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Exergy: Its Potential and Limitations in Environmental Science and Technology

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New technologies, either renewables-based or not, are confronted with both economic and technical constraints. Their development takes advantage of considering the basic laws of economics and thermodynamics. With respect to the latter, the exergy concept pops up. Although its fundamentals, that is, the Second Law of Thermodynamics, were already established in the 1800s, it is only in the last years that the exergy concept has gained a more widespread interest in process analysis, typically employed to identify inefficiencies. However, exergy analysis today is implemented far beyond technical analysis; it is also employed in environmental, (thermo)economic, and even sustainability analysis of industrial systems. Because natural ecosystems are also subjected to the basic laws of thermodynamics, it is another subject of exergy analysis. After an introduction on the concept itself, this review focuses on the potential and limitations of the exergy concept in (*1*) ecosystem analysis, utilized to describe maximum storage and maximum dissipation of energy flows (*2*); industrial system analysis: from single process analysis to complete process chain analysis (*3*); (thermo)economic analysis, with extended exergy accounting; and (*4*) environmental impact assessment throughout the whole life cycle with quantification of the resource intake and emission effects. Apart from technical system analysis, it proves that exergy as a tool in environmental impact analysis may be the most mature field of application, particularly with respect to resource and efficiency accounting, one of the major challenges in the development of sustainable technology. Far less mature is the exergy analysis of natural ecosystems and the coupling with economic analysis, where a lively debate is presently going on about the actual merits of an exergy-based approach.

1. Introduction to the Exergy Concept

In science classes everywhere, students learn “Energy can neither be created nor destroyed. It just changes forms”. This scientific fact about what science calls energy is not what people experience in their everyday lives. What is typically called “energy” comes in a myriad of tangible forms for which people and businesses pay money — energy in the form of gasoline, electricity, natural gas, etc. Although the scientific energy is conserved, this other energy, “useful energy” or “marketplace energy” is not. The word energy as used by science and the word energy as used in everyday life carry two distinct meanings. The first refers to an abstract additive, conserved property that is tremendously useful in modeling. The second refers to *exergy*, which quantifies the ability to cause change, and this is certainly not conserved. These basic thermodynamic considerations date back from the 1800s; see Supporting Information S1 for a historical overview. As will be shown in this review, marketplace or useful energy has its own value to science and technology.

By definition, the exergy (Ex) of a system or resource is the maximum amount of useful work that can be obtained from this system or resource when it is brought to equilibrium with the surroundings through reversible processes in which the system is allowed to interact only with the environment. The environment used in the calculations must be chosen properly, for example as the so-called “dead state”. The exergy concept was originally derived by Gibbs as a special case of Gibbs’s available energy. He referred to this as “the available energy of the body and medium” when the body is surrounded by a “medium at constant temperature and pressure”, see Supporting Information S1 and S2. In practice, transformation of resources through a process results in work, heat, and/or products, byproducts, and wastes that embody part of the intake exergy. The final exergy embodied in the delivered work, heat, primary and secondary products, and waste is not equal to the initial exergy content of the resources: the difference is dissipated through irreversible entropy generation. In fact Gouy and Stodola independently showed that the absolute value of this loss of exergy (Ex_{loss}) is equal to the entropy production (S_{gen}) multiplied with the temperature of the surroundings (T_0): $Ex_{loss} = T_0S_{gen}$ (Figure 1).

The exergy or work potential of a system (or resource) is usually split up into four contributions: potential exergy due to its position in a given body force field (gravitational, magnetic, etc.), kinetic exergy due to its velocity with respect to a fixed reference frame, physical exergy due to its pressure (P) and temperature (T) being different from the surroundings P_0 and T_0, and chemical exergy due to its composition being different from the surroundings. Systems without kinetic,

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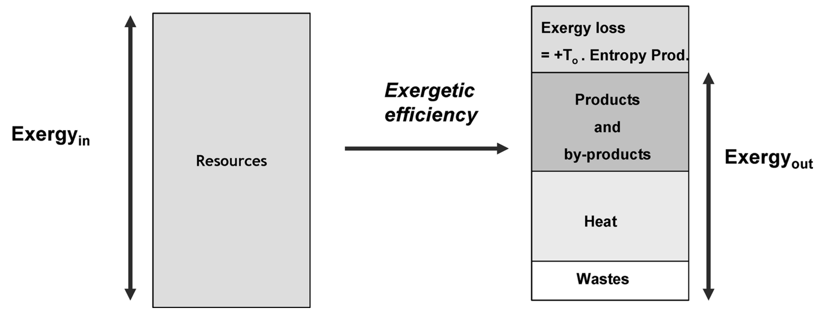

FIGURE 1. Second Law analysis of a real process.

potential, and physical exergy are considered to be at the environmental state; systems without even chemical exergy have no potential at all and are considered to be at the dead state, being in full equilibrium with the surroundings: they cannot produce any work.

Potential and kinetic exergy are equivalent to potential and kinetic energy; physical exergy can be calculated from the enthalpy (h) and entropy (s) of the system at its actual T and P and at environmental T_0 and P_0 (eq 1).

$$\mathrm{Ex_{ph}} = (h - T_0 s) - (h_0 - T_0 s_0) \quad (1)$$

Equation 1 represents the physical exergy transport by a flowing stream, per unit of mass flow. The physical exergy content of a material, per unit mass, equals $u + P_0 v - T_0 s - g_0$, where u is the internal energy, v is the volume, and g is the Gibbs free energy, each per unit mass. The calculation of chemical exergy is somewhat more complex. For a resource, one considers a reference compound in the natural environment for each chemical element in the resource material, for example, O_2 for O, $Cl^-_{(aq)}$ for Cl, and SiO_2 for Si. These ground states are the most probable (i.e., most common in the lito-, hydro- and atmosphere) products of the interaction of the elements with other common compounds in the natural environment and typically display a high chemical stability. A reference species can be selected from the atmosphere (gaseous compounds), hydrosphere (dissolved ionic compounds), and the lithosphere (solid compounds). The exergy value of a pure reference compound is prescribed by geochemical data: its relative occurrence in the natural environment. Starting from the exergy of the reference species, the chemical exergy of any resource substance can be calculated through thermochemistry. The first chemical exergy data were mainly published in the 1970s and were later summarized in the books of Kotas (*1*) and Szargut et al. (*2*), with recent updates by Szargut et al. (*3*) and De Meester et al. (*4*). Given the standard Gibbs energy of the reference reaction ΔG°_{r} (kJ/mol) (*4*), the chemical exergy of a compound i, $\mathrm{Ex}^0_{\mathrm{ch},k}$ (kJ/mol), is computed by eq 2,

$$\mathrm{Ex}^0_{\mathrm{ch},i} = \Delta G^0_{\mathrm{r}} + \sum_k \nu_k \mathrm{Ex}^0_{\mathrm{ch},k} \quad (2)$$

where ν_k and $\mathrm{Ex}^0_{\mathrm{ch},k}$ are the number of moles and the standard chemical exergy (kJ/mol) of the kth reference species, respectively. The suffix "0" denotes that the reference system is assumed to be at the standard "environmental" temperature T_0 (usually 298.15 K) and pressure P_0 (usually, 1 bar or 101325 Pa).

In practice, two techniques have been proposed to approximate the chemical exergy: the group contribution methods (e.g., ref (*2*)) and the use of so-called "β values", exergy-to-energy ratios that link, in a lumped sense, the energy to the exergy content of an energy stream. The β values depend on the atomic composition of the resource under consideration (*2, 5*).

TABLE 1. Summary of Exergy (Ex) Calculations for Different Kind of Resources, Where β is the Exergy-to-Energy Ratio

resource	exergy value or calculation method
	β in $\mathrm{kJ_{exergy}/kJ_{energy}}$
potential energy	$\beta = 1$
kinetic energy	$\beta = 1$
physical energy	$\mathrm{Ex} = (h - T_0 s) - (h_0 - T_0 s_0)$
chemical energy	$\beta = \sim 0.8$ to 1.0, depending on composition
heat at temperature T	$\beta = 1 - T_0/T$ [a]
pressure of an ideal gas at T_0	$\mathrm{Ex} = nRT_0 \ln (P/P_0)$
solar irradiation (whole spectrum)	$\beta = 0.9327$
nuclear energy	$\beta \approx 1$
electricity	$\beta = 1$
radiation	$\beta = 1 + (1/3)(T_0/T)^4 - (4/3)(T_0/T)$

[a] Note that when $T < T_0$, β is negative. This is because the resulting exergy flow is in the opposite direction of the energy flow.

TABLE 2. Exergy Destruction and Loss in a Simple Steam Power Plant (*6*)

description	type	exergy destruction or exergy unrecovered in % of the fuel exergy
steam generator combustion	destruction	30
steam generator heat transfer	destruction	30
turbine	destruction	3
condenser	destruction	5
pump	destruction	negligible
stack gas	loss	3
cooling water	loss	2

The above are "classical" exergy forms, but the exergy of radiation, electrical, and nuclear energy can also be calculated. As a summary, a number of rules of thumb are summarized in Table 1.

Although (scientific) energy is adequate for successful modeling of thermal processes, it is, at best, highly misleading when it is applied for analysis purposes, that is, to identify the process inefficiencies and to provide insight on how to reduce these inefficiencies. The superiority of exergy is readily demonstrated by considering a simple natural gas fired steam Rankine cycle, operating at 6000 kPa with "typical" values for stack gas temperature, cooling water temperature rise, etc. Carrying out the modeling, followed by writing exergy balances on each component, yields the results in Table 2. The "ratio" gives the percent of fuel exergy either destroyed in a component or exhausted into the environment. The results contrast with a traditional energy analysis. Here, energy is conserved, so all inefficiencies are attributed to energy losses. Thus, in this plant, all losses would be attributed to the stack gas (2%) and cooling water (6%). Because this plant has only a single product, an energy analysis thus suggests that to improve the process efficiency, the energy losses associated with the cooling water and the stack gas should be reduced. This is clearly not true, and an exergy analysis clearly points at the true sources of inefficiency.

The major process inefficiencies occur here in the steam generator, where nearly sixty percent of the fuel exergy is destroyed. This is due to (a) heat transfer from very high temperature combustion products to the relatively low temperature boiling water and (b) the combustion process itself. The next largest source of inefficiency is the condenser, although the 5% destruction and 2% loss are an order of magnitude smaller than those of the steam generator. Note that the cooling water exergy loss, 2%, is negligible compared to the 60% that an energy analysis would attribute to cooling water; also, the 3% stack loss is significantly less than the 10−15% energy content.

The utility of exergy analysis goes beyond technical systems; it can also be applied to complete chains as observed in natural and industrial processes, as discussed in Sections 2 and 3, respectively. Moreover, it is also enlightening to look at the exergy flows in national economies as it was done for the United States (*7*), Ghana (*8*), Sweden (*9*), Brazil (*10*), Turkey (*11*), Norway (*12*), Italy (*13*), and even for the whole earth system (*14–16*). Exergy, and not energy, is the true measure of something's ability to cause change; it is also the unit to which costs should be assigned. The relationship between exergy and money has been referred to as "thermoeconomics", "exergoeconomics", or "exergy cost accounting", and is discussed in Section 4. Finally, because exergy analysis is also applicable to overall production and consumption chains, that is, from cradle to grave or from resource intake down to emission, it has also been used to assess the environmental impact of production chains (section 5).

2. Exergy in Natural Systems Analysis

2.1. The Ecosystem Exergy Concept. Several 20th century scientists such as Lotka, Morovitz, and Prigogine have tried to make use of thermodynamics to explain the most probable behavior of complex natural systems at macroscopic scales, and more ecosystem development theories emerged, as illustrated in Supporting Information S3. Based on these early works, Schneider and Kay (*17*) proposed a reformulation of the second law as to adapt it to open systems far from equilibrium. It explains the development of self-organizing structures exposed to exergy flows, as well as the ability of complex systems to dissipate exergy flows at the fastest rate possible. This so-called ecosystem exergy concept suggests that ecosystems tend to develop structural and functional attributes that lead to more effective degradation of the energy flows passing through the system. Consequently, it has been formalized as being derivable from two axiomes: the maximum storage and the maximum dissipation principle (*18*). The maximum storage principle means that for any site with given abiotic features and a given local gene pool the ecosystem tends to develop toward the state with the highest possible exergy content in terms of biomass, genetic information, and complex structural networks (*19, 20*). The maximum dissipation principle means that for any site the ecosystem strives to attain the maximum degradation of the input exergy flows (*21*). Both principles were linked by Svirezhev and Steinborn's minimax principle (*22*) stating that during the process of self-organization ecosystems tend to maximize their exergy in respect to the increment of information and to minimize it in respect to their radiation balance. This link could be considered as a generalization of the Carnot cycle to open systems far from equilibrium: the more exergy is captured, the more work is available for maintenance and for dissipation (*23*). Therefore, the exergy concept may be consistent with Paltridge's hypothesis of maximum entropy production (MEP) (*24, 25*). It must be stated that the maximum exergy dissipation principle has not yet been proven or demonstrated experimentally. In the cover story of the New Scientist of October 5, 2004, the late James Kay hypothesized that exergy dissipation is a goal function of ecosystems and human systems because they operate in agreement with the second law as entropy machines, contributing to a faster entropization of their environment. Recent work by Dewar (*26, 27*) tried to give a stronger theoretical underpinning for maximum entropy production as an organizational principle, but was criticized by Bruers (*28*).

The ecosystem exergy concept constitutes an attractive proposition, having parallels with other ecosystem theories and showing as varied as promising applications (land use impact assessment, sustainability evaluation of ecosystem management), but its premises and conclusions are still being strongly debated. Some of the criticism on the ecosystem exergy concept is perhaps based on a misunderstanding: it seems contraintuitive that maximum exergy storage and dissipation by the ecosystem would be compatible with entropy maximization of the environment. Another problem has been the ongoing confusion about the information exergy concept and about the difference between informational exergy storage and information entropy (also called Shannon entropy (*29*)). The news featured in Nature stating that "MEP theory can possibly explain why the places with most energy, the tropics, are also the most diverse — or in other words, entropic" (*30*) is illustrative for this confusion. Both of these issues are addressed in Supporting Information S4.

Finally, it is necessary to highlight the relationship between exergy analysis in natural and human-industrial systems. The essential difference is that in natural systems exergy dissipation is assumed to be maximized whereas in human-industrial systems exergy consumption is minimized, or better, the efficiency of its use is optimized. This apparent paradox can be explained by the fact that the human-industrial system is somehow a subsystem that separated itself from the ecosystem, but is still strongly depending on it for its life support. As a consequence, maximizing exergy dissipation by the human system might entropize the ecosystem and ultimately reduce the overall entropy production of the combined natural−human-industrial system.

2.2. Exergy as Ecological Indicator. The 24 heuristic criteria to estimate ecosystem maturity proposed by E.P. Odum (*31*) can be considered the first list of ecological indicators derived from ecosystem theory. Ever since, several attempts have been made to use the ecosystem exergy concept to derive indicators quantifying the degree of self-organization, or integrity, of an ecosystem (*32, 33*). Such indicators are particularly relevant in the context of an ever-expanding anthroposphere that endangers the natural life-support systems (*34*). Rosen (*35*) confirmed that the biggest asset of ecosystem exergy analysis is that it can measure the increase in disorder in ecosystems associated with human environmental impact. The two main indicator approaches found back in literature are exergy storage and exergy dissipation.

The exergy content of ecosystems cannot be measured straightforward, but it can be calculated from the exergy stored in its various components. Bendoricchio and Jørgensen (*20*) proposed to calculate the exergy content of an ecosystem component as the probability of producing the considered component at thermodynamic equilibrium. For the biological components of an ecosystem, this probability consists of the probability to produce the organic matter (classical exergy term) and the probability (P_i) to find the genetic code, that is, the correct nucleotide sequence of the DNA (informational exergy term). On the basis of this reasoning, they derived the following formula for ecosystem exergy (eq 3) (*20, 36*),

$$\mathrm{Ex} = (\mu_1 - \mu_1^{\mathrm{eq}})\sum_{i=1}^{N} c_i - RT_0\sum_{i=2}^{N}(c_i \ln(P_i)) \qquad (3)$$

where Ex is exergy, μ_1 is the chemical potential of organic matter at actual environmental conditions, μ_1^{eq} is its chemical potential at thermodynamic equilibrium, and thus the difference ($\mu_1 - \mu^{\mathrm{eq}}{}_1$) is the specific free energy of detritus (18.7 kJ/g), c_i is the concentration of the ith component (in g), N is the number of components (taxa) in the ecosystem, and T_0 is the temperature of the environment (in K). Component $i = 1$ is detritus (dead organic matter); components from $i=2$ are taxa (commonly species). In the second (informational) term the summation starts from $i=2$ because detritus contains no active genetic information anymore. The chosen reference state for this calculation is composed by all inorganic elements that form a living organism in their highest oxidation state when no chemical exergy is left (*36*). In the original formula, P_i was calculated as 20^{-700g} where 20 is the amount of essential amino acids used in proteins of living organisms, g is the amount of genes in species i, and 700 is the average amount of encoded amino acids in a gene, which is a rather rough approximation, given the occurrence of nonsense DNA and the lack of data on the amount of genes (*37*). Susani et al. (*36*) improved the formula by calculating P_i as $4^{-a_i}(1-g_i)$ where 4 is the amount of nucleotides coding amino-acids in living organism, a_i the amount of nucleotides in the genome, and g_i the percentage of repeating genes. Using the formula shows that the informational part of the exergy is much higher than the chemical exergy of organic matter (*36*), which makes the formula highly criticized (see Supporting Information S4). Accounting for the exergy storage for a whole ecosystem including all taxa remains rather impractical.

Exergy storage can also be roughly estimated by simple proxy indicators (*38*): total biomass or free net primary production (the fraction of net primary production that is not harvested and stays available for life support functions (*39*)) for the classical exergy term, and species richness relative to the regional species pool (*40*) for the informational term.

The exergy dissipation activity by an ecosystem is determined and compared with that of a reference system. Schneider and Kay (*21*) hypothesized that because the main exergy source in ecosystems comes from the sun, ecosystem thermal indicators would be suitable for measuring the exergy dissipation of an ecosystem. This assumption was supported by measured data from groundborne (*41*), airborne (*42, 43*), and satellite remote sensing (*44*), which showed an unmistakable trend that, under constant site and measurement conditions, more developed ecosystems degrade the reradiated energy more and thus show a cooler surface temperature (*45*). On the basis of these observations, Luvall et al. (*46*) proposed to calculate solar exergy dissipation (SED) from thermal remote sensing as follows,

$$\mathrm{SED} = \frac{R_{\mathrm{n}}}{K^*} \qquad (4)$$

where R_{n} is the net all-wave radiation in W m^{-2}, that is, the net available energy dissipated through storage, evapotranspiration, and sensible heat, and K^* is the net shortwave (0.3–3.0 μm) radiation in W m^{-2}. This ratio produces the fraction of net radiation that is converted to lower exergy thermal heat. It embodies the exergy degradation rate of an ecosystem. It is larger for more developed ecosystems, which also show lower surface temperatures (*46*). Exergy dissipation

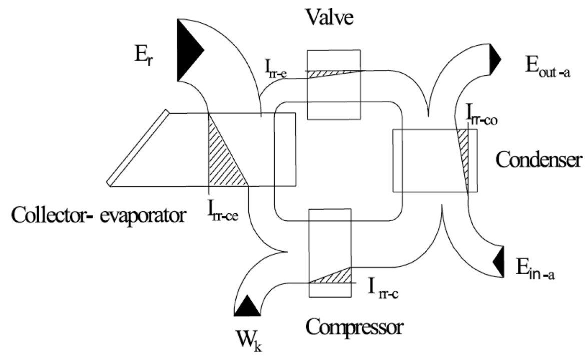

FIGURE 2. Visualisation of the exergy analysis of a solar assisted heat pump, with exergy flows (E, in W) and irreversibilities (I_{rr}, in W) associated with solar radiation r, electric power W_k, ingoing air in-a, outgoing air out-a, expansion valve e, condensor co, compressor c, and collector-evaporator ce (based on ref *51*).

measurement has found relatively little application so far, mainly because of the technological limitations (limited availability of satellite or aerial instruments, low spatial and thermal resolution, difficult calibration, problems with emissivity (*45*). An example of ecosystem evaluation using exergy storage and exergy dissipation indicators is given in Supporting Information S5.

3. Exergy in Industrial Systems Analysis

Analysis of industrial systems has probably been the most common application of exergy, and several books (*1, 2, 47–50*) and hundreds of papers have been published over the last four decades. The research in this area may be broadly categorized into (a) methodological developments and (b) applications to specific industrial processes and their supply chains. In addition, decision-support systems and techniques based on exergy and traditional cost or economic analysis have also been developed. The focus of this section is primarily on methods for and applications of exergy analysis to industrial processes. Some extensions to account for industrial supply chains are also briefly discussed.

Most of the publications on exergy analysis of industrial processes focus on the flow and loss of exergy through the specific process units, as illustrated in Supporting Information S5. This information is then used to identify opportunities for improving process efficiency by modifying parts of a process that have maximum loss of exergy.

3.1. Analysis Methods. Exergy analyses of industrial systems often result in different types of graphical representations, the most popular being the Grassmann diagram, as illustrated in Figure 2 (*51*). Japanese researchers frequently make use of vector diagrams. Yamamoto and Ishida (*52*) make use of process vectors on a thermodynamic compass representing exergy and enthalpy changes of substances through a process. By drawing the vectors on a process flow diagram, characteristic features of an entire process can be represented on a single diagram. Exergy vector diagrams have been applied to several typical processes and reactions (*48*). In the vector diagram, endothermic processes occupy the third and fourth quadrants, and exothermic processes occupy the first and second. Similarly, spontaneous processes occupy the second and third quadrants, and nonspontaneous processes occupy the top first and fourth. This diagram is best used to quantify the net exergy loss of processes consisting of multiple reactions or other operations. Such insight can help in selecting efficient subprocesses and reactions among several alternatives.

Among the thermodynamic process design methods, those based on pinch analysis (*53*) have been very popular for the synthesis of heat exchanger networks. Extensions to other exchange networks including mass, water, waste, etc. have also been developed. The relationship between pinch analysis and exergy analysis has also been explored by many researchers. Pinch analysis has evolved into a widely used approach for the design of networks in chemical processes. Exergy analysis permits a more comprehensive analysis of process systems and different energy types but cannot be a direct substitute for pinch analysis (*54*). The reverse is also true, because pinch analysis makes no direct and explicit use of an entropy concept. Combinations of exergy analysis and pinch analysis have been shown to be quite effective for design and improvement of processes (*55–58*), including ways of accounting for reactions in composite curve analysis (*59*). Applications of exergy analysis have been mostly on mechanical processes, and challenges and opportunities for using exergy analysis for chemical process optimization and synthesis have been identified (*60, 61*). Furthermore, exergy analysis tools integrated with chemical process simulation tools such as AspenPlus have also been developed (*62, 63*).

3.2. Illustrations. Exergy analysis has been applied to a variety of thermo-mechanical, chemical, and other manufacturing processes. Some of these are briefly discussed in this section.

Energy Technologies — Nonrenewable. A large number of studies have focused on exergy analysis of processes based on conventional coal combustion, and more recently on more advanced methods such as gasification and chemical looping. Theoretical and application studies on coal-based power plants have used exergy analysis to identify that the steam generating boiler is a dominant source of inefficiency (*64–66*). These papers suggest various ways of enhancing process efficiency by reducing gradients, like adjusting the condenser back pressure or decreasing the excess combustion air. A survey of such methods is found in Rosen and Dincer (*67*). Other coal-based processes have also been areas of active research, including gasification, simultaneous generation of power and chemicals (*68*), integrated gasification and coal combustion (IGCC) processes, and a coal gasification fuel cell based cogeneration plant (*69*). IGCC processes have been analyzed for improving their performance (*70*) via approaches such as reducing exergy destruction during combustion by recuperating waste heat from gas turbine exhaust (*71*) or by integrated production of chemicals such as dimethyl ether (*72*). The added value of an exergy analysis for detection of inefficiencies is illustrated in Supporting Information S6.

Methods that exploit the chemical exergy of fossil fuels without direct combustion have been receiving increasing attention due to their promise for greater efficiency and the likely ease of separating carbon dioxide for sequestration or other uses. Many variations of chemical looping have been studied via exergy analysis. This includes systems based on fossil fuels such as methane and coal (*73–75*), using hydrogen (*76*), and solar hybrid systems (*77*). As in other applications, almost all papers use exergy analysis to identify opportunities for improving efficiency and demonstrate the higher second law efficiency of chemical looping combustion versus conventional combustion.

Gasification of biomass (*78–81*) shows that exergetic efficiencies are comparable to those of coal gassification, and wet biomass needs to be dried to improve its efficiency. Solar thermal decarbonization of fossil fuels has also been analyzed for improved efficiency (*82*). Rosen (*83*) compares coal versus nuclear based electricity by exergy analysis to show the higher efficiency of coal based processes. Most of the exergy losses are due to high gradients created by combustion and heat transfer. Hydrogen production and fuel cells have also been analyzed via an exergy analysis (*84*).

Energy Technologies — Renewable. Despite a history of being ignored, exergy analysis of renewable energy technologies has been receiving increasing attention as exemplified by the following representative papers. A full exergetic analysis for solar thermal, wind, and geothermal power generation systems is described by Koroneos et al. (*85*). The authors calculate exergy flows, losses, and exergetic efficiencies for each of these systems. They also include a general discussion comparing renewable sources with nonrenewable sources of energy. Their main conclusion is that renewable energy sources can not convert as much of the available energy to useful energy as nonrenewables do. However, according to the authors, this disadvantage is negligible compared with the depletion of resources when nonrenewable sources are used. Literature about photovoltaic cells is reviewed by Charalambous et al. (*86*). Several cell designs are compared on the basis of thermal and electrical efficiency, as well as a small mention of exergetic performance. Insight from exergy analysis does not seem to be the main focus of this article and is not referenced in their conclusions. Another study was performed on photovoltaic cells based on a facility tested in Colorado, but again the exergy analysis was superficial, and they simply recommend further exergetic evaluation (*87*).

Singh et al. (*88*) directly compare energy and exergy analyses of a solar thermal power system. This work clearly illustrates the usefulness of an exergy analysis, because an energy analysis locates the largest losses in the heat engine, and the largest source of entropy generation occurs in the collector−receiver assembly. The difference is that exergy expresses the quality of energy. Losses in the collector−receiver are of much higher quality energy than those in the heat engine. Wind energy has been analyzed by Sahin et al. (*89*) via an approach very similar to their work on photovoltaic cells. It defines a new method of calculating exergy efficiency for wind turbines used to make electricity. This method is applied to experimental data for a specific wind turbine. Energy and exergy efficiencies are plotted as functions of wind speed. The authors recommend the use of exergy in this field because it is more realistic and thermodynamically rigorous. Hepbasli and Akdemir (*90*) present an exergy analysis of a geothermal district heating system. It includes a Grassmann diagram of the system and recommends areas for improvement based on irreversibility calculations. A detailed exergy analysis of a geothermal power plant (*91*) calculates exergy of all significant flows. An exergy flow diagram shows the major losses in the process, which is used to identify the condensers and turbines as candidates for improvement.

Commodity Chemicals. Exergy analysis has been applied to a variety of processes for producing bulk and commodity chemicals and to specific types of chemical technology (*2, 92*). For instance, an exergy analysis of microreactor technology shows their thermodynamic superiority to conventional reactors (*93*). De Souza et al. (*94*) study ethanol steam reforming to produce hydrogen. Exergy analysis of cement clinker burning (*95*) finds that exergy loss can be minimized by reducing sludge humidity and by optimizing fuel combustion. Sorin et al. (*96*), Fiorini et al. (*97*), and Sommariva et al. (*98*) study and compare reverse osmosis and thermal desalination processes. The exergy analysis of blast furnace in steel manufacturing was published by Ziebek and Stanek (*99*). A review of exergy analysis of internal combustion engines is provided by Rakopoulos and Giakoumis (*100*). Hellstrom (*101*) analyzes nutrient recovery processes in wastewater treatment via exergy analysis. Rivero (*102*) reviews applications of exergy analysis to petroleum refining and the petrochemical industry. Ptasinski et al. (*103*) and Okazaki et al. (*104*) use exergy analysis to study the production of methanol from synthesis gas obtained via waste treatment or other sources. Other processes analyzed via exergy analysis include pulp and paper plants (*105*), distillation processes

(*106*), metallurgical industries (*107*), chlor-alkali process (*108*), and a variety of chemical and thermal processes (*52, 109–111*).

Heating Ventilation and Air Conditioning (HVAC) Processes. The work of Wepfer et al. (*112*) is one of the early applications of exergy analysis to HVAC processes. They develop methods for calculating available energy for the elementary processes used in heating, ventilation, and air conditioning, and apply them to illustrative problems. These processes include adiabatic mixing, steam-spray humidification, adiabatic evaporation, dehumidification, and direct-expansion cooling. This work is extended further by Ren et al. (*113*) by defining a different reference state to simplify calculations. The above authors identify fan efficiency as vital to the overall efficiency. The energy and exergy consumption of residential HVAC systems is compared by Zmeureanu and Wu (*114*) both with and without independent ventilation systems. Energy and exergy analysis is done for a couple of alternatives, considering also the energy mix used. Greenhouse gas (GHG) emissions are also reported for each alternative.

3.3. Cumulative Exergy Consumption. Cumulative exergy consumption (CExC) extends exergy analysis beyond a single process to consider all processes from natural resources to the final products. It is defined as the sum of the exergy contained in all resources entering the supply chain of the selected product or process. This approach can be readily extended to the life cycle by including the demand chain, as discussed in more detail in Section 5. This approach is related to cumulative energy consumption analysis or net energy analysis, but CExC can account for material and energy inputs along with their quality. The main advantage of CExC analysis is that by accounting for exergy use throughout the life cycle it may provide insight into potential improvements and for comparing alternative products. CExC aggregates a variety of resources over the life cycle, implicitly assuming substitutability and losing detailed information. As with other life cycle approaches, boundary definition and allocation of inputs to the respective outputs are important issues in cumulative exergy consumption calculation. Allocation can be based on exergy content of the coproducts instead of typical approaches such as weight or economic value.

CExC has been calculated for many common industrial processes (*2, 108, 109*). These efforts focus on the "most important" processes. Another approach is based on input−output analysis of sectors in an economy. This approach has been popular for exergy and cumulative exergy analysis of entire economies (see Section 1). Various extensions of cumulative exergy consumption have also been developed to account for additional processes and resources. Extended exergy accounting includes contibution from labor (Section 4), whereas energy and ecological CExC accounts for the contribution of ecosystem goods and services via their exergy consumption (*115*).

4. Exergy and Economic Analysis

Once exergy is recognized to be the proper quantifier for the "usefulness" of an energy or material stream, it is also immediately clear that it can be used as a sort of "production factor" in economics. The idea was first put forth by Elsner (*116*) and Fratzscher (*117*), and of course implicitly in some parts of Georgescu-Roegen's work (*118*), and of El-Sayed and Gaggioli's first attempts at thermo-economics (*119*). Later on, a systematisation was attempted by Ayres and co-workers (*120–127*). The same group also investigated the possibility of linking economic growth to the actual exergy input into a country (*124*). Although in a slightly different form, it is presently acknowledged that exergy can be considered a production factor proper and that the pro-capite exergy input into a societal system is indeed a measure of its "operational efficiency". Along this line, the work of Wall and co-workers (*8, 9, 14, 128*) introduced the idea that the total exergy input is an econometric measure of the same relevance as the gross national product (GNP).

4.1. CExC or the Exergetic Cost ("*k*"). Any production chain can be seen as a series of elemental processes, each one of which adds some exergy to its inputs, destroys some exergy in its internal irreversibilities, and delivers a product endowed with some "added exergy value". The "final" product, that is, the one that is generated at the end of the chain, therefore has a cumulative exergy content or cumulative exergy consumption (CExC) (expressed in kJ/unit of product) that can be exactly computed once the production process is known. Starting from the bottom of the production line (mouth of the mine for extracted materials, underground reservoir for gas, oil, and coal, etc.), and properly accounting for feedbacks, wastes, and recycles, recursive application of this technique leads to the calculation of one exergy cost ("*k*") or cumulative exergy consumption (CExC) for each commodity that we use in our society, including dematerialized ones such as power, electricity etc. Again, as mentioned in the previous section, proper allocation methods and system boundary definitions are required. In Valero's "exergy cost" theory, the exergy of the products is expressed as a process-dependent function of the exergy of the inputs,

$$\mathrm{CExC} = \mathbf{A}(\mathrm{Ex}_i) \tag{5}$$

where the matrix **A** is called the structural matrix of the process, and depends on the process configuration, that is, on the connectivity of the system. **A** is easily obtained by properly assembling the exergy "balances" (including the exergy destructions) of the individual components (*129*). It must be remarked that the CExC and the *k* values are, by definition, exactly the same; in spite of their rather different formalization, Szargut's and Valero's methods are indeed equivalent. For further reference, notice that the "cost" mentioned here is the cumulative amount of exergy "embodied" in the product by the successive contributions of each step in the production chain; CExC involves no monetary calculations.

4.2. Thermo-economics. The basic idea of thermo-economics (TE) is to apply the usual procedures of engineering accounting, linking the prices of components to their operating parameters and to their exergetic efficiency and pricing not the unit mass but the specific exergy content of a stream (material or energy). In its simplest form, TE computes the costs of individual exergy streams by writing monetary balances on components or subsystems of a system.

If we attribute a monetary cost to the exergetic inputs, this cost will be incrementally increased in the various steps of the process, due to the hardware and operating costs that "add to the value" of the successive production steps. Because, in general, the production chain is not strictly linear, some outputs from a certain component may be split and may constitute the inputs for two or more of the remaining components; conversely, two or more outputs may constitute the input to a different component. Therefore, to compute the cost of the final outputs (the product streams) we need to properly allocate the hardware costs (capital and maintenance, for instance) among the various outputs of each component. This can be done mathematically by means of a Lagrangian multiplier method (*119, 130*) or in a more compact and elegant way by augmenting the matrix **A** with a proper set of auxiliary "cost allocation equations" (*129*). The result is again a matricial function in the form of eq 6,

$$\mathbf{C}_{O,j} = B(\mathrm{Ex}_{\mathrm{I},k}, C_{\mathrm{I},k}) \tag{6}$$

where each $C_{O,j}$ is the monetary cost of the *j*th output O_j. Because both $\mathrm{Ex}_{\mathrm{I},k}$ (the exergy of the *k*th input flow) and $C_{\mathrm{I},k}$

(the monetary cost of the unit of the kth input) are in turn functions of thermodynamic parameters $x_{k,m}$ (pressure, temperature, chemical composition of each kth input flow), material properties $\varphi_{k,n}$ (specific heat, lower heating value, etc.), hardware design variables d_i (type and class of equipment, geometric ratios, etc.), and allocation criteria a_s (how much of the equipment cost is allocated to the jth output), the cost function $\mathbf{C}_O$ can be rewritten formally as

$$\mathbf{C}_O = \Phi(x_{k,m}, \varphi_{k,n}, d_i, a_s) \tag{7}$$

An example of this calculation is given in Supporting Information S7. Thermo-economics provides fundamental insight in the cost−formation process; it allows process engineers to assign a monetary cost to the unit of exergy of each one of the output streams on the basis of (a) a sound estimate of the losses associated with each subprocess (because they are measured by the corresponding exergy destruction) and (b) a Second-Law coherent calculation of the influence of upstream irreversibilities on downstream exergetic efficiencies.

TE has the additional advantage of using the well-established cost-accounting procedures of engineering economics and has, therefore, become very popular among process engineers and energy conversion managers, who can easily understand its paradigm. When compared with an energy analysis/accounting, it generally produces substantially different relative cost allocations among cogenerated outputs and has been widely applied to the analysis and optimization of combined heat-and-power plants, chemical distillation and refinery processes, water desalination, trigeneration plants (power, heat, and cold), etc.

4.3. Extended Exergy Accounting. It is well-known from economic theory that the cost of a product is given by the sum of capital, labor, and fuel, plus costs associated with the environmental effects of effluents and pollutants, all together making up the production function. Without further justification we can assume that the usual form employed by economists to express such a function remains valid if the cost is expressed in exergy units:

$$c_j = f(K, L, \mathrm{Ex}, M, O) \tag{8}$$

Where c_j is the exergy cost of a unit of the (material or immaterial) commodity j (J/unit of commodity), K is the amount of monetary capital (\$ or €) required by its production, L is the amount of labor (working hours), Ex is the exergy of the energy flows (both heat and power) used in the process (J), M is the necessary materials (kg), and O is the environmental remediation cost (monetary cost of the remedial action necessary to annihilate or reduce the effects of product j on the environment). The five terms inside of the brackets in the equation are called the production factors.

Extended Exergy Accounting (EEA (*131*)) was the first theory to provide a unified treatment of these issues. The specific extended exergy (Eex) is defined as the sum of the thermodynamic exergy Ex (Section 1) and the equivalent exergy of capital ($\mathrm{Ex_K}$), labor ($\mathrm{Ex_L}$), and environmental remediation ($\mathrm{Ex_O}$) activities. These equivalent exergies are expressed in joules (their fluxes in watts), and represent the amount of primary resources required to generate one monetary unit ($\mathrm{Ex_K}$), one working hour ($\mathrm{Ex_L}$), and to annihilate a certain pollution ($\mathrm{Ex_O}$):

$$\mathrm{Eex_{commodity}} = \mathrm{CExC} + \mathrm{Ex_K} + \mathrm{Ex_L} + \mathrm{Ex_O} \quad [\mathrm{J/kg, J/J, or\ J/unit}] \tag{9}$$

where we recall that CExC is the initial exergy of the raw material inputs augmented with all of the exergetic equivalents of the various energy inputs (heat, power, and where applicable, chemical) used in the production process. The fundamental premise of EEA is that economic systems are eco-systems that function only because of the energy and material fluxes that sustain human activities. All agricultural, industrial, and economic activities can only exist as long as they exploit (use) physical, chemical, and biological resources taken from a reservoir of noninfinite capacity but of practically infinite exergy capacity. From the point of view of the proponents of this method, exergetic content (and neither capital nor labor by themselves) is the correct measure for the cost of a commodity or a service. It is important to remark that EEA maintains that the monetary price tag of a commodity should not be dismissed, but rather ought to be used in combination with the one calculated on the basis of its extended exergetic content (Eex).

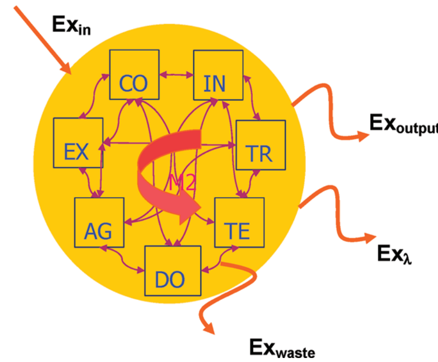

FIGURE 3. Schematic representation of the exergy flows between a society and the environment. Notice that M2 (monetary circulation) is not an exergy flow; see text for explanation. $\mathrm{Ex_{in}}$, total exergy flux into the society from its environment (J/y); $\mathrm{Ex_{output}}$, exergy content of the useful (desired) output (J/y); $\mathrm{Ex_{waste}}$, exergy content of the unused outputs (J/y); $\mathrm{Ex_\lambda}$, exergy destruction (J/y); EX, extraction sector; CO, conversion sector; IN, industrial sector; TR, transportation sector; TE, commercial/institutional sector; DO, domestic sector; AG, agricultural sector. M2 represents the monetary flow.

The numerical correlation between the Eex of the unit of labor and of capital can be established by the following reasoning: the total net exergy primary influx $\mathrm{Ex_{in}}$ (J/yr) that flows from the environment into a society (S) in the form of energy and material fluxes can be regarded as the "thermodynamic fuel" of the very large number of complex processes that describe the operation of the society. The "products" of S are all generated, used, and disposed of internally, and its only outputs are the waste materials and the waste energy that S discharges into the environment (Figure 3). The four classical production factors within S are energy (exergy), materials, labor, and capital; the first two are already contained in $\mathrm{Ex_{in}}$, whereas the last two are generated within S. We can therefore assume that both K and L are equivalent to a certain portion of the incoming exergy flux and that the extended exergy conversion factor for capital can be considered to be a certain fraction (α) of the incoming exergy flux,

$$\mathrm{ee_{K,S}} = \alpha\frac{\mathrm{Ex_{in}}}{M2}[\mathrm{J/\$\ or\ J/€}] \tag{10}$$

where α is a country-specific constant that represents the "capital intensity" of that country and, as such, is space and time dependent. The money supply, M2 (\$/y or €/y), is a proper measure of the "monetary flux": its choice is of course somewhat arbitrary, and EEA adopts the global net monetary circulation, which for each country is computed and published by the Central Bank.

By the very same reasoning Labor — and in general human services — is assigned an equivalent exergetic value equal to a portion of the total (yearly averaged) primary exergetic resource input Ex_{in} divided by the number of working hours in S:

$$\mathrm{ee}_{L,S} = \beta \frac{\mathrm{Ex}_{in}}{n_{\text{working hours}}} [\text{J/working hour}] \qquad (11)$$

The "extended exergy conversion factors" ee_K and ee_L are thus seen to represent the equivalent exergetic resource use needed for a certain society to generate one unit ($ or €) of capital and one unit (work hour) of labor. For the EEA method to be applicable, it is necessary to assume that the economic and the exergetic values are locally consistent, that is, that there are no abrupt (catastrophic) variations in either Ex_{in} or M2. Notice that the very same definition of the exergy-equivalent implies though that different countries may have different ee_K values, due to their different productive and economic structures and lifestyles and that for a country both ee_K and ee_L may vary over time, due to an evolving social structure.

The capability of attaching to the labor input (taken here to include all service-related, blue and white collar human activities) a properly computed exergetic value is perhaps the most relevant novelty of EEA. Currently, in all practical applications of engineering cost accounting, including thermo-economics, labor is either completely neglected or it is accounted for on a purely monetary basis: this is unsatisfactory, because it assigns a higher weight to market conditions and financial considerations than to social, technical, and environmental issues that, if properly valued, may so distort the objective function that new solutions emerge.

EEA may be regarded as an extension of CExC, because it adds to the "cumulative exergy cost" of a product the amount of primary resources needed to generate each one of the remaining production factors that are not considered by CExC. It can be best used as a comparative tool; if two otherwise identical products, generated by two different production chains, are compared on the basis of their monetary cost, the assessment is made solely on the basis of market economy. If they are compared on the basis of their CExC, the assessment is made only on the basis of their embodied exergy. Using EEA, the assessment can be made considering all of the production factors, and furthermore, the final result is homogeneously expressed in terms of (primary resource equivalent) exergy, which is impossible to do with either a monetary approach and with thermo-economics.

5. Exergy Analysis and Environmental Impact Assessment of Technology

Because exergy embodied in resources, products, and waste materials has potential to cause change in both the industrial environment and the natural ecosystem, exergy and entropy have been proposed not only as a measure for economic losses and dematerialisation, but for waste accounting and ecotoxicity as well, as illustrated in the work of Ayres and co-workers (*120–125, 132–136*). The environmental impact of technology or products should be viewed over the full life, relating all environmental inputs (resource intake) and outputs (emissions) to one functional unit: the product or service under consideration. Most of the classical LCA tools that are available have a major emphasis on emissions. In this sense, exergy analysis (Figure 1) is different in nature: it is much more resource and product, and hence also efficiency, oriented. Nevertheless, efforts to assess environmental impact not only through resources intake (Section 5.2) but also through emission generation have been developed on an exergy analysis base.

5.1. Environmental Impact Assessment of Emissions on an Exergy Analysis Base. Emissions as such have an exergy value because they are not in thermodynamic equilibrium with the surroundings. However, their exergy value does not represent their environmental impact. Indeed, environmental impact is the result of an exposure to emissions, frequently the result of ecophysiological and biochemical interactions that are usually out of the scope of traditional thermodynamic analysis. In this sense, it is doubtful whether environmental impact can be quantified on the pure physical mixing ratios of pollutants emitted (*137*). The approach of Dewulf and Van Langenhove (*138*) considered the full emission and exposure process, where they calculated the loss of exergy in the natural environment and in society due to health effects. On the basis of statistical thermodynamics where one is able to assign an exergy value to living organisms (Section 2), loss of natural environment and human life-years were quantified in exergy loss due to exposure of emissions. A different approach to quantify the impact of emissions is the calculation of the exergy that is necessary to abate the emissions in waste treatment facilities (*129–141*), although this abatement exergy does not reflect environmental impact straightforward. However, it may make sense when technology is confronted with stringent environmental legislation that transforms the emission into a resource requirement issue, the resources being necessary for abating the pollutants, or in case the pollutants are used as resources to produce products and/or services.

5.2. Environmental Impact Assessment of Resource Intake on an Exergy Analysis Base. All processes taking place in society, whether they are production or consumption, destroy part of the potential of the resources withdrawn from the natural environment (Figures 1 and 2). In this sense, the whole industrial society can create or produce nothing from a thermodynamic point of view; it can only target at a maximum utilization degree of the natural resources it takes in. This can be achieved through thermodynamic optimization through entropy production minimization, and through proper (re)use of the full set of products, including byproduct and wastes. In this sense, exergy analysis perfectly matches the industrial ecology theory principle: consider all wastes as potential products.

Different exergy-based resource accounting methods have been proposed. Rechberger and Brunner (*142*) proposed a method to support decision-making in resource management, based on material flow analysis and Shannon's statistical entropy function. Connelly and Koshland (*143*), Dewulf and Van Langenhove (*144*), and Soeno et al. (*145*) used exergy analysis to quantify to what extent implementation of industrial ecology principles can achieve better natural resource management.

By far, the most applied is, however, the cumulative exergy consumption (CExC) demand as a measure for environmental impact (see Section 3). It reflects well to what extent products and services depend on natural resources. When compared to other resource accounting methods, it has the major advantage that it is able to weigh different masses in a scientifically sound way and that it enables us to bring mass and energy onto one single scale, eliminating the fuel and feedstock discussion. In fact, different kind of resources — renewable resources (biomass, solar, wind, hydropower), fossil fuels, nuclear fuels, metal ores, minerals, water resources, and atmospheric resources — are quantified on one single scale, which is a unique feature in resource accounting. The resource category "land use" remains unconsidered in most of CExC calculations, but recently it is enclosed in the cumulative exergy extraction from the natural environment (CEENE) method in order to complete natural resource accounting (*146*).

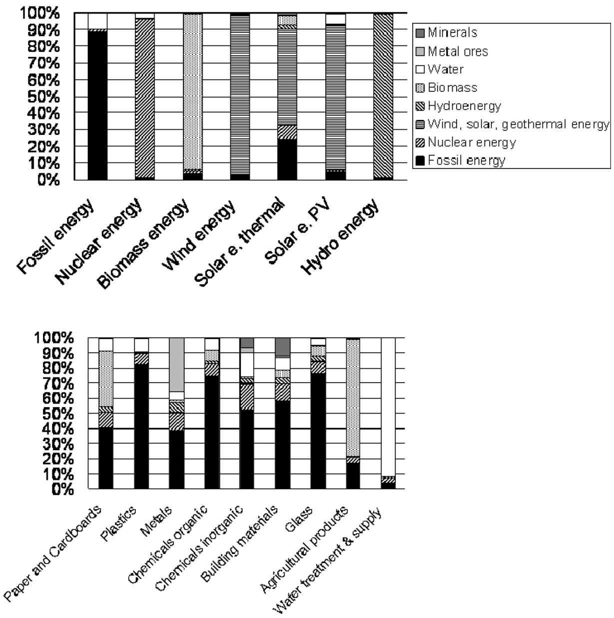

FIGURE 4. Natural resources consumption pattern for energy and materials, all quantified through exergy analysis (based on ref *151*).

CExC is maybe even more valuable when it goes beyond its classical approach, which can take place in two ways. First, if one also considers the exergy value of the products, it allows the calculation of the efficiency of the process chain, allowing the identification of weaknesses in the overall process chain. This has been illustrated for renewables-based energy (*140, 147–149*). Second, if one distinguishes different groups of natural resources contributing to the CExC, it becomes possible to identify the pattern of the natural resources a certain product "draws upon". This has been the basis for the calculation of the degree of renewability for the (so-called) renewable resources (*140, 147, 150*). Bösch et al. (*151*) divided the natural resource intake into eight different categories and illustrated this for typical energy and material products (Figure 4). By coupling recent exergy data for natural resources as available in De Meester et al. (*4*) and Dewulf et al. (*146*) with updated life cycle inventory databases, it becomes possible to calculate the exergy consumption pattern of over 2500 products and services (*146, 151*).

6. Outlook

The principles of the Second Law of Thermodynamics, established in the 1800s, have been confronted with a slow implementation in practice. This may be partially related to the fact that the Second Law is taught starting from the vague, abstract, and nontangible entropy definition instead of making students familiar with "useful energy", "ability to cause change", work potential, or exergy. Application did not begin until the 1970s, with the first ones being industrial process analyses. Today, they are far more mature and enjoy wide recognition for their powerful contribution to process optimization through inefficiency identification. Far less mature is exergy analysis of natural systems and the coupling with economic analysis, where a lively debate is presently going on about the actual merits of an exergy-based economic approach.

Exergy as a tool in environmental impact analysis may be the second most mature field of application. The assessment of the environmental impact of technologies was, for about 30 years, dominated by emission issues, which has led to implementation of waste treatment facilities due to environmental legislation. Numerous emissions are, therefore, under much better control today, such as acidification or stratospheric ozone depletion. Emission oriented life cycle impact assessment tools have been helpful in designing technology that is beneficial toward emission reduction. Now, in the beginning of the twenty-first century, there are numerous indications that technology development should go beyond emission reduction and aim at a higher degree of environmental sustainability. This requires that we consider the environment as a reservoir for our energy and material needs: a growing world population, a growing demand of pro-capite resources, a depletion of fossil resources, geopolitical implications of our resource dependency, and the likelihood that global warming is indeed a result of our resource consumption patterns. Because both academia and industry expect a drastic shift in the resource consumption pattern in the course of this century, it is obvious that technology development could strongly benefit from appropriate resource accounting and technical efficiency tools. As stated by Prof. G. Whitesides at the Green Chemistry Conference in Washington 2005, new technologies only have a chance if they are economically and thermodynamically feasible. It is in this arena that exergy analysis can play a major role. The major challenge for scientists who are well aware of the potential of exergy in resource accounting may be that of finding ways to communicate what thermodynamics has to say in this field. Exergy-based resource accounting may be at its highest value in environmental impact assessment in combination with classical emission oriented LCA, or alternatively through EEA.

Supporting Information Available

Details on the history of "exergy" and illustrative examples are presented in the Supporting Information sections S1 to S7. This information is available free of charge via the Internet at http://pubs.acs.org.

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