too flexible and it does not require basic health and safety information. From a GC & GE point of view the actual requirements of REACH are not enough because the analysis is still at the end-of-pipe. No requirements of post-use handling, life cycle analysis, double-use, design for degradation, energy intensive production processes, etc. are considered. However, the industrial sector is distrustful stating that this legislation adds even more steps for the development of new products and compounds and it will cause Europe fall behind the US, China, India and Japan in the chemical industry. It is a difficult step forward but a global policy towards sustainability is still a pending deal.

4.3.2. European integrated pollution prevention and control directive (IPPC 96/61)

The EU has a set of common rules for permitting and controlling industrial installations in the Integrated Pollution Prevention and Control (IPPC) Directive of 1996 [96,97]. In essence, the IPPC Directive is about minimising pollution from industrial sources throughout the European Union covering ca. 50,000 installations. This directive sets an ideal framework for the boosting of GE through the modification of current design conditions.

The IPPC Directive (96/61) calls for specified manufacturing operations to comply with its requirements and have a permit to operate under the regime by 2007. The manufacturing operations covered by IPPC are defined within Annex 1 of the Directive and cover a range of industries; from chemicals production, refining, power generation through to intensive farming and food and drink operations.

Under the legislation an operator of an IPPC installation must apply for a permit through the submission of a technical application. The application needs to address actual operational conditions demonstrating that Best Available Techniques (BAT) are used at the installation to ensure an acceptable environmental impact. A brochure of BAT is created for each particular case and the further analysis will depend on the installation and the system boundaries. Currently, a total of 33 activities have been analysed, approximately in half of them the final document has been formally adopted by the Commission; all of reports (final and draft) are ready available online [97]. Examples of sectorial guidance notes are large volume organic chemicals, refineries, chlor-alkali industry, paper industry, etc. There are also cross sector (horizontal) guidance notes, covering general industry issues such as wastewater treatment, cost benefit analysis, cooling systems, energy, etc.

Procedurally, IPPC places a great emphasis on having a good Environmental Management System (EMS) whereby the impacts of operations and environmental performance metrics are fully understood. This influences 'critical to environment' operating procedures, the definition of improvement projects and their design scope, amongst other considerations.

Bob Hudson, suggested that the requirements of the IPPC Directive will influence the role of the European process engineer in many areas [103]. In affecting the role of the process engineer, IPPC will influence the design remit of a project, its commissioning strategy, promoting the use of 'Green Engineering Principles' within the project from the early stages of the design including, for instance, decommissioning plan at the end of the asset life in design.

Legislative frameworks are, in essence, a 'cradle to grave' approach to sustainability which indirectly cover benefit operation from new equipment and system design through to decommissioning of assets. But, in practical, all the efforts done to modify existing installations to comply with this strict legislative framework will help in the understanding of current technologies and finding opportunities of their transformation into more sustainable technologies. Thus, IPPC Directive is based on several principles, namely (1) an integrated approach, (2) best available techniques, (3) flexibility and (4) public participation.

1. The integrated approach means that the permits must take into account the whole environmental performance of the plant, covering e.g. emissions to air, water and land, generation of waste, use of raw materials, energy efficiency, noise, prevention of accidents, and restoration of the site upon closure. The purpose of the Directive is to ensure a high level of protection of the environment taken as a whole.
2. The permit conditions including emission limit values (ELVs) must be based on Best Available Techniques (BAT). As a result of this a number of BAT Reference Documents (the so-called BREFs) are free available. These documents concisely explain the fundamental guidelines for design towards sustainability analysing precisely both existing and novel innovative technologies.
3. The IPPC Directive contains elements of flexibility by allowing the licensing authorities, in determining permit conditions, to take into account: the technical characteristics of the installation, its geographical location and the local environmental conditions.
4. The Directive ensures that the public has a right to participate in the decision making process, and to be informed of its consequences, by having access to permit applications in order to give opinions, permits, results of the monitoring of releases and the European Pollutant Emission Register (EPER) [104]. In EPER, emission data reported by Member States are made accessible in a public register, which is intended to provide environmental information on major industrial activities. EPER will be replaced by the European Pollutant Release and Transfer Register (E-PRTR) from 2007 reporting period onwards.

4.3.3. The European initiative, SusChem

The European Technology Platform (ETP) for Sustainable Chemistry (SusChem) was initiated jointly by Cefic and EuropaBio in 2004 aimed at fostering and focus European research in chemistry, chemical engineering and industrial biotechnology [105]. The platform is integrated by three subplatforms, namely, Industrial Biotechnology, Materials Technology and Reaction & Process Design. Firstly, Industrial Biotechnology, includes different research areas, i.e. Novel enzymes and microorganisms, Microbial genomics and bioinformatics, Metabolic engineering and modelling, Biocatalyst function and optimisation, Biocatalytic process design, Fermentation science and engineering, Innovative downstream processing. Secondly, Materials Technology which combines fundamental understanding of structure property relationship, computational material science, novel analytical techniques, scale-up strategies, bio-based performance and nanocomposite materials and chemistry for Nanoscience. Finally, Reaction & Process Design, catalysis, biotechnological processing, process intensification, in-silico techniques, purification and formulation engineering and plant control and supply chain management.

The initiative is ambitious and comes almost half a decade later than the US and Japan. SusChem aims to revitalise chemistry and biotechnology innovation in Europe. The vision that the platform proposes is very product-development-oriented and it is divided in a large number of different sectors of research which will require of a good coordination, but on the other hand it covers almost all of the fields within the chemical industry. There is not specific funding within the European Framework Program for Research, FP7, for the period 2007 to 2013 addressed directly to sustainable technologies. This means that the research in this way will be camouflaged somewhere in between of the different specific themes and as a result of this the achievements will be difficult to measure and evaluate. The importance of the platform in joining efforts and merging opportunities is obvious.

4.4. Industrial issues

General guiding principles reinforces the idea of sustainability for the chemical and process industry designs but specific actions are required at practical levels. Thus, for instance, principle 4 of GE accounts for the maximization of mass, energy, space, and time efficiency, but it is rather generic to decide whether we need to integrate or not a heat exchanger of our cooling system. The European Integrated Pollution Prevention and Control Bureau (EIPPCB) methodology is a good example of a combination of both horizontal and vertical approaches. At the first stage, basic issues about energy efficiency are answered, such as definitions of energy efficiency, how to measure/calculate energy efficiency, how to find relevant indicators and boundaries (installation, site, etc.), energy efficiency indicators and how to use them, benchmarking may be possible/desirable within a company/plant but not between several companies, best existing or future practices (best available technologies) and provision of energy audits [106]. Then, the list of best available techniques (BATs) is given, such as, heat recovery systems, steam production and networks, heat pumps, energy storage or heat exchangers.

Invista Technologies in collaboration with the Clean Technology Group at the University of Nottingham, UK, has patented a novel process for the synthesis of TA [107]. They achieved a continuous selective partial oxidation of *para*-xylene (*p*-X) in supercritical water catalyzed by $MnBr_2$ in high yield. Supercritical water has been shown to be a very effective reaction medium for this synthesis. The reaction is a partial oxidation of *p*-xylene to TA with oxygen as oxidant (cleavage of H_2O_2 by temperature). And the operation conditions are: $T = 200–400\,^{\circ}C$; $p = 24–28$ MPa. This new reaction pathway avoids completely the generation of undesired intermediates which are difficult to separate from the final TA product. This original process simplifies the equipment enormously, even when it adds an inherent complexity in the design of the new equipment because of the higher pressures and temperatures.

Another striking example using supercritical fluids is found in the textile industry. In traditional textile dyeing processes, water is used as solvent for dye. However, this causes environmental and economic problems. The water that remains after the process contains residual dye and its purification is costly. Furthermore, an energy demanding drying step is required after dyeing with water. Dyeing using $scCO_2$ at 30.0 MPa and 100 °C instead of water mitigates these problems, the dye can be separated easily from the CO_2 and hence both can be recycled at once [108]. Furthermore, no drying step is needed after the process. The heat and mass transfer enhancement at supercritical conditions allow this process to be competitive achieving high dyeing rates.

One application of ionic liquis not yet implemented but with good expectations is the electrodeposition of metals from ILs studied by Prof. Abbot. The main problem with metals is the corrosion. One of the best methods to control this corrosion is the electrodeposition of a metallic coating that passivates on contact with the environment and prevents the oxidising agent reaching the substrate. This surface engineering has applications in a wide range of industrial sectors. Hard chrome plating plays a critical role in civil, automotive, maritime and naval industries. The major disadvantage of the current process is that requires the use of chromic acid-based electrolites comprising hexavalent Cr(VI), highly toxic and carcinogenic. ILs choline-metal based are conductors and can be used as electrolytes for the electrodeposition of the desired metal, Cr(III) for instance. Running the process like this, vapours are not produced and efficiencies up to 90% are achieved. The process is currently in the beta-test scale using 50 litre baths to coat hydraulic systems with chromium [109].

Segars et al. examined EcoWorx product under the framework of the 12 principles of GE [79]. EcoWorx product is a carpet tile, which is a particular product category that bridges almost all commercial market services. It is used as a floor in a great number of buildings, from housing to plan office environments. Within the analysis the authors issued important parts of the integral design, such as the replacement of PVC and phthalate plasticizer by low-density polyethylene (LDPE) and other minor materials (principle 1), or the minimization of energy by using LDPE extrusion. The authors presented an exhaustive analysis principle by principle. The analysis represents again a cradle-to-grave approach, but improving the current technology augments the knowledge-base a great deal for future designs.

In a recent paper Davis applies the principles of GE to the concept of low-impact development (LID) [110]. LID represents the application of Pollution Prevention and waste minimization policies to land development focussed on water and pollutants balances. The author analyses the design, management practices and system boundaries, including societal and economic issues, encountered during the application of LID-GE principles to achieve sustainable development in land and water use. Thus, in order to reduce run off flow of pollutant loads (e.g. ammonia, nitrate, iron, copper, etc.) a porous paving and swales were installed into a parking lot of the Florida Aquarium Tampa. As a result of this, the entire water-pollutants volume was kept on-site during small storm events and eventually infiltrated or evapotranspired. This solution leaves behind traditional development infrastructures which tend to move the problem to other place by flushing of pollutants into the local waterways ('the solution to pollution is dilution'). However, as the author pointed out, solving the problem like this raises other environmental issues, such as pollutants ownership, which needs to be fixed too, e.g. removing layer of pollutant bioretention periodically. From our point of view, as we have repeated several times through the manuscript, the application of one technique or discipline alone to cope with a complex problem is not always efficiently enough towards sustainability. Here, the idea of waste is present from the beginning to the end (e.g. garbage trucks, pollutant emission, etc.); therefore the solution given applying the principles of GE cannot be fully implemented.

Good examples of green product development are the designs of Haworth and Steelcase, two office-furniture makers that have developed two chair designs, Zody and Think, which have won an environmental certification from McDonough and Braungart Design Chemistry firm (MBDC) [111]. In both chairs recycled materials account for more than 98% but it should be noted that, as these designers claim, a virgin material can be also a good option when the recycling process is more harmful than the use of fresh material. One of the keys of design is the 'design for disassembly' (DFDA) which allows for the complete recycling of all functional parts. Think chair's back have been made of short-glass filled nylon as a more convenient alternative in the afterlife than long-glass nylon. Nevertheless, as short fibbers exhibit lower flexural modulus a better frame's geometry have been required, i.e. extra engineering time. This leads to a 36% reduction in materials use (from 50 lbs to 32 lbs per chair). Less weight implies fewer materials, lower shipping costs and less environmental impact of transportation. Moreover, Think's back treaded connection allows for the back being flipped down and more chairs can be loaded per truckload. The Zody uses a single bolt assembly which results in a simpler, more reusable and quicker assembly. In addition to this, the complicated chair control system has been redesigned taking inspiration from cockroach's forward-bending, bouncy legs. The result 'spring' control system produces more fluid adjustments and saves a lot of weight (see Fig. 8).

Fig. 8. Hayworth's Zody chair's spring control system detail.

McDonough and Braungart have defined their own "Index of Sustainability" as: 'MBDC's service and design tool that evaluates a product's materials and processes so that redesign for sustainability can take place. The index is a proprietary service and design tool that can be used to continuously track and monitor progress toward sustainability during the process of redesign' [112].

Ecoefficiency was defined as a management philosophy by the World Business Council for Sustainable Development (WPCSD [113]) in 1993 following the 1992 Rio Summit [4]. Ecoefficiency expresses the ratio of economic creation to ecological destruction. As defined by the WBCSD, "ecoefficiency is achieved by the delivery of competitively priced goods and services that satisfy human needs and bring quality of life, while progressively reducing ecological impacts and resource intensity throughout the life-cycle to a level at least in line with the Earth's estimated carrying capacity." This institution has developed a comprehensive ecoefficiency learning module. It includes practical approaches may help organizations in the integration of eco-efficiency into their thinking, practices and processes [11]. BASF has successfully developed a tool of ecoefficiency analysis to address strategic, politics, research and market place issues [114–118]. These tools are based in different target areas of sustainability as schematised in Fig. 9.

How can an engineer convince his or her boss in '5-min time' that an idea is both economical and environmentally worth? Many times, if not in most of the cases, ideas thrive at industrial management level only if they are economically attractive. BASF's portfolio is both rigorous and enjoyable presenting economic and environmental features at similar levels, calculated over the whole life cycle of products and processes. Environmental impacts are determined on the basis of five six main aspects: the consumption of raw materials, the consumption of energy, resulting emissions, the toxicity potential, the abuse and risk potential and the use of area. Preparation of specific life cycle analysis follows the rules of ISO14040ff. This methodological approach ensures that, a lot of detailed data are available additionally to the final result, which is shown in the portfolio of the study. When two products have the same ecoefficiency index these products are represented at the same distance from the diagonal. Four main types of products are identified: star (right-up corner) when the product has a great economic value and is environmentally friendly, dinosaur (left-bottom corner), is the opposite to star, i.e. when the product is both cost-intensive and harmful, frog (left-top corner), means a environmentally friendly product which need to reduce its production costs and finally the pig (right-bottom corner) is a economically profitable product which is harmful to the environment and needs to be redesigned with a greener criteria (Fig. 10) [116]. Sensitivity analyses are performed to identify all hypothetic scenarios in which the product may be or may be not ecoefficient. These analyses are represented as different 'ways' within the plot.

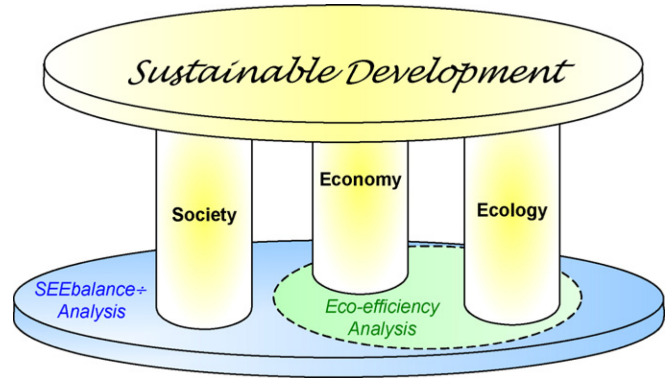

Fig. 9. BASF's Sustainable development tools.

BASF group presented the method analysing one of their basic products, Indigo dye for jeans and five different dyeing processes with using it. More than 800 products and processes have been analysed so far, some of them are available within BASF's website. For instance, Figs. 11 and 12 shows the portfolio for

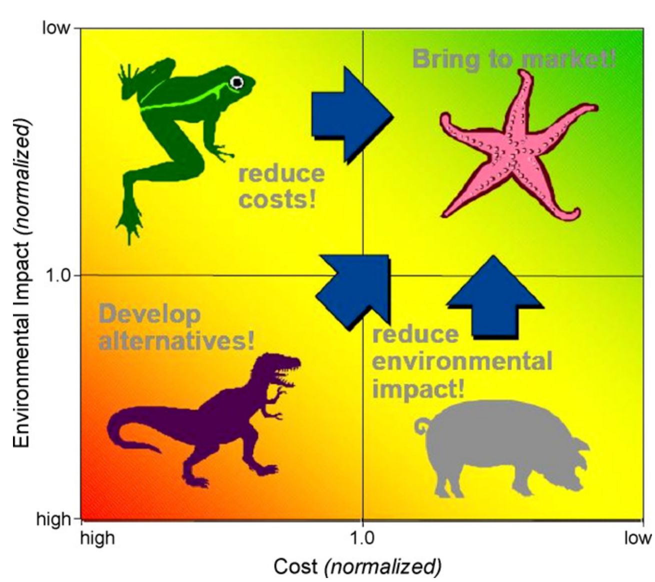

Fig. 10. BASF's ecoefficiency analysis.

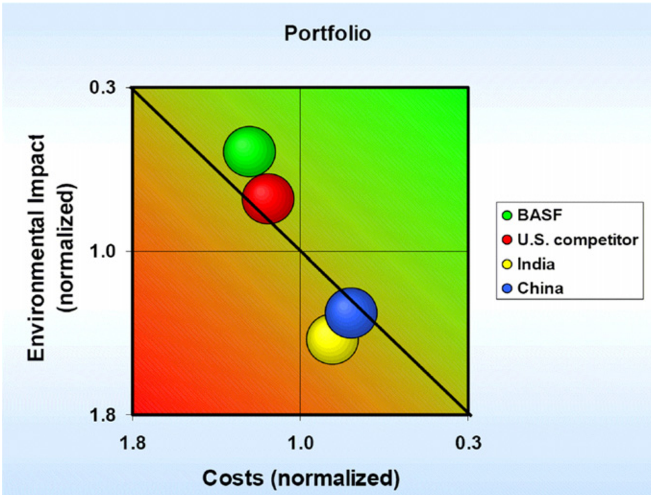

Fig. 11. BASF ecoefficiency portfolio for ibuprofen.

case of the production of ibuprofen the portfolio comparing eco-efficiency among four different industrial manufacturers. The ibuprofen from BASF and its US competitor exhibit similar eco-efficiency levels, as it can be seen from the figure. On the other hand, the ibuprofen made in India and in China is clearly less ecoefficient than the other two.

BASF group has recently developed another tool which includes also societal dimension, SEEbalance® [119,120]. This novel evaluation tool represents the three-dimensions not in a plain triangle but in a spatial cube where a vector quantifies how much of each of the dimensions is fulfilled within the system under observation.

Jenck et al. have published an excellent review of a range of industrial case studies showing that 'industrial sustainable chemistry is not an emerging trend, but is already a reality through the application of 'green' chemistry and engineering expertise' (using their words). They have identified six main industrial challenges, namely, renewable resources, eco-efficient products, energy efficiency and sustainable energy, waste reduction and waste reuse, reduction of greenhouse gases and other emissions and inherently safer processes [121].

4.5. Useful tools for green engineering

In order to help in the design, several computerised-aided solutions are currently available. Most of this software is prepared for and end-point analysis, i.e. at the end of the process design; only few of them can be applied at early stages. Table 2 compiles many of these solutions both commercial and freeware. A brief description is included.

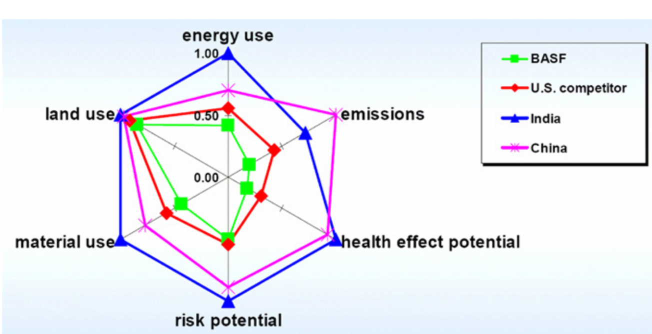

Fig. 12. BASF ecoefficiency fingerprint for ibuprofen.

Among the different software solutions designed to help engineers of both university and industry world in processes Aspen Suite is one of the most popular, which covers a wide range of applications. For instance, Aspen HYSYS® and Aspen Plus™ for process simulation and optimization, Aspen DMCplus™ for advanced process control, Aspen PIMS™ for advanced planning & scheduling, and Aspen InfoPlus.21™ for plant information management are useful utilities for design within Chemical Engineering. AspenONE includes a full complement of specific software for Oil & Gas, for Petroleum, for Chemicals, for Specially Chemicals, for Consumer Products, for Pharma and for Engineering & Construction [126]. Its importance is due to a wide range of companies in the world employ this software in their processes. Campbell, Degussa, Dow Chemical, DSMa and Dupont are an aliquot of these companies. Many of these specific software packages, applied in the right way, may help in the improvement of green techniques for the design of products and processes. These tools should be introduced at early stages of design and included chemical engineering curriculum, so that, future engineers will be able to design towards sustainability.

Our research group has presented recently a guidance tool for assessment, Green HAZOP (g-HAZOP), oriented to process improvement in terms of GE [127]. The main structure of g-HAZOP is based on the widespread Hazardous and Operability analysis (HAZOP) and ENVOP technique. We have taken this similarity as a design objective to prepare the Green HAZOP tool for three main reasons are: (1) the learning of how to use the resulting tool will be easier and quicker, (2) sharing data will save man-hours and (3) the implementation of the tool within an engineering company will have more chances of success. g-HAZOP is a useful tool for finding problems and non-green situations of chemical plants. Several guide words (e.g. no, less, more) are applied to different areas and target variables such as raw materials and products, process, efficiency, integration, controllability, and life cycle, analysing how the system would evolve under different deviations. The results are recommendations for improvement towards sustainability. It must be noted that the g-HAZOP analysis requires detailed design information and an expert team to be carried out properly. This means that this tool is better to be used during detailed engineering phase, commissioning or operation of the plant. At these stages the design is firmly defined and only small changes are allowed.

5. Main challenges in education

The role of engineers and designers at all scales, molecular, products, processes, and systems, is going to be central and essential in determining what tomorrow will look like. A chemical engineer, as the designer of products and processes also has a central role in designing chemical processes that have a minimal impact on the environment. Green Engineering uses the same traditions of brilliance, innovation, and creativity, which

Table 2
Green engineering software

Software	Description	Source or company
SRD	*Source Ranking Database* performs a systematic screening-level review of over 12,000 potential indoor pollution sources to identify high-priority product and material categories for further evaluation. Can also identify the products that have contained a specific chemical Produces risk-based rankings by multiplying an estimated indoor-air concentration by a hazard score for each chemical in a given product or material and for each environment in which the product/material is used	EPA and Versar Inc. [122]
UCSS	*Use Clusters Scoring System* identifies and screens clusters of chemicals ("use clusters") that are used to perform a particular task. A use cluster is a set of chemicals that may be substituted for one another in performing a given task Also UCSS identifies clusters of potential concern and provides an initial ranking of chemicals using human and environmental hazard and exposure data from a number of sources	EPA [122]
ChemSTEER	*Chemical Screening Tool For Exposures and Environmental Releases* estimates occupational inhalation and dermal exposure to a chemical during industrial and commercial manufacturing, processing, and use operations involving the chemical Also ChemSTEER estimates releases of a chemical to air, water, and land that are associated with industrial and commercial manufacturing, processing, and use of the chemical	EPA [122]
E-FAST	*Exposure and Fate Assessment Screening Tool* provides screening-level estimates of the concentrations of chemicals released to air, surface water, landfills, and from consumer products Estimates provided are potential inhalation, dermal and ingestion dose rates resulting from these releases. Modeled estimates of concentrations and doses are designed to reasonably overestimate exposures, for use in screening level assessment	EPA [122]
EPI SUITE	The Estimation Programs Interface (EPI) Suite^{TM} is a Window based suite of physical/chemical property and environmental fate estimation models. EPI Suite^{TM} uses a single input to run the different estimation models	EPA [122]
ReachScan	Estimates surface water chemical concentrations at drinking water utilities downstream from industrial facilities serving as a database for the identification of facilities and utilities. Estimates the number of days per year that an aquatic ecotoxicological concern concentration will be exceeded in the subject stream or stream segment	EPA and Versar Inc. [122]
IGEMS	Internet Geographical Exposure Modeling System (IGEMS) brings together in one system several EPA environmental fate and transport models and some of the environmental data needed to run them. IGEMS includes models and data for ambient air, surface water, soil, and ground water, and makes the models much easier to use than their stand-alone counterparts. IGEMS will have graphics and Geographical Information System (GIS) capabilities for displaying environmental modeling results	EPA [122]
MCCEM	*Multi- Chamber Concentration and Exposure Model* estimates average and peak indoor air concentrations of chemicals released from products or materials in houses, apartments, townhouses, or other residences. The model can be used to assess other indoor environments (e.g. schools, offices) if the user can supply the necessary inputs MCCEM estimates inhalation exposures to these chemicals, calculated as single day doses, chronic average daily doses, or lifetime average daily doses. (All dose estimates are potential doses; they do not account for actual absorption into the body)	EPA and Versar Inc. [122]
WPEM	The Wall Paints Exposure Assessment Model estimates the potential exposure of consumers and workers to the chemicals emitted from wall paint which is applied using a roller or a brush	EPA and Versar Inc. [122]
LCA	LCA systematically describes and assesses all flows to and from nature, from a cradle to grave perspective. The basis of any LCA study is the creation of an inventory of the inputs and outputs of most processes that occur during the life cycle of a product. This includes the production phase, distribution, use and final disposal of the product. It is also known as Life Cycle Analysis or Ecobalance	PER [123]
SimaPro 7	The SimaPro family allows you to implement Lifecycle Assessment in a flexible way. The new SimaPro 7 provides you with a professional tool to collect, analyze and monitor the environmental performance of products and services. You can easily model and analyze complex life cycles in a systematic and transparent way, following ithe ISO 14040 series recommendations	PER [123]
Umberto	Umberto visualizes material and energy flow systems. It is the tool for advanced process, flow and cost modeling. With its graphic interface even the most complex structures can be modeled: production facilities in a company, process and value chains and product life cycle	German ifu Hamburg GmbH in cooperation with Ifeu. PER [123]
ECO-it	ECO-it software allows you to model a complex product and its life cycle in a few minutes. ECO-it calculates the environmental load, and shows which parts of the product's life cycle contribute most. With this information you can target your creativity to improve the environmental performance of the product. ECO-it uses Eco-indicator scores to express the environmental performance of a product's life cycle as a single figure	PER [123]
Eco-indicator	The Eco-indicator 99 is a state of the art, "damage oriented" impact assessment method for LCA, with many conceptual breakthroughs. The method is also the basis for the calculation of eco-indicator scores for materials and processes These scores can be used as a user friendly design for environment tool for designers and product managers to improve products	PER [123]
SDLC	Software Development Life Cycle is also known as Classic Life Cycle Model (or) Linear Sequential Model (or) Waterfall Method. This model performs activities such as System/Information Engineering and Modeling, Software Requirements Analysis, Systems Analysis and Design, Code Generation, Testing and Maintenance	Stylus Systems Inc. [124]
Gabi4	GaBi 4 provides solutions for different problems regarding cost, environment, social and technical criteria, optimization of processes and managing your external representation in these fields	PE Europe GMBH Life Cycle Engineering, IKP University of Stuttgart [125]

are the legacy of the engineering disciplines, within the context and perspective of environmental, economic, and social benefit [76]. Introducing GE design guidelines at the start of the design process can lead to sustainable processes and products and so to a sustainable future. This new application of engineering excellence towards sustainability is definitely a complex and important challenge that science and technology have to face as soon as possible.

The changing nature of engineering education provides additional motivation for the insertion of 'environmentally conscious design' in engineering curricula. Programs must have a 'major design experience that incorporates engineering standards and realistic constraints that include the following considerations: economic, environmental, sustainability, manufacturability, ethical, health and safety, social and political' [128].

Education is crucial to expand understanding, skills, and motivation to shift society towards sustainable development [129]. The educational system produces professionals who ultimately develop products and processes and who run and manage production systems. For the case of engineering, education is an essential premise to promote concepts such as sustainability, GE and pollution prevention, especially at universities and other institutions of higher education which are closer to professionals. Sustainability-oriented teaching and research is not only important in natural and technological sciences, but also in economics and business administration [130].

The need to introduce GE concepts to undergraduate and graduate students has become recognized to be increasingly important by industry and the general populace. Major chemical companies such as DuPont, BP, Dow, Merck and Rohm and Hass have adopted a green approach, to move toward a sustainable future [131]. Obviously educators and universities have a role to establish appropriate educational materials and information for societal consumption and also judge the effectiveness of the knowledge transfer [132].

Stewart and Hesketh, Professors of Chemical Engineering at Rowan University have reported their education experience in the introduction of GE within CE curriculum. For them, introductory material and energy balances course is a logical place to initiate the students in the basic terminology and concepts of GE. The level of GE material is quite elementary since the objective is to give students some familiarity with concepts that would form the basis for more substantial GE problems in subsequent courses such as transport phenomena, thermodynamics, reactor design, unit operations, separations, plant design, process control and even specialized courses in biotechnology and nanotechnology. The authors suggest that GE elementary knowledge may be introduced at the first-semester sophomore level and therefore integrates concepts in a way that the student starting a chemical engineering program can readily understand [133].

Moreover, one practical way to teach GE into freshman engineering is to take advantage of students' knowledge in their customary life. For example, students usually are very familiar with products such as coffee machines, computers, hair dryers and common household toys, because they have been exposed to these items since birth. They can discover a large number of individual components and are ask to conduct a life-cycle assessment of these materials. Rowan University professors as educators employ this technical and they can prepare their students to use the risk assessment tools of GE to design new processes and modify existing processes.

In Europe the scenario is completely different now. GE has not been fully understood yet, and this is the first step to be included in the curriculum. European higher education institutions have accepted the challenge and undertaken a main role in constructing the European area of higher education from the joint declaration of the European Ministers of Education convened in Bologna on the 19th of June 1999 (in the wake of the fundamental principles laid down in the Bologna Magna Charta Universitatum of 1988). Universities have independence and autonomy to ensure that higher education and research systems continuously adapt to changing needs, society's demands and advances in scientific knowledge. The construction of the new European higher education framework will be a long way where consensus among the different agents, i.e. students, teachers, university managers and governmental representatives, is critical. This particular moment is an exceptional occasion to adapt Chemical Engineering studies to the newest requirements including Green Engineering within Chemical Engineering curriculum.

A common method to introducing GE has been through a senior/graduate level elective course on environmental engineering or pollution prevention with emphasis on the end of the processes treatment. Actually, GE material is incorporates in a number of ways: as a require course, as an elective and as a modules in core courses. As a result, GE could become a central component of the engineering curriculum. So instead of having only an optional course in environmental or GE, it would be more appropriate to integrate GE concepts and principles into a range of courses within an engineering discipline and often into the design sequence.

When the selected approach is to place GE courses at the end of their university formation period (for example as a master or PhD formation) it can leave the impression that environmental aspects should be considered when the design is already finished. Since one of the precepts of GE is that it should be conducted at all levels of engineering practice and design it is necessary the creation of the suitable framework for the right inclusion of GE at early stages of the formation.

Within the process of adaptation we spot the following steps but not limited to: (1) identification of the current state-of-the-art, capabilities and future necessities, (2) analysis of core and special courses, topics and activities, (3) find core and special training opportunities, (4) find cross-linking training opportunities, (5) definition of the Agenda of implementation within the structure i.e. grade, master and doctorate, (6) pilot project implementation and testing, (7) modifications to the plan, (8) final approval and implementation and (9) monitoring of the plan.

The 20th century will be remembered because of the industrial development and because of the explosion of scientific and technological ideas and inventions that have revealed the main basis of Science. However, it was at the end of this century when the term sustainable development entered on the scene. We believe that it wasn't a coincidence; it was an imperative necessity of equilibrium, because all that promising technological development grew up following short or mid-term objectives, creating dramatic environmental consequences.

Now, at the beginning of the 21st century we are ought to develop novel guidelines, methods and procedures for design and innovation towards sustainability. Unfortunately, the last two decades have shown that the movement towards sustainable development has more inertia than the movement towards technological development and economic growth.

6. Conclusions

Chemical Engineers will play an essential role as designers and managers of hundreds of different products, processes and production systems which are currently or might be in the future the base of the welfare state. Green Engineering aims at transforming traditional Chemical Engineering practices into a more practices. There are two possible ways of approach: and inductive approach where general rules are given and designers follow these rules to create and improve PPSs and a deductive approach, where successful sustainable case studies are presented as the model for design. The deductive approach is often more common because it only depends on one's criteria, so, a broad portfolio of green solutions is available in the literature. The inductive or 'academic' approach has been adopted in this paper.

Green Engineering feeds on a wide variety of muse-disciplines and theories, it is of crucial importance to identify the needs for an specific applying the correct approach to the general design philosophy, to safety, to the chemistry, to the product and to the process and to the auxiliary facilities. Our hypothesis is that the continuous adaptation of GE is the very base of sustainability in the chemical and process industry and that is the main reason to feed on all these disciplines. Principles of GE cannot be static, because environment, society and economy are dynamic. Therefore, Chemical Engineers are called to identify, assimilate and study the way in which these disciplines can be included within the design criteria to achieve sustainable solutions.

In this review manuscript, we have compiled several successful examples at both professional and academic levels which are the basement of sustainable design in the chemical and process industry. As a result of the dissemination of these examples designers can 'deduce' what have done other colleagues towards sustainability.

Finally, it must be highlighted that education in GE is the key weapon to tackle the current needs. GE has to be introduced at academic and industrial levels to create a critical mass of engineers and scientists to undertake this challenge as soon as possible.

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