A thermodynamic perspective on technologies in the Anthropocene: analyzing environmental sustainability

Liao, W.

Citation

Liao, W. (2012, July 3). *A thermodynamic perspective on technologies in the Anthropocene: analyzing environmental sustainability*. Retrieved from https://hdl.handle.net/1887/19206

Author: Liao, Wenjie
Title: A thermodynamic perspective on technologies in the anthropocene : analyzing environmental sustainability
Date: 2012-07-03

Chapter 2

Thermodynamic analysis of human-environment systems: A review focused on Industrial Ecology

(Published as: Liao W, Heijungs R, Huppes G (2012) *Ecol Model* 228: 76-88)

Abstract

The term Anthropocene, which is used by many scientists to refer to the current era, reflects various environmental issues caused by anthropogenic activities. The energy flows and conversions in the anthroposphere and the anthropogenic impacts on the ecosphere, as two major aspects of the physical part of Industrial Ecology (IE), are both subject to the laws of thermodynamics. After an introduction to human-environment systems and IE in the Anthropocene, this review focuses on the role and applications of thermodynamic analysis in IE based on a thermodynamic definition of human-environment systems at four levels, *i.e.*, the ecosphere (A), the anthroposphere (B), the supply chain (C), and the foreground system (D). It argues that process engineering thermodynamics (at level D) and ecological energetics (at level A) are the most mature applications, and the primary benefit added by thermodynamic analysis to IE lies in the physical validation and quantitative formulation of thermodynamics. The review also indicates that the challenges of using thermodynamic analysis to understand the physical complexity of IE and to guide sustainability decision-making call for a joint effort by thermodynamic analysis and ecosystems ecology and for more insights from social sciences.

2.1 Introduction

2.1.1 The Anthropocene

We are currently in the era sometimes called the Anthropocene where humanity and human activities have become global geophysical forces and major drivers of global environmental change (Crutzen, 2003; Steffen *et al.*, 2007). Rockström *et al.* (2009) suggested that humanity has transcended the "safe operating space" of the planet with respect to climate change, nitrogen loadings, and biodiversity loss, and threatens to do so for six other major global environmental issues as well. Allenby (2009) pointed out that the planet's radiation spectrum carries a human signature which can be captured in the night-time image of the Earth from space. All the attributes of global environmental change are related to the interaction between people and their environments. Traditionally, the discipline of ecology studies the flows of energy and matter in the ecosphere, and the discipline of economics studies such flows in the anthroposphere. Increasingly, boundaries between disciplines have vanished, as can be seen by the emergence of cross-disciplinary fields such as ecological economics and Industrial Ecology (IE). Also, journals that traditionally focused on one discipline increasingly recognize the areas of overlap or contact with the neighboring disciplines, as is evident from publications like Ayres (2004), Svirezhev and Svirejeva-Hopkins (1998), Suh (2005), Nielsen (2007), *etc.*

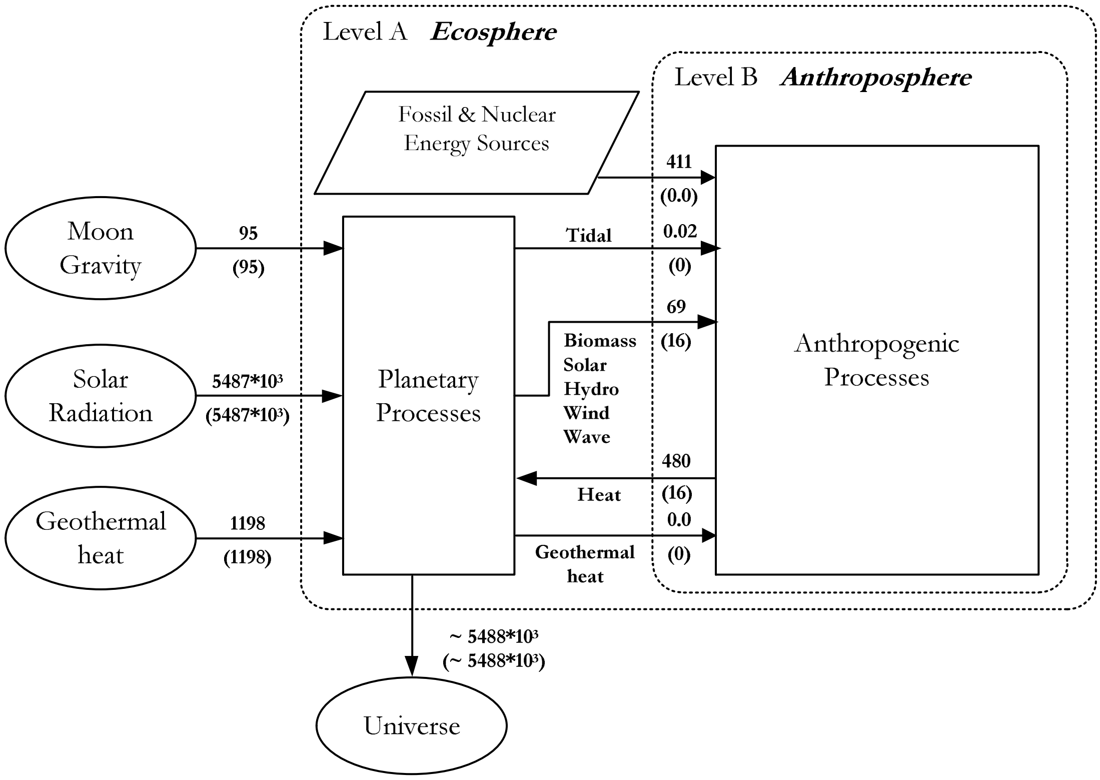

Figure 2.1 Global energy flows in the Anthropocene. Numbers represent energy flows in EJ/yr, for the year 2010 and in brackets for 1800. The ellipses stand for sources or sinks, the parallelogram for stock, and the rectangles for processes. Dashed lines represent the boundaries of the levels. Sources: BP (2010), IEA (2008), Kostic (2004), Price (1995), and Brown and Ulgiati (2010).

The historical development of primary energy supply for humanity in the Anthropocene can be taken as a typical example of the Anthropocene. Figure 2.1 shows that, prior to the Anthropocene, biomass, together with peats, satisfied nearly all energy demands, and there was hardly any consumption of fossil fuels (except for coal), uranium ore, or geothermal heat. With industrialization, human consumption of non-renewable energy sources, mainly fossil fuels increased and then outpaced that of renewable energy sources derived from solar radiation, hydropower, and biomass. Since WWII, human society has witnessed a dramatically escalating consumption of fossil fuels and fission energy. The utilization of biomass, hydropower, and other new renewable energy sources, such as wind power and solar radiation collected directly by solar cells, continues to increase at a moderate pace, but still accounts for less than 16% of the current total primary energy production.

2.1.2 Human-environment systems and Industrial Ecology

All the environmental problems, whether at global or at regional level, have invoked environmental concerns and have called for a re-examination of human-environment systems where social and ecological aspects are interacting at multiple temporal and spatial scales (Clark, 2010). It is against this background that IE has emerged in the last few decades as a field aiming at a sustainable development of the anthroposphere which is the interface between the ecosphere and society (Figure 2.2). The ecosphere includes the lithosphere, the hydrosphere, the biosphere, and extends to 100 km above the surface. While society consists of social aspects such as economy, culture, institutions, and politics. The very name of anthroposphere indicates the content of IE. IE is 'anthropogenic' in that it focuses on humanity and production and consumption activities which are important sources of environmental repercussions. IE is 'spherical' in that it includes the investigation of the part of the ecosphere which is modified by humans and serves as the source of resources in the society and the sink of environmental emissions. IE as such requires a description of (1) the energy and material flows and conversions in the anthroposphere and (2) the impacts of the anthroposphere on the ecosphere, and (3) the influence of other societal aspects on the anthroposphere.

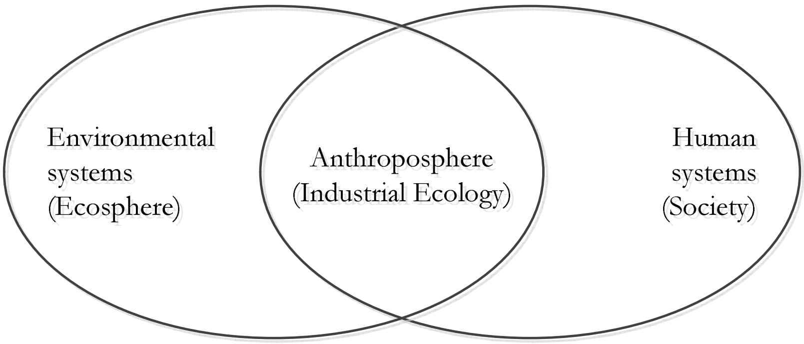

Figure 2.2 Human-environment systems and Industrial Ecology.

Energy flows and conversions are intrinsically the subject of thermodynamic analysis. The concept of Anthropocene summarizes the impacts of the anthroposphere on the ecosphere, especially in the aspect of global energy metabolism. Therefore, leaving the influence of other societal aspects out of consideration allows us to conceptually model the physical part of IE, that is, the content of (1) and (2), from a thermodynamic systems perspective by zooming in on the anthroposphere at level B in Figure 2.3, where the supply chain is a sub-system of the anthroposphere, consisting of components, processes and interactions that convert resources into products that are used to deliver services, and the foreground system is a specific production process to make a specific product.

The development of thermodynamics as a perspective into the reality has witnessed abundant publications to model and analyze various components in the anthroposphere as well as the ecosphere, as will be discussed in following sections, but few to review the role of thermodynamic analysis in a specific field. Two of such few publications worth mentioning are those of Sciubba and Wall (2007) and Dewulf *et al.* (2008). Sciubba and Wall (2007) presented a comprehensive historical account of the exergy concept and its applications from 1800 to 2004 in order to provide the idea of an "epistemological uniformity" in the development of exergy. Dewulf *et al.* (2008) offered a critical review on the potential and limitations of the exergy concept in ecosystem analysis, industrial system analysis, thermo-economic analysis, and environmental impact assessment and argued, "The major challenge for scientists … may be that of finding ways to communicate what thermodynamics has to say in this field (of environmental science and technology)." The article builds upon their work, extends exergy to other thermodynamic concepts, and focuses on the role and application of thermodynamic analysis in IE as well as its related processes in human-environment systems. The processes and hence the literature are categorized at four levels in the hierarchy of energy metabolism as shown in Figure 2.3. In addition, by pinpointing the limitations and challenges of thermodynamic analysis in current IE research, the article aims to bring more objective and new insights from thermodynamics as well as ecology and systems analysis which are already theoretical and analytical base to the evolving field of IE.

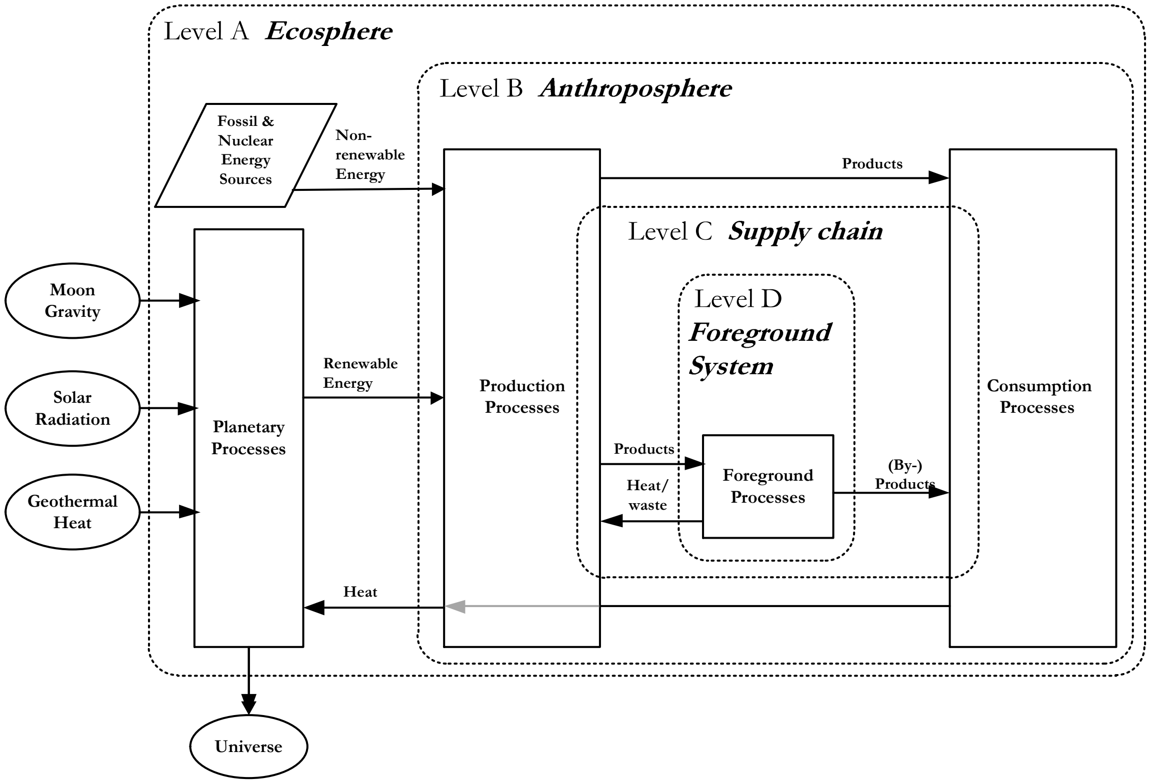

Figure 2.3 Energy metabolism in the anthroposphere.

2.2 Thermodynamic analysis and human-environment systems

2.2.1 Thermodynamic analysis

The basis of thermodynamic analysis is stated in several laws of thermodynamics, mainly the first and second laws. The first law expresses the conservation of quantity of energy, while the second describes the change of quality of energy. Thermodynamics has long been recognized as a fundamental approach to modeling systems at various levels. Thermodynamic systems can be the environmental systems such as single organisms or the ecosphere, or human systems such as a single production process or an entire economy. In principle, any thermodynamic metric based on or derived from the first law or the second law can be adopted for thermodynamic analysis. The most common methods of thermodynamic analysis are energy analysis (EA) based on the first law (IFIAS, 1978), entropy analysis (EnA) (Berry, 1972; Costanza and Herendeen, 1984; Kleidon and Lorenz, 2005) and exergy analysis (ExA) (Keenan, 1951; Fratzscher, 1959; E. Schmidt, 1956; Beyer, 1970; Brodyanski, 1973; Wall, 1977a; Szargut *et al.*, 1988; Chen GQ, 2005) based on the second law, and emergy analysis (EmA) (Odum, 1996).

Review as below is based on two general categorizations (a) theoretical and methodological developments and (b) applications to various processes in human-environment systems, which can be the foreground processes at level D, supply-chain processes at level C, anthropogenic processes at level B, and planetary processes at level A.

2.2.2 Foreground processes (at level D)

Applications of thermodynamic analysis in chemical production processes are common practice for engineers. EA at level D basically aims to evaluate the direct energy inputs to a specific foreground process, which only include "process energy", *i.e.*, energy products from supply-chain processes. ExA at level D concentrates on the exergy flows and losses through the specific unit process to identify the potentials for efficiency improvement.

1) Graphical representation and pinch analysis

Thermodynamic analysis for foreground processes frequently results in Sankey diagrams and Grassmann diagrams, respectively, as illustrated, for instance, in Yamamoto and Ishida (2002). Sankey diagrams produced by EA focus on the distribution of energy flows to various sources or sinks, represented by arrows, whose width indicates the magnitude of energy flows (Schmidt, 2008). The use of Sankey diagrams has also been extended to display material flows, CO_2 emission, and monetary flows (Chancerel *et al.*, 2009; Cheah *et al.*, 2009; Nakamura *et al.*, 2009). Grassmann diagrams produced by ExA distinguish themselves from Sankey diagrams in that an arrow in a Grassmann diagram becomes narrower at each stage, indicating the exergy loss and identifying the parts amenable to efficiency improvement.

Pinch analysis was first used to identify the system targets prior to designing heat exchange processes (Linnhoff, 1979) and has developed into an energy minimizing method for the design of various processes which also involve exchanges of materials, water, waste, and so on. While pinch analysis has been shown to be a poorer method than ExA in studying processes where threshold problems occur and heat pumps are available (Wall and Gong, 1996), the combination of ExA and pinch analysis has been suggested as an effective method for process design and optimization (Dewulf *et al.*, 2008)

2) Applications

Steam power generation was investigated by EA and ExA as a fundamental process in the early years. Conventional coal combustion and many coal-based advanced power generation methods are the most common subjects of EA and ExA. ExA of renewable energy engineering has also drawn increasing attention. Koroneos *et al.* (2003) reviewed the exergy analysis of solar energy, wind power, and geothermal energy systems and compared their exergy efficiencies with fossil fuel-based systems. Hepbasli (2008) extended Koroneos and colleagues' work by including biomass and hybrid systems and presenting the exergy utilization efficiency of various renewable energy resources in Turkey as well. Solar energy engineering is thought to be the most suitable candidate for ExA (Sciubba and Wall, 2007). Other renewable energy sources, such as wind (Sahin *et al.*, 2006) and geothermal energy (Hepbasli and Akdemir, 2004) have also been investigated by EA or ExA.

ExA has been applied to various processes for producing different commodity chemicals including ammonia, hydrogen, arsenic, ethanol, methane, pulp and paper, chlor-alkali, and so on. The conversions between chemical exergy and thermal or mechanical exergy involved in many chemical processes, such as micro-reaction, distillation, desalination, steam reforming, petroleum separation, drying, and wastewater treatment, have also been the subject of thermodynamic analysis (Sciubba and Wall 2007; Dewulf *et al.*, 2008).

The built environment, which accounts for 30-40% of the total energy consumption, is another typical field for the application of thermodynamic analysis. Studies have included the calculation of exergy flows of various elementary processes of heating, ventilation, and air conditioning (Wepfer *et al.*, 1979), the application of ExA in a changing reference environment (Sakulpipatsin, 2008), the relationship between exergy consumption and visual and thermal comfort (Maki and Shukuya, 2009), and optimized selection among different house energy consumption patterns (Lu and Wu, 2010).

2.2.3 Supply-chain processes (at level C)

The foreground processes are the typical domain where most "end-of-pipe" techniques are deployed for environmental pollution control and prevention. It is the shifting of an environmental problem from the foreground system (at level D) to their supply chain (at level C) or even the whole anthroposphere (at level B) which invokes IE as a systems perspective on environmental problems. Applications of thermodynamic analysis combined with other existing analytical tools for IE, such as life-cycle assessment, material flow analysis, and input-output analysis, are reviewed in Section 3.2. There are also combinations of thermodynamic analysis with other non-IE tools at level C, such as the exergo-economic analysis proposed by Tsatsaronis *et al.* (1993), Tsatsaronis (2008) who developed an exergy-based cost-accounting method and applied it to process integration (Abusoglu and Kanoglu, 2009).

2.2.4 Anthropogenic processes (at level B)

It has been argued that the global economy and various regional economies as well as other metabolic processes as described within sociological sciences should be a subject of thermodynamic systems, since every social-economic activity involves flows and conversions of energy and is driven by exergy (Wall, 1977b). Although there is a long history of using physical concepts, such as thermodynamic metrics, in economic theory, research into thermodynamic analysis in economic systems is less structured and systematic than that in physicochemical production processes. The school of ecological economics is a typical example of an approach applying the second law in economics (Georgescu-Roegen, 1971, 1975; Daly, 1991, 1996; Costanza *et al.*, 1997; Ayres, 1998), but the distinction between methods and applications even in ecological economics is not so obvious. The literature of applications of thermodynamic analysis in economic systems is preliminarily categorized as below.

1) Waste theory and joint production

In the view of many environmental economists, the occurrence of excess waste as emissions is due to market failure, *i.e.*, the consequence of waste generation is not internalized in the market price. This failure could be avoided by applying suitable economic instruments (Bisson and Roops, 2002). This viewpoint has been criticized by a group of scientists who favor the theory of joint production and irreversibility of waste production as an entropy carrier. Georgescu-Roegen (1971, 1975) pointed out that the thermodynamic nature of economic processes implies that waste is an output just as unavoidable as the input of natural resources. Baumgärtner (2000) proved that every process in industrial production is a joint production in the sense that the joint inputs as high entropy raw material and low entropy fuel are transformed into joint outputs as low entropy product and high entropy waste. Besides, the raw material and fuel are complementary and the product and the waste (both in terms of materials and energy) are necessarily produced together. Baumgärtner and De Swaan Arons (2003) further discussed the degree of thermodynamic efficiency which determines the actual amount of waste generated using current technologies.

2) Economic growth and national economy

Conventional economic growth theory assumes that resource consumption is a consequence rather than a cause of growth. Resource economists have investigated the relation between energy and economic development, but treated all kinds of natural resources as substitutable by man-made resources such as labor and capital (Conrad, 1999). Both ignored the thermodynamic fact that biophysical resources are used up as exergy in most production processes but cannot be produced by economic activities. Based on the hypothesis that all natural resources are the non-substitutable basis for economic growth, Ayres *et al.* (2003), Ayres and Warr (2005), Wall and Ayres (2006), Williams *et al.* (2008) investigated the possible link between the input of exergy, such as useful work and exergy service, and economic growth, from the perspective of supply-driven economic growth. They suggested that exergy can be another production factor besides capital and labor. This allows the operational efficiency of an economy to be determined and the “efficiency dilution” to be observed in national economies. Wall (2002) introduced the idea that total exergy input is just as relevant as GDP in economic modeling. Along this line of thermodynamic modeling and economic systems analysis, mainly using exergy metrics, studies have investigated various national economies, such as those of Sweden (Wall, 1987), Japan (Wall, 1990), Norway (Ertesvag and Mielnik, 2000), Canada (Rosen, 1992), Turkey (Ileri and Gurer, 1998), Italy (Wall *et al.*, 1994), Ghana (Wall, 1997), Brazil (Schaeffer and Wirtshafter, 1992), the U.S. (Reistad, 1975), and China (Chen *et al.*, 2006)

3) Value, labor, and cost accounting

If exergy, and thus negentropy, is recognized as another scarcity or as the ultimate resource, it can be used as a proxy of value. Based on the statistical definition of entropy, J. Chen (2005) suggested that both economic value and information represent reductions of entropy. Following the usual procedure of engineering accounting and linking the prices of components to their operating parameters and to the upstream irreversibility and downstream exergy efficiency, thermo-economics allows a monetary cost to be assigned to the specific exergy content of each energy and material output stream (Valero *et al.*, 1986; El-Sayed and Evans, 1970). Extending the concept of energy and material flows to include capital, labor, and environmental remediation costs allows the total actual exergy cost of a product to be calculated by extended exergy accounting (Sciubba, 2005). All of these attempts to apply thermodynamics-based value and cost accounting theory distinguish themselves from the current mainstream economics, which only considers monetary flows.

2.2.5 Planetary processes (at level A)

Energy conversions and material cycles, mainly biogeochemical cycles, are the core processes comprised in all ecosystems; an ecosystem is a supply-driven network of various flows of energy and materials. Besides, it is the energy flows that drive the material cycles (Odum, 1997). An ecosystem is thermodynamically an open non-equilibrium system; it takes up all its matter as necessary nutrients from other ecosystems in the biosphere; it gets exergy from solar energy and produces matter while producing entropy, generally in the form of heat (Jørgensen and Svirezhev, 2004). The application of thermodynamic analysis to other subsystems in the ecosphere, such as the atmosphere, hydrosphere, lithosphere, and so on, is only slightly relevant to IE research. There have been many publications on this, such as Curry and Webster (1999) and Kleidon and Lorenz (2005), but a review of them is beyond the scope of this article.

1) Energetics of ecosystems

It was Tansley and Lotka who independently proposed the idea of an ecosystem as a major functional unit in the biosphere, which shares energy as a single common factor with other Earth systems. Lotka also introduced thermodynamics into ecosystem ecology (Lotka, 1922; Odum, 1997). Exergy from solar radiation is the main source supporting all ecosystems, *i.e.*, the whole biosphere in Figure 2.1. Energy is concentrated and exergy is lost as solar energy flows through the ecosystem. This is demonstrated in the solar energy flow diagram through biological food chains and the concept of trophic pyramids (Miller *et al.*, 2008; Odum, 1971).

2) Thermodynamic goal functions for ecosystems

As suggested by Prigogine *et al.* (1972a, 1972b), ecosystems as well as organisms and the whole biosphere are dissipative systems "far from equilibrium". In order to maintain their highly organized, low-disordered state, ecosystems require a continuous exergy input, storage capacity, and the means to dissipate entropy. These three attributes of ecosystems form the common basis for various proposed thermodynamic principles serving as goal functions for ecosystem development. These principles include minimum entropy production (Prigogine, 1955; Bejan, 1996), maximum entropy production (Paltridge, 1979; Swenson, 1997; Kleidon *et al.*, 2010), maximum power (Lotka, 1922; Odum and Pinkerton, 1995), maximum exergy storage (Jørgensen and Mejer, 1979; Jørgensen and Svirezhev, 2004), maximum ascendency (Ulanowicz, 1986), depletion of gradients or maximum dissipation (Schneider and Sagan, 2005), and the constructal law (Bejan and Lorente, 2006). All of these hypotheses are inspired by the second law of thermodynamics.

3) Thermodynamic concepts for ecological indicators

The first list of ecological indicators in ecosystem ecology was proposed by Odum (1969) to estimate ecosystem maturity. Ever since, several attempts have been made to use thermodynamic concepts such as ecosystem exergy to derive ecological indicators that can quantify the integrity, the degree of selforganization, the health, and the status of an ecosystem (Kay and Schneider, 1992; Costanza *et al.*, 1992). These indicators are especially relevant when investigating the interaction between the anthroposphere and the ecosphere. Dewulf *et al.* (2008) confirmed that exergy storage and exergy dissipation are the two main indicator approaches found in the literature. The exergy of an ecosystem component, as suggested by Jørgensen and Nielsen (2007), could be calculated from its genetic content. And the environmental degradation under anthropogenic impact can be measure through entropy (Svirezhev, 2000).

4) Applications

Thermodynamic analysis has been applied to ecosystems at various levels of organization, such as the dynamic energy budget theory for organisms (Sousa *et al.*, 2010), the ExA of organic matter in water flow (Martinez and Uche, 2010), the ExA of water and water quality (Zeleta-Aguilar *et al.*, 1998; Chen and Ji, 2007), the ExA of lakes (Xu, 2005), exergy-based indicators for ecosystem growth (Jørgensen *et al.*, 2000) and biodiversity (Petrovskaya *et al.*, 2006). Applications of ExA in many other ecosystems have been reviewed by Jørgensen and Fath (2004) and Jørgensen and Nielsen (2007).

2.3 Thermodynamics in IE

2.3.1 Thermodynamics as one basis of IE

One of the two physical attributes of IE, that is, the flows and conversions of energy and materials, intrinsically follows the thermodynamic laws, and can be described using thermodynamic concepts and linked directly to practical environmental questions. The other physical attribute, *i.e.*, the relationship between the anthroposphere and the ecosphere, is reflected by the analogy between the anthroposphere and an ecosystem, *i.e.*, industrial ecosystems may behave in a similar way to ecological systems wherein material flows get recycled (Lifset and Graedel, 2002). Thermodynamics, which is suggested by ecological energetics and systems ecology to be a core perspective of the ecosystem, is applicable to the anthroposphere to depict its physical structure. This structure can be regarded as consisting of components of the ecosphere, such as industrial symbiosis which is the sharing of services and byproduct resources by companies in a relative geographical proximity (Chertow, 2000), and can model the interaction between the anthroposphere and the ecosphere, for instance in terms of resource consumption, environmental emissions, pollution dilution, and carrying capacity. The early effort by Bryant (1982) to treat economic value and energy value as fundamental equivalents suggests another analogy between thermodynamics and economics and may offer new insights when investigating the influence of economic factors. As such, thermodynamics services as one basis of the three key contents of IE mentioned in Section 1.2.

2.3.2 Review on combination of thermodynamic analysis with IE analytic tools

The main application of thermodynamic analysis in IE is the combination with three analytical tools that are of particular importance, *i.e.*, life-cycle assessment (LCA), material flow analysis (MFA), and input-output analysis (IOA).

1) Thermodynamic analysis and life-cycle assessment

There has been a close link between LCA and EA since the early 1970s, when the so-called "embodied energy" of a specific product was the main scope for LCA studies on household products such as beverage containers, detergents, and diapers (Udo de Haes and Reijungs, 2007; Guinée *et al.*, 2011). The current combination of thermodynamic analysis and LCA operates mainly in three ways at level C. The first involves employing thermodynamic metrics in life-cycle impact assessment as an impact category of resource depletion. The second involves using thermodynamic metrics to approximate environmental impact, while the third involves incorporating thermodynamic analysis into life-cycle thinking, mainly for specific multi-criteria studies.

Exergy consumption or entropy generation is used for resource accounting and the characterization resource depletion in life-cycle impact assessment (Wall, 1977a, 1986; Ayres *et al.*, 1996, Finnveden and Ostlund, 1997; Gößling-Reisemann, 2001; Stewart and Weidema, 2005; Steen, 2006). By far the most commonly applied indicators of this type are cumulative exergy demand (Bösch *et al.*, 2007) and cumulative exergy extraction from the natural environment (Dewulf *et al.*, 2007a), whose applications are sometimes grouped as life cycle exergy analysis (Gong and Wall, 1997, 2001a,b) or exergetic life-cycle assessment (Cornelissen, 1997; Cornelissen and Hirs, 2002; Dewulf *et al.*, 2008). Cumulative exergy demand is the sum of all exergy that is connected to the supply chain of a product or service and is equivalent to cumulative exergy consumption as proposed by Szargut and Morris (1987). Cumulative exergy extraction from the natural environment distinguishes itself from cumulative exergy demand by taking the actual transformed exergy into account. For instance, an analysis of the solar exergy input to crop planting for bio-fuel production only considers the portion that is extracted by photosynthesis rather than the total insolated exergy. Both cumulative exergy demand and cumulative exergy extraction from the natural environment can include water use and some aspects of land use (Finnveden *et al.*, 2009). The resource aggregation based on both indicators is appealing. However, both indicators can give counterintuitive results since they seldom address their presumption of the substitutability between various exergy resources adequately (Baral and Bakshi, 2010; Zhang *et al.*, 2010b; Bakshi *et al.*, 2011). Zamagni *et al.* (2009) further pointed out that exergy-based indicators are to be preferred but not recommended for resource depletion with regard to the inherent property of resources. A less implemented indicator is ecological cumulative exergy consumption, which extends the scope of conventional life-cycle inventory analysis to include the inputs from ecosystem goods and services, allowing the impact on biodiversity caused by land use to be modeled and assessed by the ecologically based LCA (Zhang *et al.*, 2010a, 2010b).

Wall (1977b) first indicated that the effect of resource use and waste disposal on the ecosphere is strongly related to the amount of exergy in the utilized resource or the disposed waste. Rosen and Dincer (1997), Rosen (2001, 2002) explained the relationship between exergy and environment impact and suggested waste exergy emission, i.e., release of chemical exergy associated with emission flows, is one type of environmental impact while the other two types are resource degradation and chaos creation. Emission flows possess exergy and hence have the potential to cause instability to the ecosphere, since they are in disequilibrium with the environment. Ao *et al.* (2008) further suggested that exergy associated with emission flows is especially detrimental when it is released to the ecosphere on a large scale. The environmental impact of emission flows can thus be quantified based on their exergy value (Seager and Theis, 2002) or indirectly reflected by determining the total exergy that is needed to dispose of the emission flows in waste treatment facilities under the requirement of "zero-impact" or specific legislative pollution limits (Sciubba, 2001; Dewulf *et al.*, 2008). For instance, Ometto and Roma (2010) assessed the atmospheric impacts of emissions from fuel ethanol production based on their chemical exergy. Kirova-Yordanova (2010) compared the environmental impacts of different processes for ammonium nitrate production based on abatement exergy. Ulgiati and Brown (2002) suggested quantifying the impacts of emissions by calculating the emergy of environmental services needed to dilute and abate the emissions. This method is applied to production of electricity (Ulgiati and Brown 2002) and steel (Zhang *et al.*, 2009a) and sewage treatment (Zhang *et al.*, 2010a). However, it is worth mentioning that except for potential instability to the ecosphere, other types of environmental pollutions pertinent to human and ecological health should not be measured based on exergy or other thermodynamic metrics until any plausible relation between thermodynamic analysis and bio-physiological effects on human and ecological health is suggested. In this sense, the approach developed by Dewulf and Van Langenhove (2002a) to model the full waste emission and exposure process and calculate the loss of eco-exergy in the ecosphere due to health effects is theoretically enlightening but subjected to more valid proof.

The quality of life-cycle inventory of a unit process can be enhanced via data reconciliation with the first and second laws (Hau *et al.*, 2007), and one physical basis for allocation of environmental burdens between products is the energy or exergy content of the products (Ekvall and Finnveden, 2001; Rosen, 2008). Thermodynamic analysis of energy technologies incorporates not only cumulative energy demand and cumulative exergy demand, which are already standardized in existing LCA databases, but also other types of LCA studies, which are applied in a more *ad hoc* way to calculate the energy balance and assessment the environmental performance of a specific technology like biofuel production (Van der Voet *et al.*, 2010; Von Blottnitz and Curran, 2007; Sheehan *et al.*, 2004), information and communication technology ("Skip" Laitner, 2003; Yi and Thomas, 2007), e-commerce (Sivaraman *et al.*, 2007; Williams and Tagami, 2003), bio-based materials (Hermann *et al.*, 2007; Dornburg *et al.*, 2004), and nano-products (Olapiriyakul and Caudill, 2009; Grubb and Bakshi, 2011). ExA or EmA is sometimes coupled with LCA by using the same inventory data to provide multi-criteria analysis (Portha *et al.*, 2010; Cherubini *et al.*, 2008; Pizzigallo *et al.*, 2008; Ulgiati *et al.*, 2006; Duan *et al.*, 2011). Most results of the analysis show that LCA and ExA or EmA are complementary methods.

2) Thermodynamic analysis and material flow analysis

MFA serves as the main method to understand the structure of societal metabolism and the interaction between the anthroposphere and the ecosphere, by focusing on the material throughput of the anthroposphere or its subsystems. While MFA stems from the concept of material input per service unit as proposed by Schmidt-Bleek (1993a, 1993b), the concept of material flows has been described as exergy flows by Wall (1977b). MFA is typically conducted between level B and level C. The basis of MFA is the accounting of physical inputs and outputs of a sector, a city, a region, or a nation, in mass units. As any material conversion in the anthroposphere or the ecosphere is driven by some energy flows and causes exergy loss, any material flow accounting scheme, in principle, has its parallel energy accounting scheme. This is indeed the underlying idea of material and energy flow analysis in economics and ecology (Suh, 2005), as well as in IE and other human-environment systems (Haberl *et al.*, 2004). Material and energy flow analysis is the most common framework to combine thermodynamic analysis. In the framework, MFA distinguishes itself from the analysis of energy or exergy flows by including the stocks of materials, setting aside the energy significance of the anthropogenic material flows, and regarding them as flows of material significance in building up artifacts, such as the biophysical structure of the anthroposphere (Lifset, 2006).

The framework of material and energy flow analysis is applied to a specific subject either by historical analysis or by scenario analysis, or both. For instance, Michaelis and Jackson (2000a,b) reported a result for the UK steel sector from 1954 to 2019. Sundin *et al.* (2002) made a material and energy flow analysis of UK pulp and paper production, based on their life-cycle perspective, from 1987 to 2100. Muller *et al.* (2004) used a dynamic model for material and energy flow analysis to analyze regional timber management in Switzerland from 1900 to 2100. However, most applications of the framework imply a discrepancy in categorization of energy and materials, which is sometimes due to the difference between available energy statistics and material statistics. The approach of energy flow accounting developed by Haberl (2001a, 2001b) focuses on biomass as such a difference in comparing the different energy sources from agriculture and renewable fuels between developing and developed economies. Haberl *et al.* (2006) also used this approach to assess the energy inputs of the EU from 1970 to 2001 and the US from 1980 to 2000. Other metabolism analysis shows that ExA or EmA can be also used to compensate for the discrepancy, for instance, in the study of industrial metabolism of UK steel sector (Michaelis and Jackson, 2000a), urban metabolism of some Chinese megacities (Zhang *et al*, 2009b, 2010d, 2011), and the social metabolism of Taiwan (Huang *et al.*, 2006; Huang and Chen, 2009; Lee *et al.*, 2009). However, more attention is required to determine the scope of metabolism analysis when corresponding data availability is always limited.

In addition to the framework of material and energy flow analysis, other types of joint use of thermodynamic analysis and MFA are found in the analysis of recycling in the MFA of metals based on changes in exergy concentration or statistical entropy (Amini *et al.*, 2007; Rechberger and Graedel, 2002; Yue *et al.*, 2009), in the method of “exergetic material input per unit service” (Dewulf and Van Langenhove, 2003), in exergy-modified footprint analysis to include non-renewable resource consumption (Nguyen and Yamamoto, 2007), in entropy-based footprint analysis of copper production (Gößling-Reisemann, 2008), and in other ad hoc analysis (Dahmus and Gutowski, 2007; Kaufman *et al.*, 2008).

3) Thermodynamic analysis and input-output analysis

As the two established analytical tools, LCA and MFA have their modeling basis in general input-output (IO) models. Theoretical endeavors to create a general framework for thermodynamic analysis and IOA have been crucial to the development of IE. These endeavors can be dated back to Costanza’s work on “embodied energy and economic valuation” in the 1980s (Costanza, 1980; Costanza and Herendeen, 1984). However, a survey of the recent literature yields only isolated attempts to incorporate thermodynamic metrics into IO modeling from various perspectives. Two highlighted methods for this are thermodynamic IOA developed by Bakshi *et al.* (Hau and Bakshi, 2004a; Ukidwe, 2005; Ukidwe and Bakshi, 2005) and extended exergy accounting by Sciubba (2005). Thermodynamic IOA includes the contributions of ecosystem goods and services, human resources, and the impact of emissions in an economic IO model. The core of thermodynamic IOA is the ratio of ecological cumulative exergy consumption as natural capital to money as economic capital. Thermodynamic IOA has been applied to the US economy in 1992 and 1997. The results showed that the ecological cumulative exergy consumption/money ratio decreased going from basic infrastructure industries to value-added service industries, and suggested that the service industries are better at valuing ecosystem contributions than the resource extraction and manufacturing industries (Ukidwe and Bakshi, 2004, 2007). Extended exergy accounting calculates the cost of a product based on its physical value by including the exergy flows equivalent to capital, labor, and the environmental remediation costs (Sciubba, 2005). The results reported by extended exergy accounting studies suggest its superiority over pure monetary or even thermo-economic approaches to perform more complete assessments of complex systems (Sciubba, 2003; Sciubba *et al.*, 2008). However, both modeling attempts imply internal inconsistency in time by paralleling cumulative-type exergy quantity with snapshot-type of economic capital, which is shared by placing the micro-level technological model directly into the macro-level sustainability analysis.

2.3.3 Thermodynamic metrics for environmental sustainability indicators

Thermodynamic metrics can be readily used to describe the environmental performance of any energy- or material-based technology. Indicators based on such thermodynamic metrics have been suggested for the assessment of environmental sustainability. Wall and Gong (2001a,b) and Wall (2010) examined the concept of sustainability related to exergy flows in the ecosphere and applied exergy as an indicator to assess emissions as differences in the environment. Dewulf and Van Langenhove (2002b) proposed a set of sustainability indicators for technology assessment by taking "resource intake" (at level C) and waste generation as the two direct boundary conditions and efficiency as a third, indirect, condition. The indicators have been applied in case studies of bio-fuel production (Dewulf *et al.*, 2005), waste gas and waste plastics treatment (Dewulf *et al.*, 2001; Dewulf and Van Langenhove, 2002c), electricity production (Dewulf and Van Langenhove, 2005), pharmaceutical ingredient separation and production (Dewulf *et al.*, 2007b; Van der Vorst *et al.*, 2011), transportation service (Dewulf and Van Langenhove, 2003), and the built environment (De Meester *et al.*, 2009). Lems *et al.* (2002) revised the indicators to assess the sustainability of resource utilization. Three of the indicators, *i.e.*, exergy renewability, exergy efficiency, and environmental compatibility, have been selected and refined by Zvolinschi *et al.* (2007), who showed their generality in IE by applying them to two gas-fired combined-cycle power plants. Liao *et al.* (2011) assessed the environmental sustainability of ethanol production in the US by using indicators based on energy, exergy, and emergy and showed that bioethanol cannot be simply regarded as a renewable resource. Huijbregts *et al.* (2006, 2010) indicated that cumulative fossil energy demand can be used to approximate the environmental impact of specific categories of chemical products based on regression analysis. Undoubtedly, as will be discussed in the following section, besides the aforementioned, more thermodynamic-based indicators are desirable to link the technology assessment to other environmental issues, such as climate change (Lenton and Vaughan, 2009), or even to the economic and social aspects if certain boundary conditions could be determined.

2.4 Further discussions

2.4.1 Quantitative formulation of thermodynamic metrics

What we have reviewed above is mainly about energy and exergy, and of course there is much more to say about the role and applications of entropy in thermodynamic analysis, which is beyond the scope of this article. Defined as the ability to perform work, the absolute value of energy cannot be measured. Only the transition of energy can be measured, based on a specific zero-point set by a specific reference frame. The same applies to exergy, defined as the maximum work that can be performed according to a specific reference environment. On the one hand, the lack of mathematical definition of the absolute value of energy and exergy allows wide applications of the metrics in describing various elements of a system and quantifying their specific attributes (Figs. 2.1 and 2.2) in two different ways: computational and conceptual. The computational applications of thermodynamic metrics have been demonstrated as the application of thermodynamic analysis to a specific production process (at level D) and to the atmosphere, hydrosphere, lithosphere, and so on (at level A). The conceptual applications of thermodynamic metrics have been illustrated by using exergy as a measure of waste impact (Gaudreau *et al.*, 2009) and incorporating the information content of complex systems via the concept of eco-exergy. Sciubba and Wall (2007) criticized that the conceptual use of Jorgenson's eco-exergy and Shannon's information-entropy imply no relationship with exergy or entropy as thermodynamic metrics. And Kleidon *et al.* (2010) commented that the various hypotheses about ecosystem goal functions have mostly been proposed at a highly qualitative level, with many ambiguities that impede their quantitative verification.

On the other hand, the lack of a mathematical definition accounts for the ambiguous quantitative relationship between energy and other metrics. While there have been few case studies combining EA, ExA, and EmA (Nilsson, 1997; Hovelius and Wall, 1998; Liao *et al.* 2011), the quantitative relationships between various thermodynamic methods and the basic concepts have seldom been elaborated in case studies. A typical example is that of emergy. Hau and Bakshi (2004b), with conceptual novelty, discussed the features and criticisms of emergy and revealed the link between emergy and ecological cumulative exergy consumption. The current debate on whether energy or exergy is the basis from which the emergy concept is derived illustrates that a quantitative definition of emergy can substantially affect the result of EmA (Brown and Herendeen, 1996; Sciubba and Ulgiati, 2005; Brown and Ulgiati, 2010; Sciubba, 2010).

Unlike LCA or MFA, thermodynamic analysis is being implemented in various contexts, such as exergy used in engineering as chemical exergy (Sciubba and Wall, 2007) and in ecology as eco-exergy (Jørgensen and Svirezhev, 2004). What is lacking is a standard procedure which could make the implementation of thermodynamic analysis more consistent across different case studies. A more consistent implementation of various thermodynamic analysis based on solid quantitative definitions of the core thermodynamic metrics can help to communicate thermodynamic knowledge to other sub-disciplines in IE in more consistent language (Ehrenfeld, 2008).

2.4.2 Challenges in understanding the physical complexity of IE

Thermodynamic analysis as applied in current IE can hardly depict its physical complexity. It has been suggested that the ecosphere and Gaia are complex adaptive systems (Levin, 1993, 1998). The anthroposphere, as a subsystem of the ecosphere that is thermodynamically open to energy and materials, is also a complex adaptive system. The majority of IE publications have concerned the metabolic and structural relationships in the anthroposphere (Ehrenfeld, 2007), both of which have been described by thermodynamic analysis in many of the studies referred to above. However, these studies typically apply thermodynamic analysis as static linear models, and the causality of the interactions in the anthroposphere is pre-assumed and treated from a mono-disciplinary perspective (Valero, 2006). The agents and networks at the lower levels of complexity in the anthroposphere (levels D and C) can be analyzed based on the thermodynamic laws, and the whole system at higher levels of complexity (levels B and A) can be conceptualized as a thermodynamic system. But how the interactions at the lower level shape the structure of the anthroposphere as a whole and how the anthroposphere evolves from one regime to another are subjects seldom investigated in current IE research. From a viewpoint of analogy, the efforts invested in investigating complexity and dynamics in ecosystems, such as Holling (2001) and Kay (2002), may help guide IE research into a more complexity-oriented direction.

Thermodynamic analysis may also help formalize the emergent system structure of the anthroposphere in future IE, despite the fact that the future physical part of the anthroposphere can hardly be fully predicted by merely applying thermodynamic analysis, since thermodynamics serves as only one perspective to understand the anthroposphere. Such an understanding requires a multi-perspective approach (Nikolic, 2009) and many important exogenous human factors contribute to the evolution of the anthroposphere. The historical development of the anthroposphere can be reviewed in terms of energy flows and conversions. Given any thermodynamic threshold value of a specific part of the ecosphere which is modified by humans, it is possible to check whether the current anthroposphere transcends the safety boundary beyond which a catastrophic transition could happen. Undoubtedly, an individual analytical tool, be it LCA, MFA, or IOA, or even a hybrid of them, can hardly capture the real attributes of the mechanism via which the collective property emerges at the system level. However, thermodynamic laws are valid wherever an energy-related attribute of the mechanism is located. This is the case, for instance, in the physical modeling of many LCA-based frameworks, such as life-cycle sustainability analysis (Heijungs *et al.*, 2009), where thermodynamic constraints to the anthroposphere can be set up.

2.4.3 Challenges for supporting sustainability decision-making

There are more opportunities for using thermodynamics to model and analyze consumption processes in IE. As Hertwich (2005) pointed out, only by taking consumption into account can IE provide the analysis required by the decision-makers. The efforts to pay more attention to consumption have been motivated and reflected by the term sustainable consumption (Jackson, 2005) and related studies demonstrate the role of thermodynamic analysis in conceptualizing the physical basis and describing the level and pattern of consumption (Hertwich, 2005). But as a physical approach per se, the role of thermodynamic analysis in addressing other ethical and behavior-related questions of consumption, as proposed by Reisch and Ropke (2004), remains highly uncertain.

On the production side of the anthroposphere, the relevance of thermodynamic analysis to guide decision-making is not free of debate. Thermodynamic analysis focuses on the metabolism of the anthroposphere rather than what it takes from and emits to the ecosphere. With regard to the outflows of a production system, the energy or exergy used to dilute or abate the emissions reflects the legislative standards as policy factors, despite the fact that this abatement exergy or dilution exergy does not straightforwardly reflect environmental impact. The energy or exergy efficiency of a production system compared to the average value of efficiency based on current technology is typically used as a criterion in screening technology alternatives. However, with regard to the inflows and stocks of resources considered in LCA, energy- or exergy-based resource accounting provides less policy relevance than other methods that are better able to reflect the problem of resource scarcity. Allocation of environmental impacts based on energy or exergy shares the same problem of less policy relevance.

Thermodynamic analysis applied as it is in IE provides valuable information about empirical mechanisms and relations in the physical models for sustainability analysis and covers the majority of the "environmental pillar" and part of the "economic pillar" of sustainability. However, thermodynamic analysis does not explicitly capture anthropocentric value judgments which at least co-determine choices among processes that convert materials and energy, despite it provides valuable information about empirical mechanisms and relations in the physical models for sustainability analysis. And it may be desirable that more questions could be formulated by thermodynamic analysis to tackle the multi-faceted sustainability issues in more width or even in the "social pillar" by incorporating thermodynamic concerns into the real participatory procedure of sustainability decision-making. Admittedly, what sustainability question should be raised depends on the definition of the sustainability concept in return. In this sense, the recent work by Sciubba and Zullo (2011a, 2011b) provided a constructive example to discuss the thermodynamic meaning of sustainability by looking into the population dynamics caused by exergy resources in a two-population system.

2.5 Conclusions and outlook

This article has reviewed the importance of thermodynamic analysis for the study of human-environment systems, with an emphasis on IE. Human-environment systems were defined as a thermodynamic hierarchy at four levels: the ecosphere (A), the anthroposphere (B), the supply chain (C), and the foreground system (D). Process engineering thermodynamics at level D and ecological energetics at level A may be the most mature applications of thermodynamic analysis. The energy flows and conversions in the anthroposphere and the anthropogenic impacts on the ecosphere, as the main content of IE, are modeled and analyzed based on several thermodynamic metrics. IE as such regards the combination of energy and exergy with life-cycle assessment at level C and the incorporation of energy metabolism into the scheme of material flow analysis at level B as the two most typical implementations, both, while not free of limitations and subjected to improvement, demonstrating the primary benefit added by thermodynamic analysis to IE, which lies in the physical validation and quantitative formulation of thermodynamics. The added value can be enhanced if the mathematical relationship between thermodynamic metrics is clarified and a standard procedure for implementing thermodynamic analysis is set up. More benefit can be added by shifting from static linear models of thermodynamics to non-equilibrium thermodynamics and systems complexity, as IE evolves to reflect the essential complexity of the anthroposphere. Moreover, the link between environmental impacts and thermodynamic loss would have to be verified, the resource scarcity relevance of characterization based on thermodynamic metrics, and time factor in the combination of cumulative exergy and input-output analysis leaves room for improvement. As a last remark, it is a challenge for physicists, just as for other natural scientists working in the study of human-environment systems, to find better ways to communicate even the basic and indispensable knowledge provided by thermodynamic analysis to decision-makers.