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

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Wenjie Liao

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Wenjie Liao 廖文杰

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COLOPHON

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知人者智，自知者明。
胜人者有力，自胜者强。
知足者富，强行者有志，不失其所者久，死而不亡者寿。

——老子《道德经·第三十三章》

Understanding others is knowledge; understanding oneself is enlightenment.
Conquering others is power; conquering oneself is strength.
Contentment is wealth; forceful conduct is willfulness.
Not losing one’s rightful place is to endure; to die but not be forgotten is longevity.

Laozi, Dao De Jing, chap. 33, tr. V.H. Mair

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Chapter 1

Introduction and research questions

1.1 Human imprint in the Anthropocene

Humans have been modifying the ecosphere since about 2.3 million years ago when *Homo habilis* appeared as one of the earliest *Homo* species. During the major part of that time humans had changed the ecosphere mainly by muscle and sinew, supplemented by primitive tools and fire which were used for hunting for instance megafauna. Human impacts on the ecosphere remained quite slight even after the appearance of *Homo sapiens* around two hundred thousand years ago, as suggested by rare traces of humans in the rock from the Pleistocene. From about ten thousand years ago, agriculture, with various forms of plant and animal domestication, evolved independently in several different places of the world. This Neolithic revolution of agriculture transformed the world from hunter-gatherers to a more sedentary lifestyle based in villages and towns which eventually developed into complex civilizations as seen in Mesopotamia, Egypt, China, the Indus River Valley, Mexico, and Peru. Land-clearing, irrigation, and other specialized food-crop cultivating technologies affected large areas of the land surface. Forests were logged; bushwood was used to heat houses and to fire smelters; lead, iron, copper, gold, *etc.* were digged and refined. But the extent of influence, as pointed out by Steffen *et al.* (2011), was tightly constrained by the availability of mechanical work; only human and animal power was available.

However, since the onset of the Industrial Revolution around 1800, humans have substantially influenced the ecosphere. Human population increased from around 1 billion in 1800 to 7 billion in 2011 (UN, 2010; UN Day, 2011), growing by a factor of four during the past century alone (McNeill, 2000), and by 1 billion in the last 12 years alone. This growth in human population was accompanied by a roughly 40-fold increase of energy use and a roughly 50-fold increase in economic output (McNeill, 2000). Virtually all human wealth, 97%, was created just in the last two centuries, *i.e.*, in 0.01% of our history (Beinhocker, 2006). In the same period the fraction of the land surface devoted to intensive human activities rose from 10% to about 25-30% (Labim and Giest, 2006). Concentrations of CO_2 and CH_4 rose by 30% and 100%, respectively, mainly as a result of dramatic increase of human activities such as burning fossil fuels, agriculture, and deforestation (IPCC, 2007). In 1995, more than half of all accessible fresh water was used by humans. Fisheries removed more than 25% of the yearly primary production of the oceans in the upwelling regions and 35% in the temperate continental shelf regions (Pauly and Christensen, 1995). In the same year more atmospheric nitrogen was fixed by humans than by all natural terrestrial sources combined (Vitousek *et al.*, 1997). There were clear rate-changing steps in global human impact associated with both the industrial revolution and the post WW II boom (Steffen *et al.*, 2011). Figure 1.1 shows other global changes in the ecosphere as a result of increasing human activities from 1750 to 2000 (Steffan *et al.*, 2004). As pointed out by Zalasiewicz *et al.* (2011) human-driven changes are taking place and comparable in the level of influence to those associated with major changes in the geological past. By these and other standards, it is clear that we may view the current era as being sufficiently different from other parts of the Holocene to refer to it as the Anthropocene, either involving the period since the start of agriculture, as advocated by several geologists or since the start of the Industrial Revolution (Crutzen, 2003).

1.2 Changing an unsustainable situation: Technological choice

Human consciousness of environmental problems increases as the past two centuries witness the escalating influence of humans on the ecosphere. Significant examples of these environmental concerns, as listed by Graedel and Allenby (2003), are shown in groups in Table 1.1. Similarly, a series of "planetary boundaries" for various ecospheric processes were proposed by Rockström *et al.* (2009) to define a "safe operating space" for humanity, *i.e.*, climate change, biodiversity loss, nitrogen and phosphorous cycles, stratospheric ozone depletion, ocean acidification, global freshwater use, atmospheric aerosol loading, and chemical pollution. There is substantial overlap with the effect categories in the impact assessment of life cycle assessment (LCA) as has developed in the nineties of last century (Fava *et al.*, 1991, 1993) It is further suggested that humanity has transcended the "safe operating space" with respect to climate change, nitrogen loading, and biodiversity loss and threatens to do so for the other major global environmental concerns as well. This concept of "planetary boundaries" has rapidly drawn attention from various stakeholders for action on climate change and sustainable development (*cf.* Ban, 2011; Moberg and Simonsen, 2011)[1].

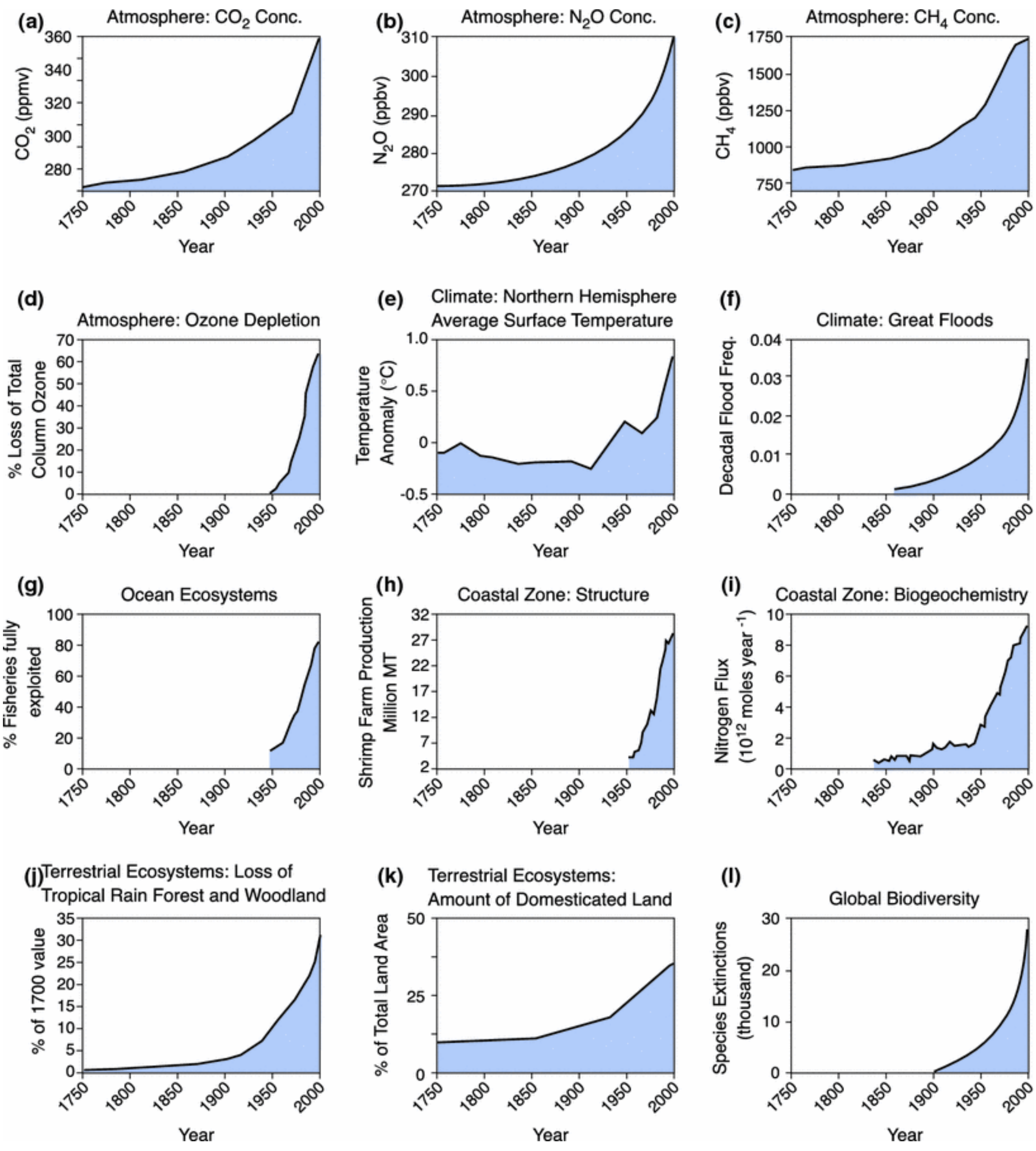

Figure 1.1 Global changes in the ecosphere as a result of increasing human activities from 1750 to 2000 (Steffan *et al.*, 2004, and reference therein)

[1] This concept has been coined with "milieugebruiksruimte" (environmental utilization space) developed by Siebert (1982) and Weterings and Opschoor (1992) in the Netherlands.

Table 1.1 Significant environmental concerns

Crucial	Highly important	Less important
Global climate change, human health damage, water availability and quality, depletion of fossil fuel resources, loss of biodiversity, stratospheric ozone depletion, land-use patterns	Depletion of non-fossil-fuel resources, acid deposition, smog, esthetic degradation	Radionuclides, landfill exhaustion, thermal pollution, oil spills, odor

Modified after Graedel and Allenby (2003)

In the political arena, sustainability was defined as a goal for the world on a global scale in late 1980s when the Brundtland Report *Our Common Future* was published, introducing the term of sustainable development (WCED, 1987). For the first time, sustainable development, as an intuitive and yet weighty concept, was simply but constructively formulated as the development that "meets the needs of the present without compromising the ability for future generations to meet their own needs". Although being understood differently by different people, sustainable development is clearly linked with many other concerns such as environmental quality, poverty, equity, justice, safety, population control, *etc* (Heijungs *et al.*, 2009). The core of sustainability is the idea of three value dimensions to be satisfied together, *i.e.*, social, environmental, and economic sustainability, which is also referred to in short as people-planet-profit or triple bottom line.

By now, it is clear that humans have been pursuing economic growth and creating wealth in an unsustainable way. Transition to a sustainable future requires sound stewardship of natural resources (both energy and materials) and the "life support system" (*e.g.*, atmosphere, hydrosphere, climate, biodiversity, *etc*.); in return requiring a shift in economic mindsets and pertinent social aspects. Economies rely on the existence of technologies: physical techniques to enable humans to create products and services that are worth trading, and social technologies that smooth the way for cooperation in creating and trading these products and services between large communities (Beinhocker, 2006). In this sense, transforming unsustainable economies requires changes technologies. This intention is expressed in, among others, proposing new technologies such as biotechnology, nanotechnology, robotics, artificial intelligence, information and communication technology, and applied cognitive science (*cf.* EC, 2011) as a solution towards more sustainable economies. Various geoengineering schemes can also be interpreted as global technological solutions to climate change. Allenby (2006) pointed out that the evaluating analysis of emerging technologies may pose the biggest challenge to both IE and related sustainability sciences.

1.3 Thermodynamics and industrial ecology

Technologies are related to various physical and social aspects such as natural resources, information, cultural values, institutional regimes, and political strategies, *etc*. The laws of nature play a prominent role here, and among them, thermodynamics plays even a key role (Baumgärtner and De Swaan Arons, 2003). Thermodynamics basically is the study of the relation between heat and work (Keenan 1941). It has long been recognized as a fundamental approach to model various scales of systems ranging from the living cell to the whole universe. In thermodynamic modeling, a thermodynamic system includes the defined region of the reality under consideration which is separated from its environment by a system boundary. Depending on the exchanges of energy and materials between the system and its environment, the system can be isolated, closed, or open. An isolated system has no exchanges with its environment, a closed system has only exchanges of energy, and an open system has exchanges of energy and materials. The basis of thermodynamics is stated in the laws of thermodynamics, mainly the first and second laws (Ruth, 1993). The first law of thermodynamics expresses the conservation of energy, while the second law describes the degradation of the quality of energy. In principle, any thermodynamic metric based on or derived from the first law or the second law can be adopted for thermodynamic analysis. This thesis uses the term of thermodynamics in a broad sense, extending to transformations of energy and materials since material flows and conversions are accompanied by energy flows and conversions in various processes of the ecosphere. Thermodynamics in this thesis thus covers both energy and materials. Technologies are thermodynamically open systems and hence subject to the most complex forms of thermodynamic analysis. This thesis applies a fortiori to the anthroposphere, which comprises the entire range of technologies, from the logging of trees to the launching of rockets.

Going back to human history, the start of the Industrial Revolution followed the design of a practical steam engine by James Watt in the late 18th century[2]. The invention of the steam engine marked an earth-shaking event for thermodynamicists: it was the first device enabling heat to be converted into mechanical work (motion) (Niele, 2005). It also shattered the energy bottleneck which dominated world economies before circa 1800: Prior to the Industrial Revolution, the primary energy sources, consisting of biomass, wind and water moving across the ecosphere, were tightly constrained in magnitude and location (Steffen *et al.*, 2011). They are ultimately derived from the energy flow from the sun, as shown in Figure 1.2, which also roughly sketches the energy metabolism within the ecosphere and its embedded technologies. The underlying processes have intrinsic inefficiencies: plants store less than 1% of the incoming solar radiation via photosynthesis and animals obtain only about 10% of that energy stored in plants via eating the plants. In addition, the main power source then was still muscle, *i.e.*, the "biological engine" of humans and other animals. After the Industrial Revolution, exploitation of fossil fuels and the vastly increasing scale of activities resulted in various aforementioned environmental concerns in the Anthropocene. This energy basis of the Industrial Revolution (introduced as a scientific discipline by Sadi Carnot in 1825) already indicates that thermodynamics can offer an important – thought not the only possible – perspective on technologies.

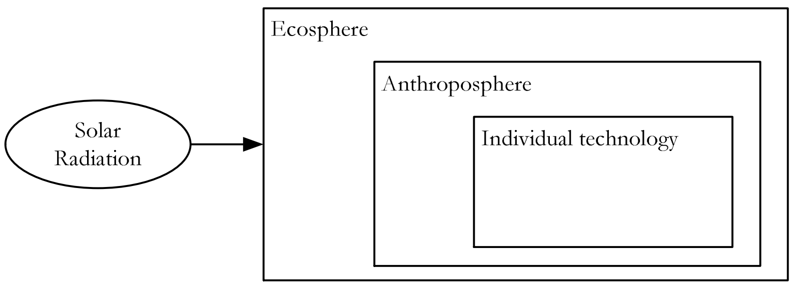

Figure 1.2 Solar radiation supporting the ecosphere and technologies

Industrial ecology (IE) has emerged in the last few decades against the background of rising environmental concerns. IE aims at a sustainable combination of ecosystems, economies, and

[2] The atmospheric engine invented by Tomas Newcomen in 1712, today referred to as a Newcomen steam engine (or simply Newcomen engine), was the first practical device to harness the power of steam to produce mechanical work. Newcomen engines were used throughout Britain and Europe, principally for pumping water, starting in the early 18th century.

technologies. As one way to explore the unknown future, IE modeling has a conceptual duality at its core. It incorporates natural science concepts relating to physical reality and social science concepts relating to symbolic reality (Huppes *et al*., 2011). The anthroposphere (technologies) as the interface between the two realities is thus the focus of IE.

The main content of IE includes a description and modeling of (1) the energy and material flows and conversions in the anthroposphere, (2) the impacts of the anthroposphere on the ecosphere, and (3) the influence of other societal aspects on the anthroposphere. Theories on (1) are intrinsically the subject of thermodynamic analysis. Main analytical tools in the context of IE - material flow analysis/accounting (MFA), LCA as well as environmentally extend input-output analysis (IOA) - have been established to investigate the content of (1) and (2).

In short, technologies and sustainable development are interrelated from a thermodynamic perspective, with IE as a major point of access for studying this relationship.

1.4 Research questions

Against the background of increasing sustainability problems, this thesis aims to contribute to the environmental sustainability analysis of technologies in the Anthropocene, by studying in which aspects thermodynamics could function as a useful element for the environmental sustainability analysis of technologies. The ultimate energy constraints for humanity are given based on the first and second laws of thermodynamics. The basic ideas underlying this thesis are the following:

- Thermodynamics covers a main physical mechanism of the interaction in human-environment systems. It sets the constraints in terms of stocks and flows and their transformation potential, and plays a key role in the analysis of life support systems like in climate system and ecology.
- Thermodynamics is essential for analyzing the environmental sustainability of technologies. It indicates the interrelations between systems in the anthroposphere and hence the potential there is for the production of useful energy within sustainable boundaries.
- Thermodynamic analysis is one basis for environmental sustainability indicators and is useful for sustainability assessment. The analysis of (in) efficiencies as in not so useful exergy loss and the rate of human appropriation of solar energy are examples.
- Thermodynamics is "value-free" and provides measurable and unambiguous indicators, in contrast to approaches where monetary preferences or ideal species distributions play an important role.

Based on these ideas, a methodological framework for the environmental sustainability analysis of technologies is developed by defining the anthroposphere as a thermodynamic hierarchy at four levels. Four main sets of research questions have been formulated in this thesis:

- Question set 1 (Q1). What is the relevance of thermodynamics for the environmental sustainability analysis of technologies? Can we link the key laws of thermodynamics to the development and use of technologies?
- Question set 2 (Q2). What are the major thermodynamic metrics and methods that can be used for the environmental sustainability analysis of technologies? Can we find a practical way to link the basic concepts of energy transformations within the boundaries of the first and second laws of thermodynamics?

- Question set 3 (Q3). How can thermodynamics be integrated with LCA and MFA to achieve a better understanding of technologies at different system levels? Can we link the thermodynamic analysis to functional systems and to the main material flows in the anthroposphere?
- Question set 4 (Q4). How can we apply thermodynamic analysis integrated with LCA and MFA to support decision-making on environmental sustainability? To what extend does the thermodynamic analysis overlap with the sustainability concepts covered in the impact categories of LCA, or is it an add-on, or can it help classify diverging mechanisms? Can we get to grips more effectively with the resource issues currently on the agenda?

For answering these questions from a thermodynamic perspective, we developed a hierarchical framework. The question sets are investigated based on this hierarchical thermodynamic framework, addressed in Chapters 2 to 5, as indicated in Table 1.2. The organization of this thesis is indicated in Figure 1.3.

Table 1.2 Overview of sets of research questions addressed in each chapter of this thesis

Chapter	Research questions			
	Q1	Q2	Q3	Q4
2	×	×	×	×
3	×	×		×
4	×		×	×
5	×		×	×

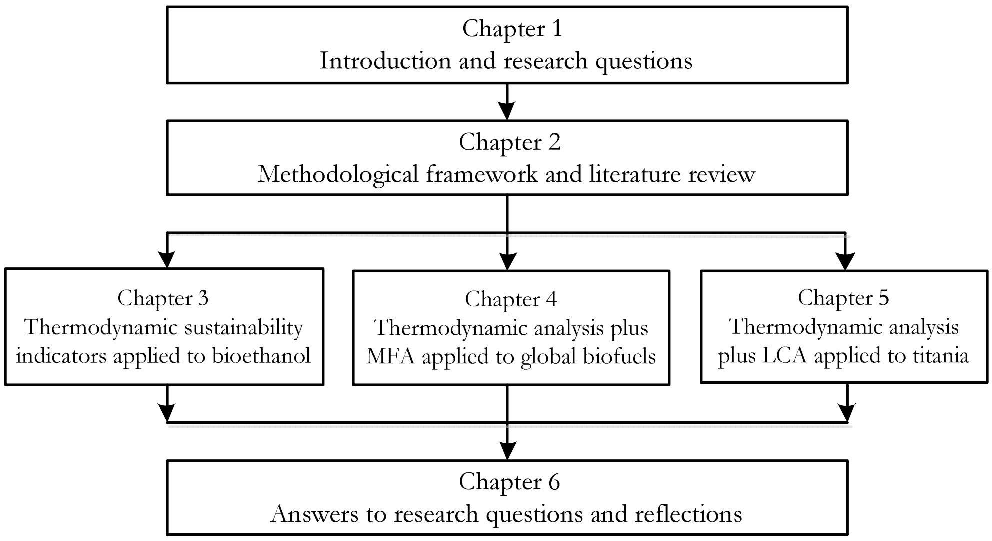

Figure 1.3 Organization of this thesis[3]

1.5 Thesis outline

Chapter 2 develops the methodological framework of this thesis and gives a literature review of thermodynamic analysis for human-environment systems. Focusing on product technology, human-environment systems are defined in terms of a thermodynamic hierarchy at four levels, *viz.*, the ecosphere,

[3] Biofuels and titania have been chosen since they are representative cases for biotechnology and nanotechnology and data are practically available in both cases.

the anthroposphere, and individual technologies, the later being further subdivided into a foreground system and a supply chain. The review focuses on the role and applications of thermodynamic analysis in IE as well as its related processes in human-environment systems. The processes and the literature are categorized within the defined thermodynamic hierarchy. The limitations and challenges of thermodynamic analysis in current IE research are pinpointed.

Chapter 3 presents an environmental sustainability assessment of bio-ethanol produced from corn stover in the U.S. by applying the framework. Energy analysis, exergy analysis, and emergy analysis are applied and four thermodynamic-based indicators are developed within the framework. The confusion about level and metric in the framework is discussed. Results on the case study of bioethanol are compared with available literature values for typical biofuel alternatives.

Chapter 4 illustrates how the natural resource demand of biofuel technology can be analyzed to assess its environmental sustainability by integrating thermodynamics and MFA based on the framework. Several existing resource demand measures are incorporated into the framework. The result on the cumulative exergy demand of nonrenewable resources of global biofuels is determined and compared with that of the anthroposphere. The contribution to climate change due to the heat emission of global biofuel production is further discussed.

Chapter 5 demonstrates the feasibility of thermodynamic resource indicators in LCA by applying the framework to the titania produced in Panzhihua city, southwest China. Four thermodynamic resource indicators are compared with three other indicators with different backgrounds. Compositions of the resource use of two mature routes for titania production are analyzed and compared. The need of identifying the best fitting resource indicator in LCA is also discussed.

Chapter 6, finally, presents answers to the question sets and a synthesis of the findings of Chapters 2 to 5 in the context of the present introductory chapter. Further development of thermodynamic analysis for sustainability is also discussed.

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.*

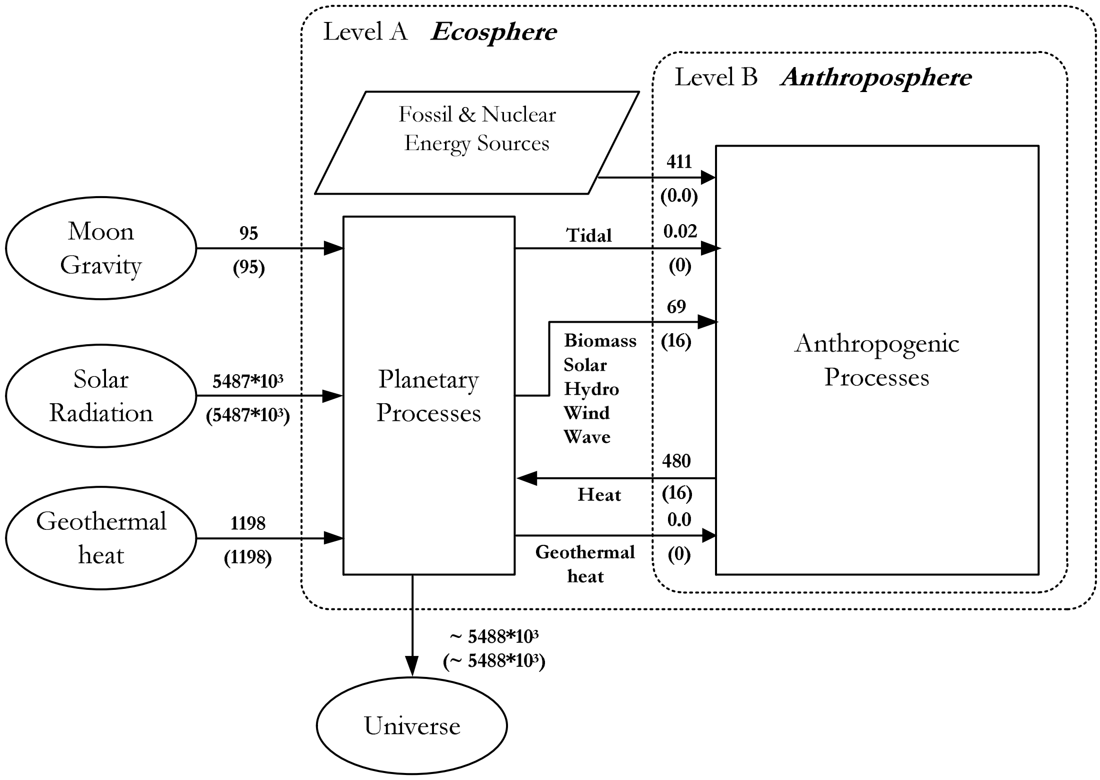

Figure 2.1 Global energy flows in the Anthropocene. Numbers represent energy flows in EJ/yr, for the year 2010 and in brackets for 1800. The ellipses stand for sources or sinks, the parallelogram for stock, and the rectangles for processes. Dashed lines represent the boundaries of the levels. Sources: 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.

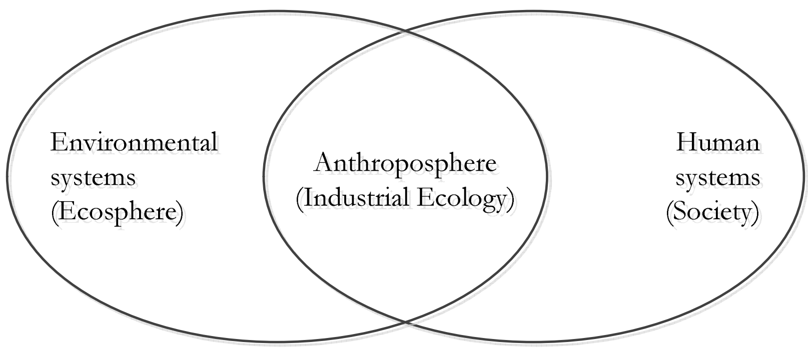

Figure 2.2 Human-environment systems and Industrial Ecology.

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.

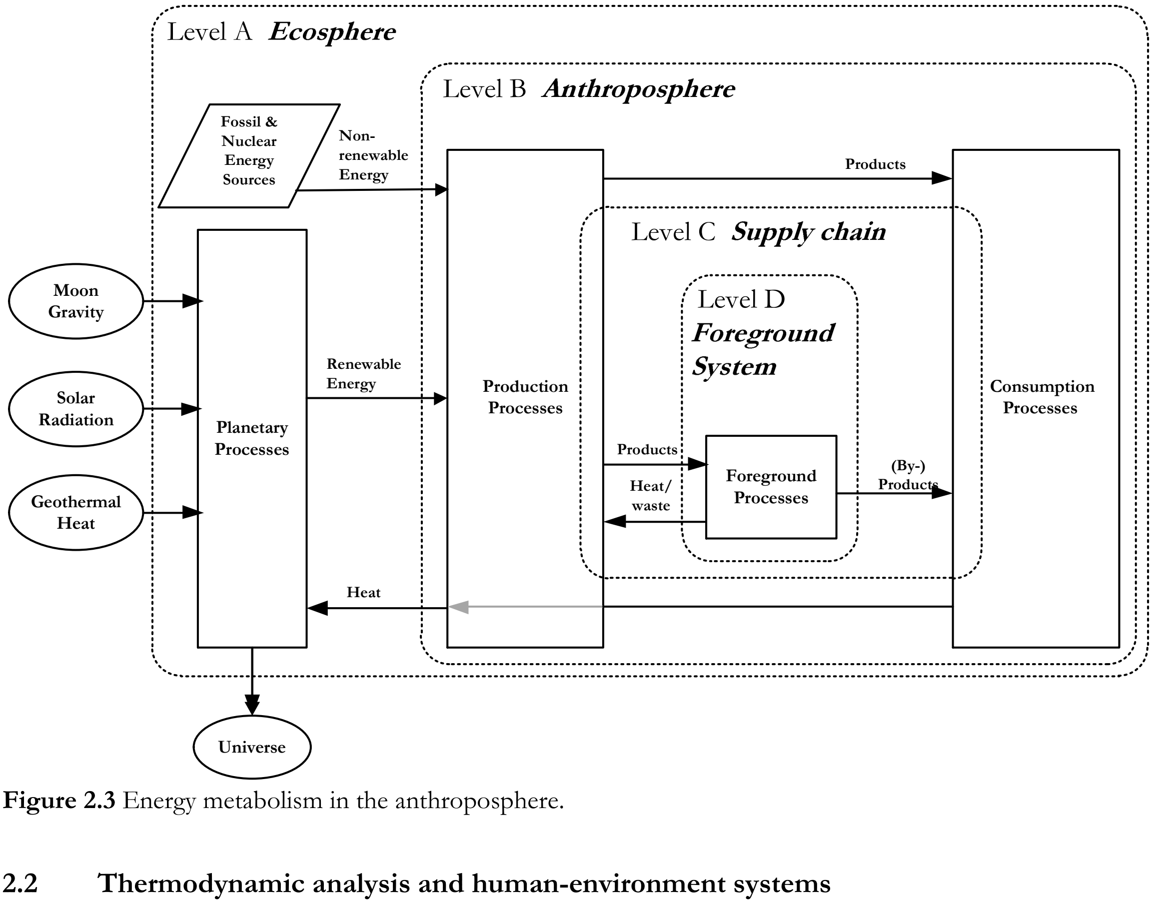

Figure 2.3 Energy metabolism in the anthroposphere.

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.

Chapter 3

Is bioethanol a sustainable energy source? An energy-, exergy-, and emergy-based thermodynamic system analysis

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Abstract

Biofuels are widely seen as substitutes for fossil fuels to offset the imminent decline of oil production and to mitigate the emergent increase in greenhouse gas emissions. This view is, however based on too simple an analysis, focusing on only one piece in the whole mosaic of the complex biofuel techno-system, and such partial approaches may easily lead to ideological bias based on political preference. This study defines the whole biofuel techno-system at three scales, *i.e.*, the foreground production (A), the background industrial network (B, including A), and the supporting Earth biosphere (C, including B). The thermodynamic concepts of energy, exergy and emergy measure various flows at these three scales, *viz.*, primary resources, energy and materials products, and labor and services. Our approach resolves the confusion about scale and metric: direct energy demand and direct exergy demand apply at scale A; cumulative energy demand and cumulative exergy demand apply at scale B; and energy is applied at scale C, where it is named emergy, while exergy also can be applied at scale C. This last option was not examined in the present study.

The environmental performance of the system was assessed using a number of sustainability indicators, including resource consumption, input renewability, physical benefit, and system efficiency, using ethanol from corn stover in the US as a technology case. Results were compared with available literature values for typical biofuel alternatives. We also investigated the influence of methodological choices on the outcomes, based on contribution analysis, as well as the sensitivity of the outcomes to emergy intensity. The results indicate that the techno-system is not only supported by commercial energy and materials products, but also substantially by solar radiation and the labor and services invested. The bioethanol techno-system contributes to the overall supply of energy/exergy resources, although in a less efficient way than the process by which the Earth system produces fossil fuels.

Our results show that bioethanol cannot be simply regarded as a renewable energy resource. Furthermore, the method chosen for the thermodynamic analysis results in different outcomes in terms of ranking the contributions by various flows. Consequently, energy analysis, exergy analysis, and emergy analysis jointly provide comprehensive indications of the energy-related sustainability of the biofuel techno-system. This thermodynamic analysis can provide theoretical support for decision-making on sustainability issues.

Nomenclature

E	Energy [J]
Ex	Exergy [J]
Em	Emergy [seJ]

Greek letters

α	Input renewability
ε	Energy/exergy efficiency
ϱ	Resource intensity

Subscripts

e	Energy
ex	Exergy
em	Emergy
pro	Product or service
agr	Agriculture
ind	Industry

3.1 Introduction

Our concerns about greenhouse gas (GHG) emissions, energy security, and rural development are motivating the development of biofuel technology (Ragauskas *et al.*, 2006; Hill *et al.*, 2006; Srinivasan, 2009). The use of biofuel, *e.g.*, bioethanol, for transportation is already being promoted as a national policy, for instance in the United States (Energy Independence and Security Act, 2007) and in Europe (Directive 2003/30/EC, 2003). The global biofuel production totaled 78 billion litres in 2008 (Bacovsky *et al.*, 2009) and provided 1.8% of total transport fuels in 2007 (Bringezu *et al.*, 2009). There is, however, ongoing debate on the extent to which biofuel could be regarded as a "sustainable energy source" (Thamsiriroj *et al.*, 2010; Niven, 2005; Escobar *et al.*, 2009) and what biofuel technology would be preferable (Campell *et al.*, 2009; Howarth and Bringezu, 2009). However, the pertinent analysis only includes a small part of the whole complex biofuel techno-system, and this lack of comprehensiveness may easily lead to ideological bias and political preference.

It has been noted that biofuel technology, like any other materials technology, inherently represents a transformation of energy and materials and their transfer to different places. The science of thermodynamics, which has formulated laws on the conversion of energy and matter, is a suitable approach to analyze the behaviour of techno-systems like that for biofuel (Guan *et al.*, 2007; Sorguven and Özilgen, 2010; Farrell *et al.*, 2006; Dewulf *et al.*, 2005). The thermodynamic analysis in this study is based on energy analysis (EA), exergy analysis (ExA), and emergy analysis (EmA), using the example case of corn stover as a cellulosic biomass used as feedstock for bioethanol production, and referring to the US as the main producer, to address that how biofuel techno-system can best be analyzed to assess its sustainability as an energy source. Results were compared with literature values, to allow them to be generalized to a broader set of typical biofuel alternatives.

3.2 Materials and methods

3.2.1 System boundary

The principle of system definition is that it should include all relevant processes. A diagram of the techno-system we investigated is shown in Figure 3.1. All relevant processes are drawn with flows mainly from left to right. Flows of energy carriers (referred to below as energy without further specification) and non-energetic materials (referred to below as materials without further specification) are indicated. The system at the broadest scale is thermodynamically speaking a closed (though non-isolated) system with energy flows, *i.e.*, incoming solar radiation and outgoing earth radiation, across the system boundary.

The three scales of the system, labeled A, B and C, can be basically defined for the various types of thermodynamic analysis conducted in this study. Scale A includes the foreground production processes, mainly the agricultural production of energy crops from seeds (process A1) and the industrial conversion of energy crop into biofuel (process A2). At scale A, the direct inputs of the foreground production are energy and materials products (EMP) and primary resources, as is also shown in detail in Figure 3.2. Scale B also includes all energy and materials conversion processes that are needed to manufacture, transport and supply the inputs to scale A. It is defined by tracing back the direct EMP inputs of scale A to primary resources, *viz.*, primary renewable resources (RRs) and primary non-renewable resources (NRRs). Scale C principally includes the biospheric processes that provide the primary resources, and the related socioeconomic processes that provide the societal resources, *viz.*, labor and services (LS), for all the industrial processes occurring at scale B.

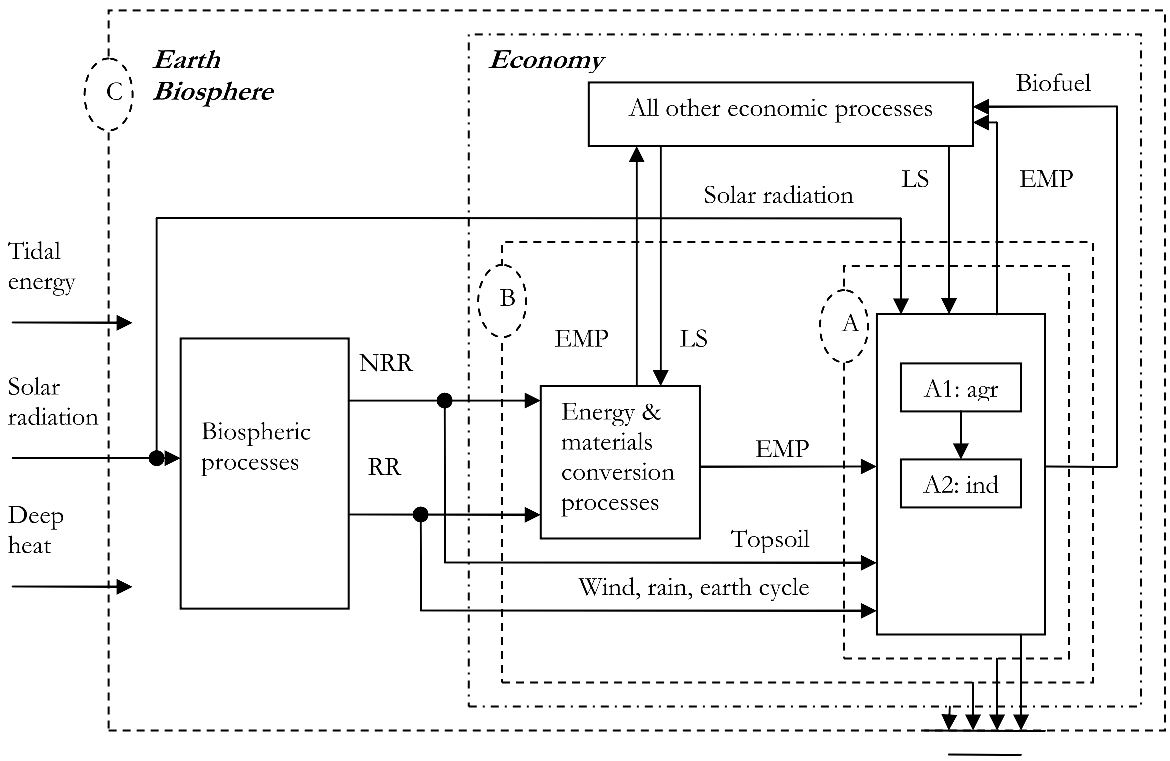

Figure 3.1 The diagram of biofuel techno-system showing various scales for thermodynamic system analysis. Level A: the foreground production; Level B: the background industrial network; Level C: the supporting Earth biosphere. RR: renewable resources; NRR: non-renewable resources; EMP: energy and material products; and LS: labor and service.

As regards the foreground production processes, the agricultural production of corn grain and stover (A1) was calculated mainly on the basis of the average situation in the US, with a corn grain yield of 8687 kg/ha/yr (12% moisture content) and a harvested stover yield of 5210 kg/ha/yr (15% moisture content). However, the industrial conversion of stover to ethanol (A2) was limited to the individual plants in the State of Iowa, where 1 kg of ethanol (99.5% by mass) was produced from 3.97 kg of stover, which means an ethanol yield of 1312 kg/ha/yr, with 1.23 kWh electricity co-produced for process use. A description of foreground production processes in detail can be found in the Swiss Centre of Life Cycle Inventories (2009), Luo *et al.* (2009), and a report by NERL (Aden *et al.*, 2002). However, due to lack of process details, transportation of corn stover from the farmland to the bio-refinery plants is left out of consideration in the study.

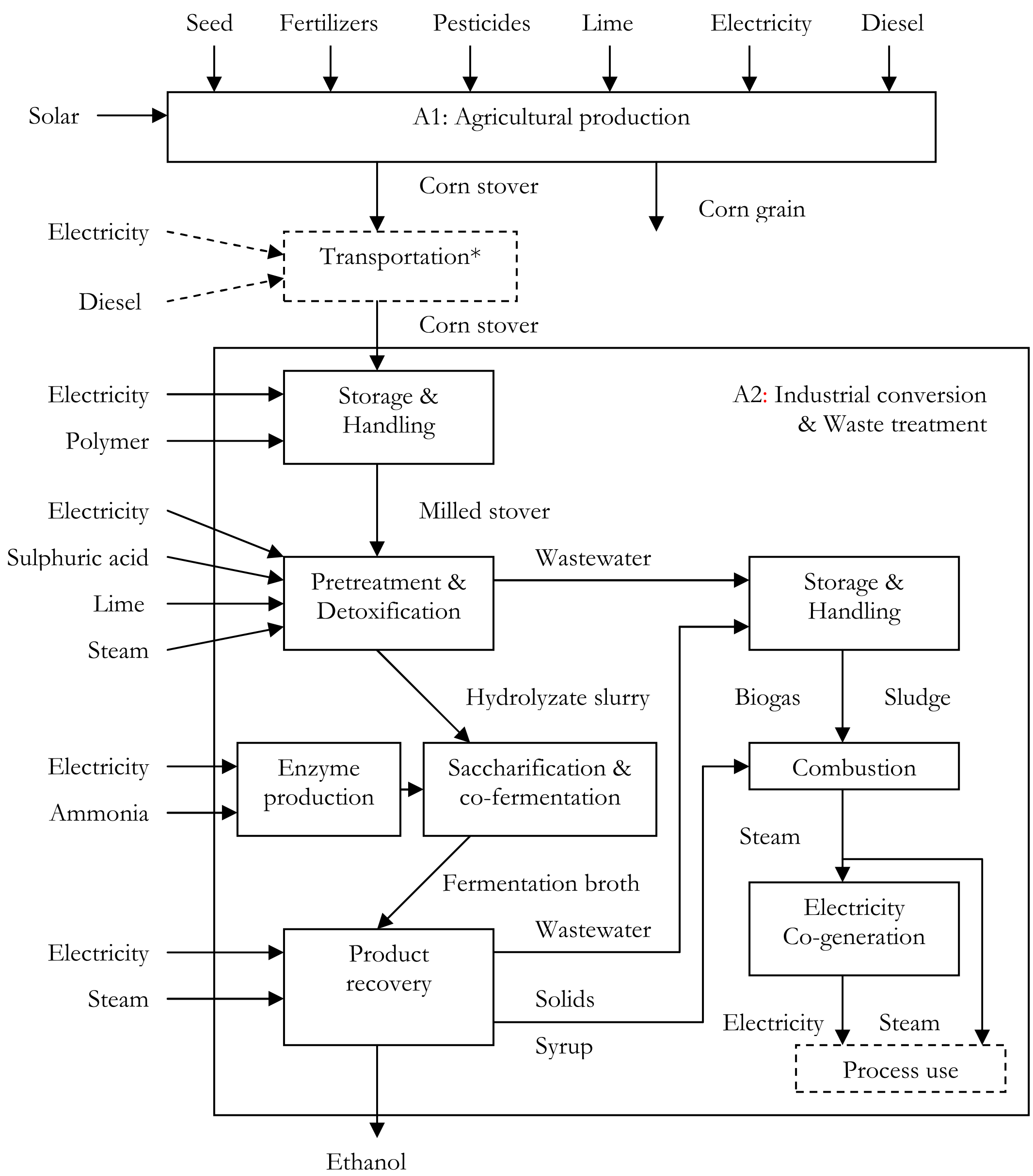

Figure 3.2 Detailed diagram of scale level A of the biofuel techno-system. Nomenclature for the diagram can be found in (Aden *et al.*, 2002). *Due to lack of process details and data, transportation of corn stover from the farmland to the bio-refinery plants is left out of consideration in the study.

3.2.2 Data sources

Data used in this study were obtained from various sources. Agricultural data and data on energy and materials conversion processes were obtained from the ecoinvent database v2.1 (Swiss Centre of Life Cycle Inventories, 2009) and Luo *et al.* (2009). Data on the industrial conversion and waste treatment were collected from a report by NERL (Aden *et al.*, 2002). Data on direct solar irradiation and other RRs were obtained from the NASA atmospheric science database (NASA, 2009), the Climatology Report by the Iowa Agricultural Department (Iowa Agricultural Department, 2008) and the Department of Commerce National Climatic Database (US DOC, 2009). Data gaps were partially filled by making various assumptions and referring to some trivial literature as noted below. Raw data were converted into flows of energy, exergy and emergy; see Appendix Table S3.1, S3.2, and S3.3.

3.2.3 Energy analysis (EA)

Various types of measurement methods are used in energy analysis (EA) to determine the direct and indirect energy inputs that a system uses to deliver a product or service (IFIAS, 1978). Energy demand can be evaluated on the basis of different valuation concepts; a discussion of the pros and cons of these concepts can be found in Frischknecht *et al.* (1998). In the present study, the direct energy demand (DED) was defined so as to account for the direct energy inputs (primary energy resources and energy products) to the foreground production processes (scale A). The indirect energy inputs which are needed to deliver the inputs as materials products can also be traced back to primary energy resources, allowing us to define the cumulative energy demand (CED) in the industrial network (scale B). CED, in this respect, extends DED so as to include the indirect energy inputs as well. Furthermore, the net energy value (NEV) can be defined by deducting CED_{EMP} from the energy contained in the products (E_{pro}) which was measured as their lower heating value in this study.

3.2.4 Exergy analysis (ExA)

Exergy is defined as the maximum amount of work which can be obtained from a flow of energy or materials when it is brought into equilibrium with the reference environment (for a commented history of the concept, see Sciubba and Wall (2007)). It has the same unit as energy, *viz.*, Joules. This study adopted the reference environment proposed by Szargut *et al.* (1988, 2005) with the natural environment subsystem by Gaggioli and Petit (1977). Exergy is consumed in all real processes in proportion to the entropy being produced. Exergy analysis (ExA) can measure exergy loss or exergy destruction and is being used in various fields, including industrial and engineering models, economics, environmental impact assessment, systems ecology, and societal systems. A comprehensive review of the use of ExA can be found in Dewulf *et al.* (2008).

Just as in EA, the direct exergy demand (DExD) is defined at scale A. The cumulative exergy demand (CExD), which is similar to the cumulative exergy consumption (CExC) defined by Szargut (2005) and the cumulative exergy extracted from the natural environment (CEENE) as defined by Dewulf *et al.* (2007), is defined at scale B. The net exergy value (NExV) is then obtained by deducting $CExD_{EMP}$ from the exergy content of products (Ex_{pro}).

3.2.5 Emergy analysis (EmA)

Emergy is defined as the total amount of available energy of one form that was originally used up, directly and indirectly, in the work of making a product or service (Odum, 1996). Emergy theory considers solar energy to be the primary source feeding all processes occurring at scale C. Hence the unit of emergy, although representing energy and thus being measured in Joules, is named solar emergy Joules (seJ). Emergy analysis (EmA) categorizes the inflows of a system used to deliver a product or service into locally renewable (RR, solar, rain, wind, earth cycle, *etc.*), locally non-renewable (NRR, topsoil, *etc.*), and purchased (F, energy and materials products, labor, service, *etc.*). The total emergy driving the system can be determined by adding up the emergy of all inflows, and is assigned to the product or service delivered (for details about the emergy algebra, see Odum (1996) and Brown and Herendeen (1996). After all the flows of interest have been quantified, a set of indicators can be developed for policy making, by assessing the environmental performance of the system itself (Brown and Ulgiati, 1997).

3.2.6 Synthesis of sustainability indicators

An energy source is environmentally sustainable when it consumes few natural resources, especially non-renewable resources, contribute to the overall energy supply chain, and is produced with high efficiency. On the basis of a thermodynamic analysis of the biofuel techno-system, the environmental sustainability of the system can be assessed against a range of indicators, *viz.*, resource consumption, input renewability, physical profit, and system efficiency. Table 3.1 below summarizes the various thermodynamic quantities of sustainability indicators for EA, ExA, and EmA at the three scales.

Table 3.1 Indicators for different types of thermodynamic system analysis

Quantity	Definition	Scale	Indication	Unit
DED	Total energy of the direct inputs	A	Resource consumption	J
DExD	Total exergy of the direct inputs	A	Resource consumption	J
CED	Total energy of the used primary resources	B	Resource consumption	J
CExD	Total exergy of the used primary resources	B	Resource consumption	J
Em_{pro}	Total solar energy used for a product or service	C	Resource consumption	seJ
α_e	$\alpha_e = E_{RR}/DED$	A	Input renewability	-
α_{ex}	$\alpha_{ex} = Ex_{RR}/DExD$	A	Input renewability	-
α_{em}	$\alpha_{em} = Em_{RR}/Em_{pro}$	C	Input renewability	-
NEV	$NEV = E_{pro} - CED_{EMP}$	B	Physical profit	J
NExV	$NExV = Ex_{pro} - CExD_{EMP}$	B	Physical profit	J
ε_e	$\varepsilon_e = E_{pro}/DExD$	A	System efficiency	-
ε_{ex}	$\varepsilon_{ex} = Ex_{pro}/DExD$	A	System efficiency	-
ϱ_e^{-1}	$\varrho_e = CED/E_{pro}$	B	System efficiency	-
ϱ_{ex}^{-1}	$\varrho_{ex} = CExD/Ex_{pro}$	B	System efficiency	-
ϱ_{em}^{-1}	$\varrho_{em} = Em_{pro}/E_{pro}$	C	System efficiency	-

3.3 Results and discussion

3.3.1 Resource consumption

Figure 3.3 represents the flows of primary resources, EMP, final product and co-products of the system on the basis of 1 kg of ethanol, in terms of EA and ExA. The balance between the inflows and outflows can be completed by taking wastes, exhausted heat, and irreversible exergy destruction into account. It is clear that RR, mainly solar radiation, dominates the resource consumption of process A1, both at scale A and at scale B. This corresponds with the nature of cropping, *i.e.*, the process of photosynthesis.

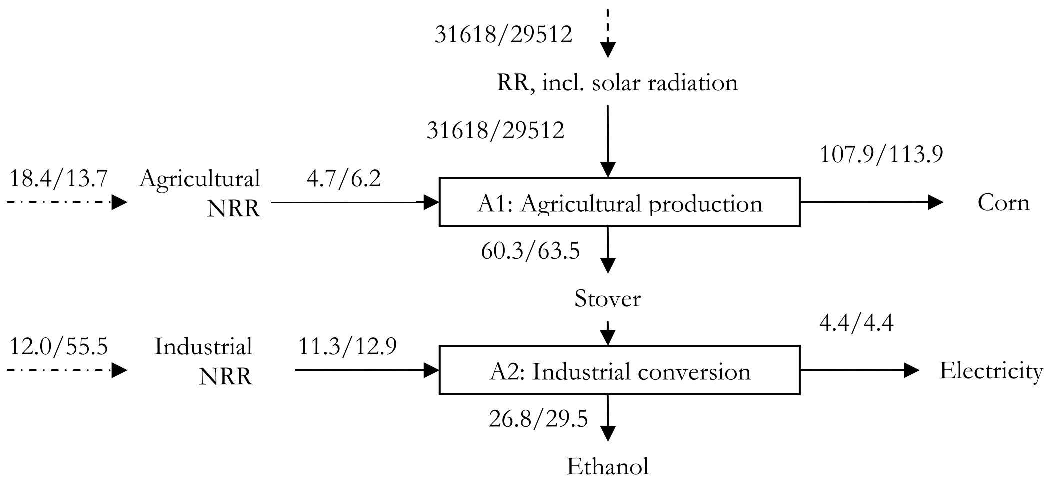

Figure 3.3 Energy/exergy flows diagram of the ethanol techno-system, in MJ/kg EtOH. Figures at dashed lines are the shares of CED/CExD. Figures at solid lines are the shares of DED/DExD and the energy/exergy of products.

Table 3.2 summarizes the results of resource consumption in terms of EA and ExA. At scale A, apart from solar radiation, the direct energy required to deliver 1 kg of ethanol is 15.98 MJ. At scale B, the CED due to EMP inputs related to process A1 that is required to finally produce 1 kg of ethanol turns out to be 18.39 MJ, 74.5% of which consists of indirect inputs such as primary energy for the production of corn seeds, chemicals, and farm machinery. Whilst related to process A2, most of the CED (94.3%) consists of the direct inputs of electricity and steam into the process, while a much lower amount of energy is used to deliver materials products.

Table 3.2 Resource consumption in EA and ExA of the ethanol techno-system

Resource consumption	Process A1		Process A2	Techno-system
(MJ/kg EtOH)	EMP	Solar [a]		EMP
DED	4.68	3.16E+04	11.30	15.98
DExD	6.15	2.95E+04	12.91	19.06
CED	18.39	3.16E+04	12.03	30.42
CExD	13.67	2.95E+04	55.47	69.14

[a] The solar energy used for electricity production and oil refinery in the supply chain of EMP is lower by several orders of magnitude than the insolation energy for cropping.

The DExD value corresponds to a direct consumption of 19.1 MJ exergy of NRRs, mainly as EMP, to produce 1 kg of ethanol. By comparison, Dewulf *et al.* (2005) found that for the corn-to-ethanol system it takes 6.39 MJ exergy of this kind to produce 1 kg of ethanol. Both exergy values are less than the exergy content of the ethanol (29.5 MJ/kg) that these two techno-systems deliver. This is because stover and corn store a certain fraction of solar exergy in their chemical structures through the process of photosynthesis. Though the fraction may be small, the stored solar exergy is generally larger than the exergy of EMP invested in the agricultural production system.

The $CExD_{EMP}$ translates into an exergy intensity for ethanol of ϱ_{ex} = 2.34 MJ_{EMP}/MJ_{pro}. In the year 2007, bioethanol production in the US was 0.6 EJ[1] (Howarth and Bringezu, 2009). This corresponds to a $CExD_{EMP}$ of 1.4 EJ, which is already of the order of magnitude of 1% of the global anthropogenic exergy consumption (13 TW, *i.e.*, 378 EJ, (Szargut, 2003)). This suggests a considerable impact of the regional application of the biofuel techno-system in the US on the Earth.

The emergy flows diagram of the techno-system is shown in Figure 3.4. It shows an Em_{pro} of 9.82 E+12 seJ, which means that 9.82 E+12 J of solar energy is used directly and indirectly to deliver 1 kg of ethanol at scale C. The emergy inputs of local RRs, local NRRs and purchased inflows account for 12.0%, 5.2%, and 82.8%, respectively, of the emergy resource consumption of the ethanol techno-system.

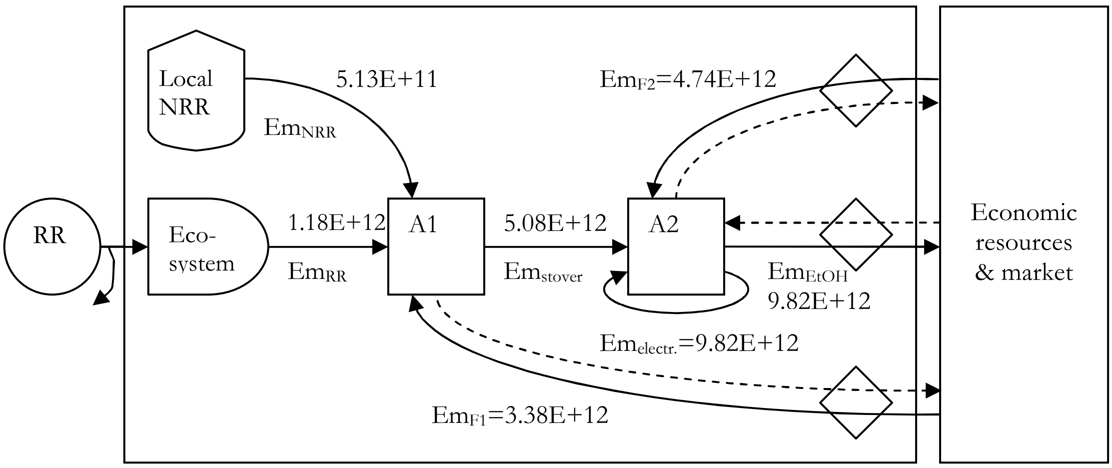

Figure 3.4 Emergy flows diagram of the ethanol techno-system, in seJ/kg EtOH

3.3.2 Input renewability

Table 3.3 summarizes the results in terms of input renewability of the techno-system. It shows that, similar to Table 3.2, the renewable resources, mainly solar radiation, account for no less than 99.9% of the direct energy/exergy inputs both for process A1 and for the techno-system. The agricultural production and the stover-to-ethanol techno-system are thus highly renewable-based. The final product (ethanol), the coproduct (corn), and the intermediate product (stover) can therefore be regarded as renewable resources for further application in the economy from an energy/exergy viewpoint. However, the α_{em} of 12.0% resulting from EmA does not support this conclusion. Other available research findings show even lower emergy-based renewability, *i.e.*, 5.36% for ethanol produced from corn in Italy (Ulgiati, 2001) and 9.45% for ethanol produced from wheat in China (Dong *et al.*, 2008). All three studies indicate that, in terms of emergy, the product ethanol cannot be regarded as a renewable energy source.

Table 3.3 Input renewability of the ethanol techno-system

Renewability	Process A1	Process A2	Techno-system
α_e	> 99.9%	84.2%	99.9%
α_{ex}	> 99.9%	83.1%	99.9%
α_{em}	n.a.	n.a.	12.0%

[1]The cited value is based on the HHV of ethanol, so the exergy value is approximately the same.

3.3.3 Physical profit

Table 3.4 summarizes the results in terms of physical profit from the techno-system. Both NEV and NExV are positive, which indicates that the ethanol techno-system contributes to the overall supply of energy/exergy resources that can be readily utilized to meet human needs. If the credits of co-products are not taken into account, EA yields a negative NEV (-3.62 MJ/kg EtOH). This is similar to the results by Pimental *et al.* (2005) and Patzek (2004), who studied corn as the feedstock for ethanol production.

Table 3.4 Physical profit of the ethanol techno-system

	EMP	Products			Physical profit
		Ethanol	Corn	Electricity	(MJ/kg EtOH)
EA	30.42	26.80	107.97	4.43	108.78
ExA	69.15	29.50	113.88	4.43	78.66

3.3.4 System efficiency

Table 3.5 summarizes the results in terms of energy/exergy efficiency and energy/exergy/emergy intensity of the techno-system. It shows that the techno-system is more efficient in terms of exergy than in terms of energy required to deliver the products. The energy/exergy efficiencies of process A1 and the overall techno-system are all very low (<1%), indicating that the techno-system is not efficient in terms of delivering energy/exergy into the products. This is mainly due to the nature of agriculture, *i.e.*, the process of photosynthesis, which inherently has limited efficiency and operation time.

Table 3.5 System efficiency of the ethanol techno-system

Efficiency	Process A1	Process A2	Techno-system
ε_e	0.53%	43.6%	0.44%
ε_{ex}	0.60%	44.3%	0.50%
ϱ_e^{-1}	0.53%	0.27%	0.44%
ϱ_{ex}^{-1}	0.60%	0.32%	0.50%
ϱ_{em}^{-1}	n.a.	n.a.	2.73E-06

The exergy intensity translates into a cumulative degree of thermodynamic perfection (CDP) of 0.005, which is much lower than the range of CDP for conventional EMP technologies (0.05 – 0.84); for instance, diesel production has a CDP of 0.835. Besides, the emergy intensities of bioethanol (2,95E+05 seJ/J (Ulgiati, 2001) – 3,66E+05 seJ/J) and biodiesel (average value 4.51E+05 seJ/J) (Ulgiati *et al.*, 1997) are much higher than those of fossil fuels (coal, crude oil, and natural gas, 6.67E+04 seJ/J – 8.89E+04 seJ/J), indicating that the biospheric processes of producing fossil fuels have been more efficient than the human dominated processes of cropping for biofuels. This is mainly because large amounts of fossil fuels and fossil-derived fertilizers and chemicals are usually used in agricultural production and industrial conversion[2].

[2] In the specific case under consideration, however, most of the electricity and steam used in the bio-refinery were produced from lignin and wastes by waste treatment, so actually only a small amount of fossil fuels was used for the industrial conversion.

3.3.5 Contribution analysis

Various inflows were taken into account and weighted by their respective conversion factors, *viz.*, exergy-to-energy ratios, CDP, and emergy intensities; see Appendix Table S3.2 and S3.3.

Since only four energy inflows, *viz.*, solar radiation, diesel, electricity, and steam, are taken into account in EA, process A1 and process A2 as different sub-processes, rather than as different inflows, to investigate their contributions to energy use. Solar radiation is explicitly left out of consideration, since it dominates CED for up to 99.9% as shown in Table 3.3. A pertinent energy signature is presented in Figure 3.5[3]. In process A1, a large amount of natural gas is used for steam reforming in the production of ammonia, which is then used in the production of nitrogen fertilizer. In process A2, a large amount of steam (5.33 MJ/kg EtOH) is used to maintain a high temperature condition for stover prehydrolysis and to prepare the boiler feed water. And the production of enzyme uses a large amount of electricity (2.59 MJ/kg EtOH) to pump air into the fermentor to ensure aerobic conditions. Figure 3.5 shows that fertilizer use, pretreatment and detoxification, and enzyme production are the three largest contributors to the energy use.

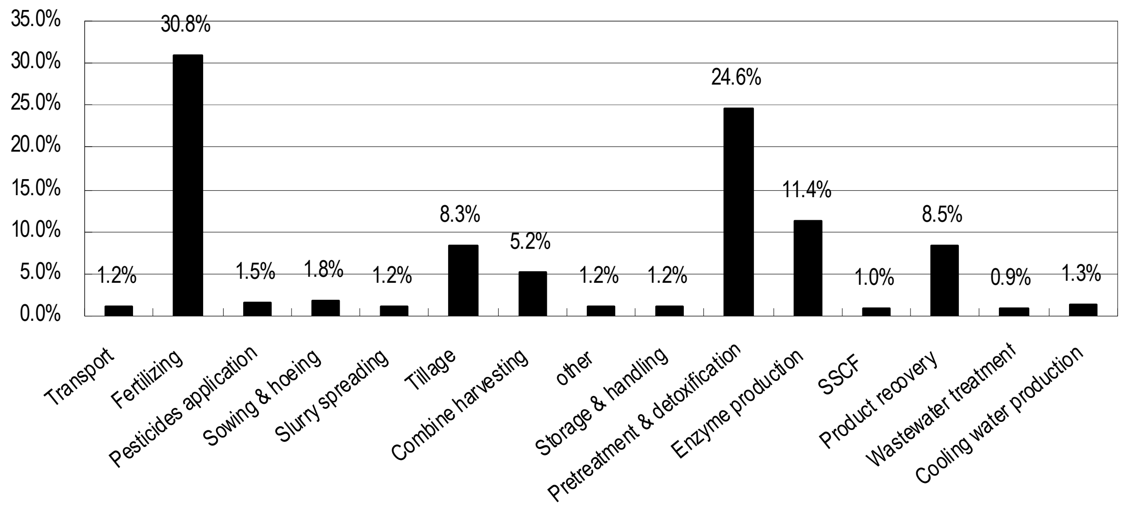

Figure 3.5 Energy signature of the ethanol techno-system

Similarly, an exergy signature can be drawn, as shown in Figure 3.6, and an emergy signature in Figure 3.7. These obviously present different outcomes of contribution analysis. They also indicate that ExA and EmA take different inflows into account at scale B and scale C.

[3] Figure 3.5 was drawn after Luo *et al.* (2009), who presented a so-called energy products-to-gate analysis. So compared to the CED in our study, the energy conversion processes were actually left out of consideration.

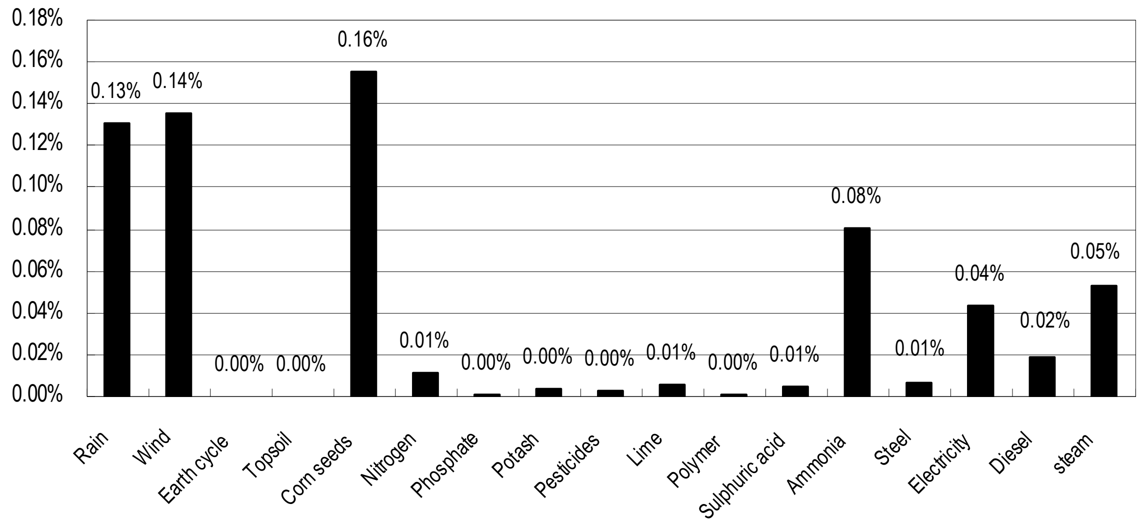

Figure 3.6 Exergy signature of the ethanol techno-system

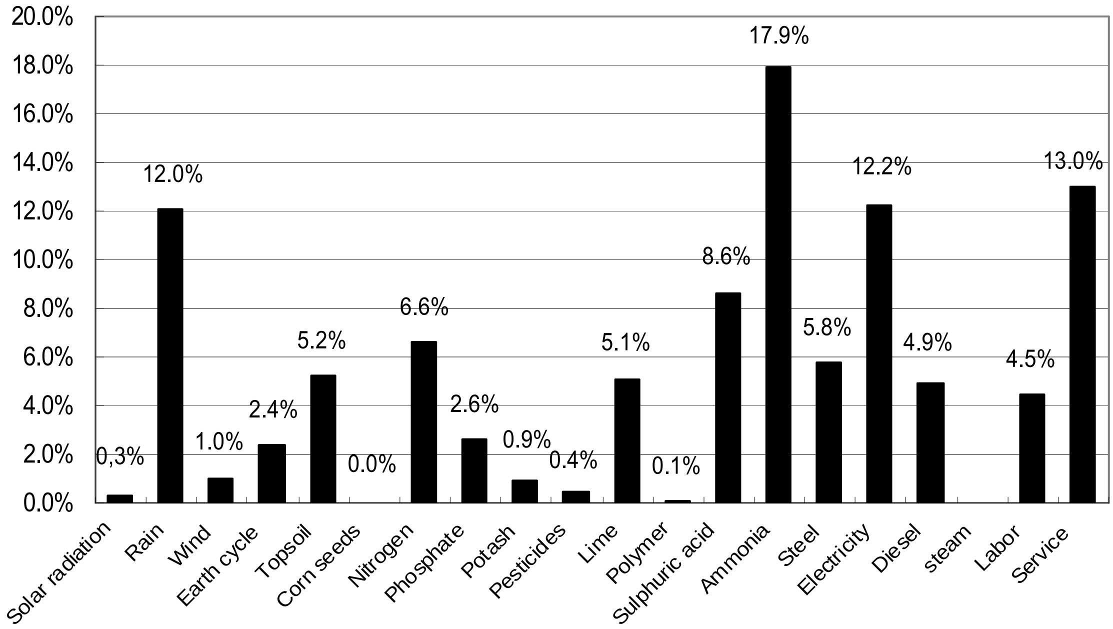

Figure 3.7 Emergy signature of the ethanol techno-system

3.3.6 Sensitivity analysis of EmA

Emergy intensity, which is equivalent to the concept of transformity used in Odum (1996) and Brown and Herendeen (1996), is a crucial concept in EmA. The emergy intensity of a product is case-specific in terms of the spatial and temporal frames and the pathway by which the product is delivered. Primary resources (RRs and NRRs) from the biosphere, which undergo natural selection and evolution and are presumed to result from long trial and error processes (Fath, 2004; Jørgensen and Svirezhev, 2004), have a range of emergy intensities, and a global average value is explicitly chosen in practice. For many manufactured products, *e.g.* electricity, steel, *etc.*, the emergy intensity varies case by case, since a product is technologically specific. This section investigates the consequences of different choices for the emergy intensity.

Table 3.6 Sensitivity to emergy intensity of emergy analysis

Emergy intensity, in seJ/J	Grid elect	Coproduced elect	Ethanol
Scenario 1[a]	2.68E+05	2.22E+06	3.66E+05
Scenario 2[b]	2.68E+05	3.27E+07	5.39E+06

[a] Scenario 1: coproduced electricity by A2 enters the national grid and the process electricity in A2 is purchased from the economy

[b] Scenario 2: coproduced electricity is reused as process energy in A2

Table 3.6 presents the outcomes in terms of emergy intensities for two scenarios that differ in the source of process electricity used in process A2. Since the difference in percentage is significant, a correspondingly different result of the contribution analysis by EmA can be expected. Despite the case study on process A2 reported by NREL (Aden, 2002), where almost all of the co-produced electricity was reused as process energy (*i.e.*, the same as in Scenario 2), when investigating future large scale applications of the bioethanol techno-system, it is more likely that the process electricity will be purchased from the national economy. This is why our analysis based on Scenario 1 was conducted as described above, in order to assess the consequences of the promotion of bioethanol technology at national level in the US. The main cause of the difference shown in Table 3.6 is undeniably the fact that Scenarios 1 and 2 model different systems, *viz.*, process A2 and the background main economy.

3.3.7 Additional discussion

As shown in Figures 3.6 and 3.7, different methods of thermodynamic analysis take different resource inflows into account. Table 3.7 summarizes the importance of four categories of emergy inflows in ethanol production from stover in the US, corn in Italy (Ulgiati, 2001) and wheat in China (Dong, 2008). Emergy inflows such as local RRs and NRRs from the biosphere account for 17.2%, 7.7%, and 19.2% of total emery consumption in ethanol production from stover, corn, and wheat, respectively, while emergy associated with labor and service from the economy contribute 17.5%, 22.3%, and 39.7%, respectively. These three categories of inflows are not taken into account in many other types of energy analysis; neither is the category of purchased labor and service in ExA. However, their importance, despite the fact that they are only being shown from an emergy viewpoint here, indicates that the complex bioethanol system may be more accurately depicted if their necessary contribution to support the system is not disregarded.

Table 3.7 Breakdown of main emergy inflow categories of ethanol production from stover, corn, and wheat

	Stover	Corn	Wheat
local RRs	12.0%	5.4%	9.4%
local NRRs	5.2%	2.3%	9.8%
purchased products, F_{EMP}	65.3%	70.0%	41.1%
purchased L & S, F_{LS}	17.5%	22.3%	39.7%

Table 3.5 also shows that the emergy intensity is about 1600 times higher than the energy intensity, *i.e.*, the unit cumulative primary energy input. This is not surprising when the necessary environmental support for the earth cycles and processes providing primary resources and ecological services is taken into account. Since process A2 is partly supported by its self-produced electricity and steam, we have mainly considered process A1, *i.e.*, the agricultural production. As shown in Table 3.2, it has a CED of 18.4 MJ/kg EtOH, *i.e.*, 18.4 MJ of primary energy, which is mainly fossil fuels, to deliver 1 kg of ethanol for the process A1. Given that the emergy intensity of the fossil fuels is about 8.00E+04 seJ/J, the above CED translates into an emergy intensity of about 1.5E+12, which is of the same order of magnitude as the result of the EmA. This shows an approximate link between CED and emergy consumption.

3.4 Conclusions and comments

This study used three types of thermodynamic system analysis, *viz.*, energy analysis (EA), exergy analysis (ExA), and emergy analysis (EmA), which can be regarded as a linear sequence of increasingly abstract types of analysis (Brown, 1996; Jørgensen and Svirezhev, 2004; Nilsson, 1997; Gattie *et al.*, 2007). The study shows that there is not really a one dimensional linear sequence, but rather basically two separate dimensions: scale and metric. The scale dimension identifies three archetypal choices: the foreground production process (A); A plus the supply chain (B); and finally B plus the biospheric processes (C). The metric dimension distinguishes two options: energy as such and energy insofar as it can be used for work with respect to a reference environment, *i.e.*, exergy. Given that EA and ExA can be performed at scales A and B, and that EmA is an analysis at scale C on the basis of the energy definition, we can now map the field as shown in Table 3.8.

Table 3.8 The place of EA, ExA and EmA in the two-dimensional diagram of scale and metric. Notice that ExA at scale C, although conceivable, has not been investigated in the present study.

Metric	Scale A	Scale B	Scale C
Energy	EA	Cumulative EA	EmA
Exergy	ExA	Cumulative ExA	–

The two-dimensional thermodynamic system analysis is proposed to depict the complex biofuel techno-system by measuring the flows and describing the processes. The environmental performance of the system can consequently be assessed against several sustainability indicators, *viz.*, resource consumption, input renewability, physical profit, and system efficiency. Conclusions can be drawn on the basis of both the case study of the stover to ethanol techno-system and the comparison with available literature results:

- Solar radiation dominates the resource consumption from an energy/exergy viewpoint, and the labor and service invested also contribute substantially to the bioethanol techno-system.
- The regional production of bioethanol in the US has considerable implications at a global scale in terms of exergy consumption.
- A straightforward conclusion on whether biofuels are renewable resources cannot be drawn for the bioethanol case investigated here, as this depends on the thermodynamic metric and scale level chosen.
- The bioethanol techno-system contributes to the overall supply of energy/exergy resources that can be readily utilized for human society.

- The bioethanol techno-system is not efficient in terms of delivering energy/exergy into the products. Also, the human-dominated processes of cropping for biofuels are less efficient than the biospheric processes of producing fossil fuels, from an emergy point of view.
- The contributions made to the bioethanol techno-system by different inflows can be investigated by the three methods of thermodynamic analysis. Each selected method has its own specific outcome.
- The choice of emergy intensity of manufactured products has a large influence on the outcomes in terms of sensitivity in EmA.

The methodology of thermodynamic system analysis developed in this study can be readily applied to other biofuel feed-stocks and other advanced biofuel techno-systems, *e.g.*, Sorguven and Özilgen (2010) and Hertwich and Zhang (2009), as well as to any other energy and materials based systems. Nevertheless, since the three methods of thermodynamic analysis are based on different theoretical assumptions and cover different flows and processes, the interrelationships among these three methods need to be investigated further and framed more consistently to offer more comparable results. Broader sustainability indicators like GHG emissions (De Souza *et al.*, 2010), biodiversity (Groom *et al.*, 2007), land and water requirements (Gopalakrishnan *et al.*, 2009; Rathmann *et al.*, 2010), and air and water pollution (Williams *et al.*, 2009) might be linked to some thermodynamic indicators to tackle the complex biofuel issue according to our different concerns. The present study, however, only supports sustainability decision making by offering information about the performance of the biofuel techno-system in the new two-dimensional scale-and-metric framework developed here.

Appendix

Table S3.1 Energy data based on Luo *et al.* (2009) and the calculation of CED

Agriculture

			Energy kJ/kg EtOH	
Primary energy for energy conversion				
	electricity production	oil refinery		
Coal	2608,00	265,19	2873,19	
Uranium	1415,32	126,74	1542,06	
Natural gas	475,66	357,04	832,70	
Crude oil	290,08	8485,55	8775,63	
Hydropower	221,00	21,05	242,05	
Wind	38,20	3,31	41,51	
Biomass	25,80	3,01	28,81	
Solar	0,50	0,04	0,54	
	5074,56	9261,93	**14336,49**	
Primary energy for materials conversion				
Natural gas			4037,60	
Coal			14,89	
			4052,49	
		CED_{agr}	**18388,98**	
		=	**24126,34**	MJ/ha/yr
Biorefinery				
Electricity			4216,95	
Steam			7167,69	
Diesel			20,61	
Light fuel oil			12,87	
Heave fuel oil			253,28	
Natural gas			224,54	
Hard coal			135,11	
		CED_{ind}	**12031,05**	
		=	**15784,74**	MJ/ha/yr
		CED	30420,03	kJ/kg EtOH
		=	39911,08	MJ/ha/yr
		LHV	26,8	MJ/kg EtOH
		=	21,2	MJ/L EtOH
		NEV=	LHV-CED	
		=	(3,62)	MJ/kg EtOH

Table S3.2 Raw inflow data and the calculation of DED, DExD, and CExD

Agricultural production

Note	**Flow item**	**Unit**	**Raw amount**	**DED MJ/ha/yr**	**Spec. Ex MJ/kg**	**Ex/E**	**DExD MJ/ha/yr**	**CDP**	**CExD MJ/ha/yr**
Input									
1	solar	MJ/ha/yr	4,15E+07	4,15E+07		0,933	3,87E+07	1	3,87E+07
2	rain (chemical potential)	MJ/ha/yr	5,09E+04			1	5,09E+04	1	5,09E+04
3	wind	MJ/ha/yr	5,27E+04			1	5,27E+04	1	5,27E+04
4	earth cycle	MJ/ha/yr	3,00E+04						n.a.[a]
5	topsoil	MJ/ha/yr	5,43E+03						n.a.
						$DExD_{agr.RR}$	**3,87E+07**	**$CExD_{agr.RR}$**	**3,87E+07**
6	N-fertilizer as N	kg/ha/yr	1,34E+02		3,68E+00		4,93E+02	0,112	4,40E+03
7	P-fertilizer as P_2O_5	kg/ha/yr	5,08E+01		2,91E+00		1,48E+02	0,387	3,82E+02
8	K-fertilizer as K_2O	kg/ha/yr	6,25E+01		3,43E+00		2,14E+02	0,14	1,53E+03
9	lime	kg/ha/yr	2,64E+02		1,97E+00		5,20E+02	0,361	1,44E+03
10	pesticides	kg/ha/yr	2,33E+00		2,40E+01		5,59E+01	0,053	1,05E+03
11	corn seeds	kg/ha/yr	1,87E+02		1,72E+01		3,22E+03	0,053	6,07E+04
12	electricity	MJ/ha/yr	4,36E+02	4,36E+02		1	4,36E+02	0,35	1,25E+03
13	diesel	MJ/ha/yr	5,71E+03	5,71E+03		1,07	6,11E+03	0,835	7,31E+03
14	steel	kg/ha/yr	1,36E+01		7,04E+00		9,57E+01	0,17	5,63E+02
15	labor	J	1,16E+08						n.a.
16	service	USD	6,27E+02						n.a.
			$DED_{agr.NRR}$	**6,14E+03**		**$DExD_{agr.NRR}$**	**8,07E+03**	**$CExD_{agr.NRR}$**	**1,79E+04**
Output									
17	stover	kg/ha/yr	5,21E+03		1,60E+01		**8,34E+04**		
18	corn	kg/ha/yr	8,69E+03		1,72E+01		**1,49E+05**		

[a] n.a.= not available

Table S3.2 Raw inflow data and the calculation of DED, DExD, and CExD

Industrial Conversion

Note	**Flow item**	**Unit**	**Raw amount**	**DED MJ/ha/yr**	**Spec. Ex MJ/kg**	**Ex/E**	**DExD MJ/ha/yr**	**CDP**	**CExD MJ/ha/yr**
Input									
19	stover	kg/ha/yr	5,21E+03		1,60E+01				
20	polymer	kg/ha/yr	1,48E+00		2,29E+01		3,40E+01	0,15	2,27E+02
21	sulphuric acid	kg/ha/yr	1,75E+02		1,67E+00		2,92E+02	0,15	1,95E+03
22	lime	kg/ha/yr	1,27E+02		1,97E+00		2,51E+02	0,361	6,95E+02
23	ammonia	kg/ha/yr	3,63E+02		1,98E+01		7,18E+03	0,229	3,14E+04
24	electricity	MJ/ha/yr	5,46E+03	5,46E+03		1	5,46E+03	0,35	1,56E+04
25	steam	MJ/ha/yr	9,41E+03	9,41E+03		0,356	3,35E+03	0,161	2,08E+04
26	steel	kg/ha/yr	5,23E+01		7,04E+00		3,68E+02	0,17	2,17E+03
27	labor	yrs	2,00E-03						n.a.
28	service	USD	2,39E+02						n.a.
			DED_{ind}	**1,49E+04**		**$DExD_{ind}$**	**1,69E+04**	**$CExD_{ind}$**	**7,28E+04**
Output									
29	ethanol	kg/ha/yr	1,31E+03		2,95E+01		3,87E+04		
		MJ/ha/yr	3,52E+04						
30	electricity	MJ/ha/yr	5,81E+03			1	5,81E+03		
			DED_{NRR}	**2,10E+04**		**$DExD_{NRR}$**	**2,50E+04**	**$CExD_{NRR}$**	**1,80E+07**
	Exergy content of EtOH =		29,52MJ/kg						

Table S3.3 Raw inflow data and the calculation of emergy value, *i.e.*, emergy analysis table (/ha/yr)

Note	Flow item	Unit	Quantity /ha/yr	Emergy intensity seJ/unit	Ref.[a]	Solar emergy seJ/ha/yr	Percent. %
Agricultural production							
renewable inputs							
1	solar	J	4,15E+13	1,00E+00	(1)	4,15E+13	0,3
2	Rain (chemical potential)	J	5,09E+10	3,05E+04	(2)	1,55E+15	12,1
3	wind	J	5,27E+10	2,52E+03	(2)	1,33E+14	1,0
4	earth cycle	J	3,00E+10	1,02E+04	(2)	3,06E+14	2,4
Non-rewable inputs							
5	topsoil	J	5,43E+09	1,24E+05	(2)	6,73E+14	5,2
purchased inputs							
6	N-fertilizer	g	1,34E+05	6,37E+09	(2)	8,54E+14	6,6
7	P-fertilizer	g	5,08E+04	6,54E+09	(2)	3,32E+14	2,6
8	K-fertilizer	g	6,25E+04	1,84E+09	(2)	1,15E+14	0,9
9	lime	g	2,64E+05	1,68E+09	(2)	4,44E+14	3,4
10	pesticides	g	2,33E+03	2,48E+10	(3)	5,78E+13	0,4
11	corn seeds	g	1,87E+05	5,88E+04	(4)	1,10E+10	0,0
12	electricity	J	4,36E+08	2,68E+05	(2)	1,17E+14	0,9
13	diesel	J	5,71E+09	1,11E+05	(2)	6,33E+14	4,9
14	steel	g	1,36E+04	1,13E+10	(2)	1,54E+14	1,2
15	labor	J	1,16E+08	4,50E+06	(5)	5,22E+14	4,1
16	service	USD	6,27E+02	1,93E+12	(6)	1,21E+15	9,4
agricultural product and by-product							
17	stover	g	5,21E+06	1,28E+09	(7)	6,66E+15	51,7
18	corn	g	8,69E+06	7,67E+08	(7)	6,66E+15	51,7
Industrial Conversion							
19	stover	g	5,21E+06	1,28E+09	(7)	6,66E+15	51,7
20	polymer	g	1,48E+03	6,37E+09	(2)	9,44E+12	0,1
21	sulphuric acid	g	1,75E+05	6,37E+09	(2)	1,11E+15	8,6
22	lime	g	1,27E+05	1,68E+09	(2)	2,14E+14	1,7
23	ammonia	g	3,63E+05	6,37E+09	(2)	2,31E+15	17,9
24	electricity	J	5,46E+09	2,68E+05	(2)	1,46E+15	11,4
25	steam	J	9,41E+09	n.a.	(2)	n.a.	n.a.
26	steel	g	5,23E+04	1,13E+10	(2)	5,91E+14	4,6
27	labor	yrs	2,00E-03	2,69E+16	(4)	5,38E+13	0,4
28	service	USD	2,39E+02	1,93E+12	(6)	4,61E+14	3,6
industrial product and byproduct							
29	ethanol	g	1,31E+06	9,81E+09	(7)	1,29E+16	100,0
	ethanol, as joules	J	3,52E+10	3,66E+05	(7)	1,29E+16	100,0
30	electricity	J	5,81E+09	2,22E+06	(7)	1,29E+16	100,0

[a] The reference of emergy transformities: (1) By definition; (2) After Odum (1996); (3) After Brown and Arding (1991); (4) After Ulgiati (2001); (5) Brandt-Williams (2002); (6) UFL (2009); (7) This study.

Footnotes of EmA

Note	Flow Item	Raw amount	Unit	Ref.
Agricultural production				
1	solar			
	Radiation	3,85E+00	KWh/m²/day	http://eosweb.larc.nasa.gov/cgi-bin/sse/sse.cgi
	Albedo	1,80E-01		http://eosweb.larc.nasa.gov/cgi-bin/sse/sse.cgi
	Conversion	3,60E+06	J/kWh	
		3,65E+02	day/yr	
	Cropped area	1,00E+04	m²/ha	
	Insolation energy	4,15E+13	J/ha/yr	Iowa State, (Lat 42, Lon -93) ; State specified in NREL report
2	rain (chemical potential)			
	precipitation	4,36E+01	in/yr	http://www.iowaagriculture.gov/climatology.asp
	Conversion	2,54E+01	in/mm or in/(L/m²)	
	Cropped area	1,00E+04	m²/ha	
	water density	1,00E+00	kg/L	
	run-off coefficient	7,00E-02		Brandt-Williams, 2002
	Gibbs free energy of water	4,94E+03	J/kg	
	energy of rain	5,09E+10	J/ha/yr	
3	wind			
	velocity	1,15E+01	mile/h	http://cdo.ncdc.noaa.gov/cgi-bin/climatenormals/climatenormals.pl
	Conversion	1,61E+03	m/mile	
		3,60E+03	s/h	
		3,15E+07	s/yr	
	air density	1,23E+00	kg/m³	
	drag coefficient	1,00E-03		Brandt-Williams, 2002
	Cropped area	1,00E+04	m²/ha	
	energy of wind	5,27E+10	J/ha/yr	
4	earth cycle			
	heat flow through earth crust contributing to uplift replacing erosion, *i.e.*, deep heat			
	average flow per area	3,00E+06	J/m²/yr	Odum, 1996
	Cropped area	1,00E+04	m²/ha	
	earth cycle energy	3,00E+10	J/ha/yr	
5	topsoil			
	organic matter loss due to soil erosion	2,00E+04	kg/ha/yr	http://www.earth-policy.org/Books/Eco/EEch3_ss5.htm

	organic matter content in topsoil	4,00E-02		Pimentel *et al.*, 1995
	water content in organic matter	7,00E-01		estimation of average value
	energy content of dry organic matter	5,40E+03	kcal/kg	
	Conversion	4,19E+03	J/kcal	
	energy loss	5,43E+09	J/ha/yr	
6	nitrogen fertilizer as N			
	ammonia, liquid, at plant	8,44E+00	g/kg corn	ecoinvent
	ammonia, liquid, at plant, as N	6,95E+00	g/kg corn	
	urea as N	3,54E+00	g/kg corn	ecoinvent
	ammonia nitrate as N	4,89E+00	g/kg corn	ecoinvent
	total N-fertilizer	1,54E+01	g/kg corn	
	corn yield	8,69E+03	kg corn/ha/yr	
	N-fertilizer	1,34E+05	g/ha/yr	
7	phosphate fertilizer as P_2O_5			
	diammonium phosphate as P_2O_5	5,85E+00	g/kg corn	ecoinvent
	corn yield	8,69E+03	kg corn/ha/yr	
	P-fertilizer	5,08E+04	g/ha/yr	
8	potash fertilizer as K_2O			
	potassium chloride as K_2O	7,19E+00	g/kg corn	ecoinvent
	corn yield	8,69E+03	kg corn/ha/yr	
	K-fertilizer	6,25E+04	g/ha/yr	
9	lime			
	mass of limestone used	3,04E+01	g/kg corn	ecoinvent
	corn yield	8,69E+03	kg corn/ha/yr	
	total lime	2,64E+05	g/ha/yr	
10	pesticides			
	total pesticides	2,33E+00	kg/ha/yr	ecoinvent
11	corn seeds			
	maize seed IP, at regional store house	2,15E-02	kg/kg corn	ecoinvent
	corn yield	8,69E+03	kg corn/ha/yr	
	total seeds	1,87E+02	kg/ha/yr	
12	electricity			
	direct-used electricity per kg corn	3,32E+02	kJ/6,62kg corn	Luo, 2009
	corn yield	8,69E+03	kg corn/ha/yr	
	total direct-used electricity	4,36E+05	kJ/ha/yr	

13	diesel			
	direct-used diesel per kg corn	4,35E+03	kJ/6,62kg corn	Luo, 2009
	corn yield	8,69E+03	kg corn/ha/yr	
	total direct-used electricity	5,71E+06	kJ/ha/yr	
14	steel			
	steel for agri. machinery (10-yr life span)	1,36E+04	g/ha/yr	after Ulgiati, 2001
15	labor			
	Minnesota case	1,16E+08	J/ha/yr	Campbell, 2008
16	service			
	Minnesota case	6,27E+02	USD/ha/yr	Campbell, 2008
17	stover			
	stover yield	5,21E+06	g/ha/yr	Luo, 2009
18	corn			
	corn yield	8,69E+06	g/ha/yr	Luo, 2009
Industrial				
19	stover			
	the same as 17			
20	polymer			
	polymer per kg ethanol	1,13E+00	g/kg	Luo, 2009
	ethanol production	1,31E+03	kg/ha/yr	
	total polymer	1,48E+03	g/ha/yr	
21	sulphuric acid			
	sulphuric acid per kg ethanol	1,33E+02	g/kg	Luo, 2009
	ethanol production	1,31E+03	kg/ha/yr	
	total sulphuric acid	1,75E+05	g/ha/yr	
22	lime			
	lime per kg ethanol	9,70E+01	g/kg	Luo, 2009
	ethanol production	1,31E+03	kg/ha/yr	
	total lime	1,27E+05	g/ha/yr	
23	ammonia			
	ammonia per kg ethanol	2,76E+02	g/kg	Luo, 2009
	ethanol production	1,31E+03	kg/ha/yr	
	total ammonia	3,63E+05	g/ha/yr	
24	electricity			
	feedstock storage & handling	2,87E+02	kJ/kg ethanol	Luo, 2009

	pretreatment & hydrolyzate condition	2,52E+02	kJ/kg ethanol	Luo, 2009
	enzyme production	2,59E+03	kJ/kg ethanol	Luo, 2009
	SSCF	2,47E+02	kJ/kg ethanol	Luo, 2009
	product recovery	2,45E+02	kJ/kg ethanol	Luo, 2009
	wastewater treatment	2,14E+02	kJ/kg ethanol	Luo, 2009
	cooling water production	3,29E+02	kJ/kg ethanol	Luo, 2009
	total electricity per kg ethanol	4,16E+03	kJ/kg ethanol	
	ethanol production	1,31E+03	kg/ha/yr	
	total electricity	5,46E+06	kJ/ha/yr	
25	steam			
	pretreatment & hydrolyzate condition	5,33E+03	kJ/kg ethanol	Luo, 2009
	product recovery	1,84E+03	kJ/kg ethanol	Luo, 2009
	total steam per kg ethanol	7,17E+03	kJ/kg ethanol	
	ethanol production	1,31E+03	kg/ha/yr	
	total steam	9,41E+06	kJ/ha/yr	
26	steel			
	steel for agri. machinery (10-yr life span)	5,23E+04	g/ha/yr	after Ulgiati, 2001
27	labor			
	labor input	2,00E-03	work yrs/ha/yr	after Ulgiati, 2001
28	service			
	plants life span	2,00E+01	yr	NREL report
	ethanol production	6,93E+01	MM gal/yr	NREL report
	Conversion	3,79E+00	L/gal	
	ethanol density	7,89E+02	g/L	
	ethanol production per ha per yr	1,31E+06	g/ha/yr	
	equivalent cropped land area	1,58E+05	ha	
	total equipment cost	1,14E+02	MM USD	NREL report
	equipment cost per ha	3,60E+01	USD/ha/yr	
	total project investment (capital)	1,97E+02	MM USD	NREL report
	project investment (capital) per ha	6,26E+01	USD/ha/yr	
	non-feedstock raw materials	1,27E+01	MM USD/yr	NREL report
	non-feedstock raw materials per ha	8,05E+01	USD/ha/yr	
	waste disposal	2,00E+00	MM USD/yr	NREL report
	waste disposal per ha	1,27E+01	USD/ha/yr	
	fixed costs	7,50E+00	MM USD/yr	NREL report

	fixed costs per ha	4,75E+01	USD/ha/yr	
	capital and service per ha per yr	2,39E+02	USD/ha/yr	
29	ethanol			
	ethanol produced in grams	1,31E+06	g/ha/yr	NREL report
	energy content of ethanol	2,68E+04	J/g	
	ethanol produced in joules	3,52E+10	J/ha/yr	
30	electricity			
	electricity co-produced	5,81E+09	J/ha/yr	NREL report

Chapter 4

Natural resource demand of global biofuels in the Anthropocene: A review

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Abstract

The Anthropocene is the later part of the Holocene where human activity has become a major driver for global ecosystem development. The demand of natural resources, renewable and non-renewable, is a crucial aspect of environmental (un-) sustainability. When considering a societal transition scheme towards sustainability, bio-based options come to the fore. The article develops a global framework for the analysis of natural resource demand of global biofuels. The framework defines the biofuel system in term of exergy at four levels, *i.e.*, the foreground system, the supply chain, the anthroposphere, and the ecosphere. Various measures of resource demand, such as cumulative exergy demand, global and anthropogenic exergy budgets are incorporated into the framework. Based on reviews of global biofuel production and natural resource demand of the anthroposphere, the study finds that the production of conventional biofuels, *i.e.*, first generation of biodiesel and bioethanol by key producer countries in 2008 consumed 9.32 E+11 MJ of exergy from non-renewable resources and accounted for 0.23% of the total anthropogenic non-renewable resource demand. In addition, it shows that the contribution to climate change due to the heat emission of the global biofuel production was 5.79 E-05 W/m^2, which would reach up to 0.002% of global greenhouse warming if anthropogenic heat flux is treated as a climate forcing.

4.1 Introduction

4.1.1 Biofuels in the Anthropocene

We are currently in the era sometimes called the Anthropocene, in which humanity and human activities have become a global geophysical force and the main drivers of global environmental change (Crutzen, 2002; Steffen *et al.*, 2007). The historical development of primary energy supply for humanity can be taken as a typical example. 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, geothermal heat, or the moon's gravitational energy. With industrialization, human consumption of non-renewable energy sources, mainly fossil fuels, outpaced that of renewable energy sources. Since WWII, human society has witnessed a dramatically increasing consumption of fossil fuels and fission energy. In recent decades, human concerns about increasing oil prices, energy security, and global warming are motivating the utilization of renewable energy sources which accounts for the minority of the current total primary energy production. The use of biofuels, *i.e.*, fuels derive from biomass, for transportation is already being promoted as a (supra-) national policy, for instance in the United States (Energy Independence and Security Act, 2007) and in Europe (Directive 2003/30/EC, 2003). The global biofuel production totaled 7.80 E+07 m^3 in 2008 (Bacovsky *et al.*, 2009) and provided 1.8% of total transport fuels in 2007 (Bringezu *et al.*, 2009).

Biofuels are commonly produced from plants, animals, and micro-organisms but also from organic wastes. They can be solid like biochar, liquid like biodiesel and bioethanol, or gaseous like biogas, biosyngas and biohydrogen. The biggest difference between biofuels and petroleum feed-stocks is oxygen content (Demirbas, 2009). The current global biofuel economy is an aggregation of a dozen of national markets. Each market provides various kinds of biofuels in terms of different feed-stocks of biomass, agricultural cultivation methods, industrial conversion technologies, and the process energy to power the industrial conversion. Liquid biofuels, mainly biodiesel and bioethanol are considered as promising fuel alternative to petroleum-derived fuels. Biodiesel is monoalkyl esters of long chain fatty acids derived from vegetable oil or animal fat. Bioethanol is ethanol derived exclusively from the fermentation of plant starches.

4.1.2 Environmental (un-) sustainability of biofuels

Like any other energy- or material-based products, the production of biofuels requires non-renewable resources in its supply chain before biofuels enter the anthroposphere for further utilization. For the environmental aspect of sustainable development, natural resources, *i.e.*, any form of energy or materials from the ecosphere that is required to deliver products and meet human needs in the anthroposphere, should not run out and emissions, mainly in terms of heat and waste, from the anthroposphere should not endanger the ecosphere or transcend the ecospherical carrying capacity (Dewulf *et al.*, 2000; Zhang and Chen, 2010). With regard to the environmental sustainability of biofuel techno-system, most attention has typically been focused on land and water requirements (Gopalakrishnan, 2009), the energy balance (Farrell, 2006; Van der Voet *et al.*, 2010), net greenhouse gas emissions (Van der Voet *et al.*, 2010; Hoefnagels *et al.*, 2010), and recently on local climate impacts caused by land-use change (Georgescu *et al.*, 2011; Loarie *et al.*, 2011). Few tackle the demand of natural resources such as primary energy and raw materials or the climate impact due to heat emission.

The study aims at addressing the question how the natural resource demand of biofuel techno-system can be analysed to assess its environmental sustainability. A global framework for the analysis is developed and exergy is introduced as a measure of the resource value. The main context of the study is organized as follows. In Section 4.2, we describe the systems diagram, the exergy-based resource measure, and the data sources. Section 4.3 and Section 4.4 present the review of the global biofuel production in 2008 and the natural resource demand of the anthroposphere, respectively. In Section 4.5, we compare the results of the reviews and discuss the implication of heat emission and entropy generation. At last, Section 4.6 gives the main conclusions of the article.

4.2 Materials and methods

In this section, we define the framework of analysis, discuss the metrics that are to be studied, and describe the data sources used.

4.2.1 Systems diagram

The principle of system definition is that it should include all relevant processes. Figure 4.1 shows the four different levels of system boundary, labelled A, B, C, and D of the conceptualized biofuel techno-system.

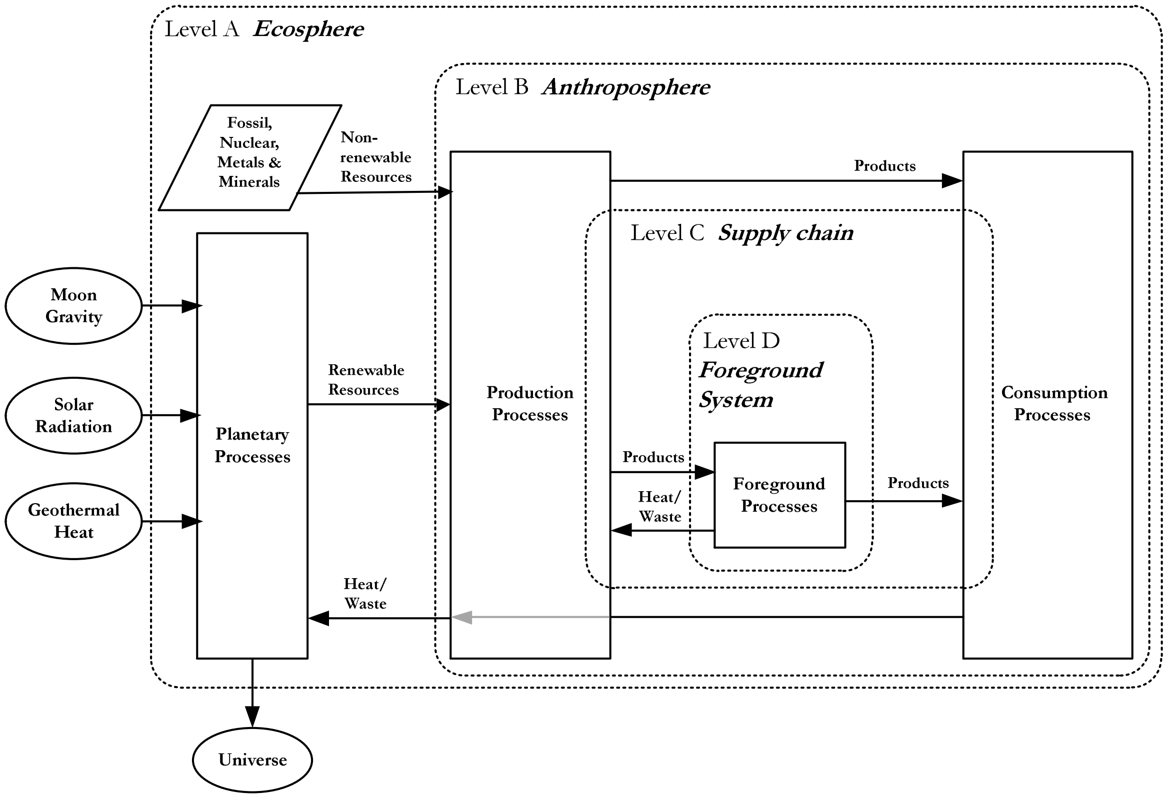

Figure 4.1 Systems diagram of resource demand analysis of energy-/material-based products. The ellipses stand for sources or sinks, the parallelogram for stocks, and the rectangles for processes, *i.e.*, conversion steps. Dashed lines represent the boundaries of the levels of analysis.

Level A (the ecosphere) principally includes the planetary processes that provide renewable resources, *i.e.*, natural resources that are generated on a human time scale (tidal, biomass, solar, hydro, wind, geothermal, and wave), and non-renewable resources, *i.e.*, resource stocks that have been accumulated on a geological time scale (fossil and nuclear fuels, metal ore, and mineral stocks). Level B (the anthroposphere) includes all the human activities, mainly production and consumption processes. Level C (the supply chain) includes part of the production and consumption processes that supplies the intermediate products. Level D (the foreground system) is defined to only account the direct inputs of the foreground processes, such as agricultural production and industrial conversion to deliver biofuels (See Figure 4.2 for an exemplified diagram of the bioethanol produced from corn stover at level D (Luo *et al.*, 2009; Liao *et al.*, 2011; Aden *et al.*, 2002)).

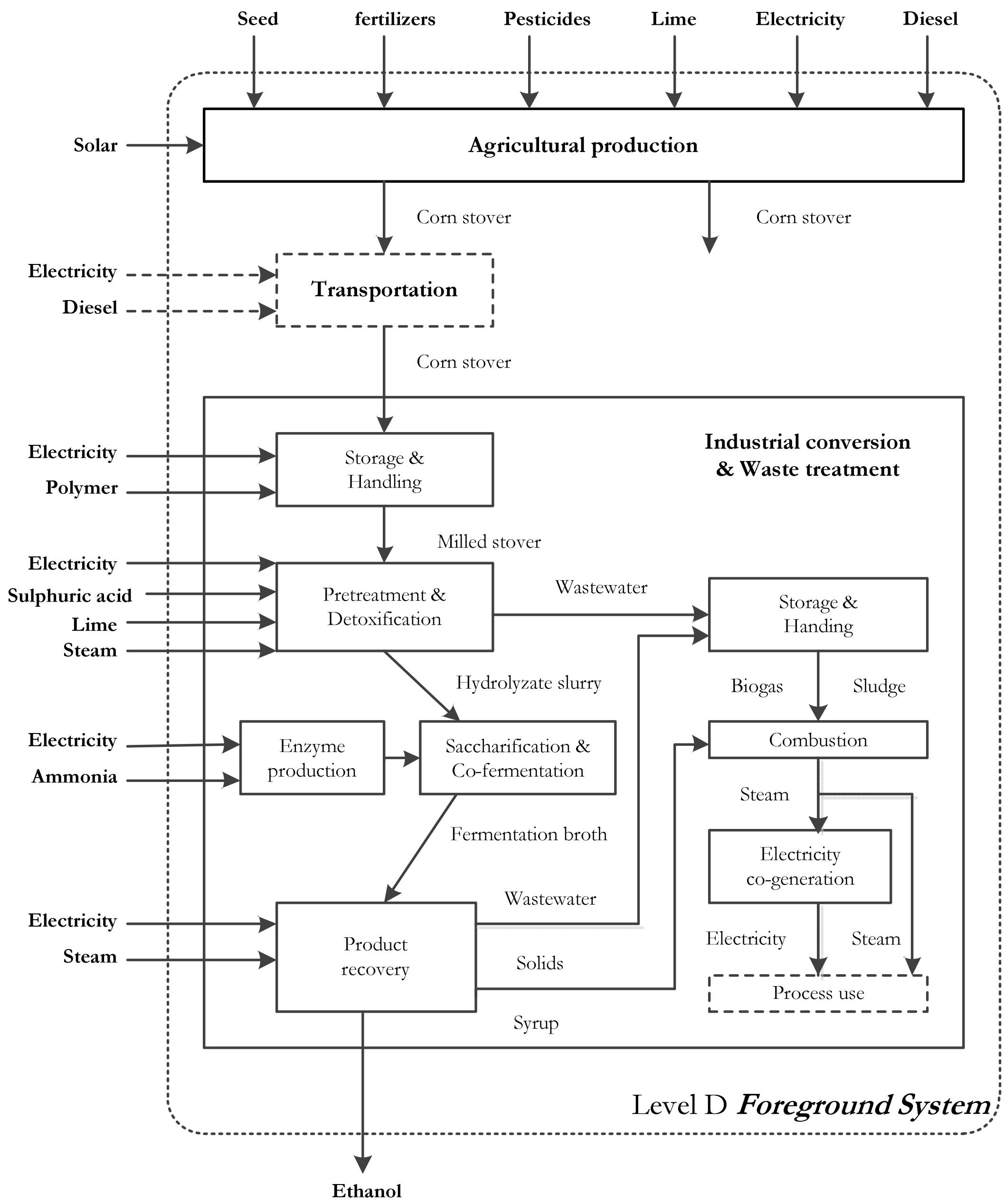

Figure 4.2 Systems diagram of the foreground processes at level D, ethanol production from corn stover (modified after Luo *et al.* (2009) and Liao *et al.* (2011)). Nomenclature for the diagram can be found in Aden *et al.* (2002).

4.2.2 Exergy-based resource measure

1) Exergy

Exergy is defined as the maximum amount of work that can be obtained from a flow of energy or materials when it is brought into equilibrium with a reference environment (for a commented history of the concept, see Sciubba and Wall (2007)). It has the same unit as energy, *i.e.*, Joules. This study adopted the reference environment proposed by Szargut *et al.* (1988, 2005), which is defined as the global average environment that has average chemical compositions of the atmosphere, seawater, and the crust under temperature of 298 K and atmospheric pressure of 1.01325 E+05 Pa. Exergy can be a proxy of the physical value of a resource since all production and consumption processes in the anthroposphere require energy and material resources from the ecosphere that feature exergy. Exergy is consumed in all real processes. The exergy being consumed is in proportion to the entropy being generated. Exergy analysis can inherently measure exergy consumption (*i.e.*, losses) and is being applied in various fields, including industrial and engineering models, economics, environmental impact assessment, systems ecology, and societal systems (Sciubba and Wall, 2007; Dincer and Rosen, 2005; Dewulf *et al.*, 2008; Liao *et al.*, 2012b).

2) Cumulative exergy demand

Cumulative exergy demand (CExD) expresses the gross exergy of all natural resources required to deliver a product (Bosch *et al.*, 2007). CExD is equivalent to the definition of cumulative exergy consumption of Szargut (Szargut, 2005). In Figure 4.1, CExD measures the exergy value of all renewable natural resources and non-renewable natural resources at the interface of level A and level B that are needed to deliver the final product at level D. This study defines the cumulative exergy demand of non-renewable natural resources, *i.e.*, energy resource including fossil fuels (F) and nuclear fuels (N), and material resources including metal ores (O) and minerals (M), as $\mathrm{CExD_{NRR}} = m_O\alpha_O + m_M\alpha_M + n_F\beta_F + n_N\beta_N$, where, "$m$" stands for the mass of a material resource in kg, "α" for the chemical exergy density of a material resource in mega-joules (MJ), "n" for the amount of energy from an energy resource in MJ, and "β" for the exergy-to-energy ratio of an energy resource.

4.2.3 Data sources

Data used in the study were obtained from various sources. Data on the biofuel production capacity of key producers were collected from a report to the International Energy Agency (IEA) Bioenergy Task 39 (Bacovsky *et al.*, 2009) and reconciled with a report to the United Nations Environment Programme (UNEP) by the International Panel for Sustainable Resources Management (Bringezu *et al.*, 2009), a special report on renewable energy resources by the Intergovernmental Panel on Climate Change (IPCC) (Chum *et al.*, 2011), and various literature values (Dewulf *et al.*, 2005; The Royal Society, 2008; Howarth and Bringezu, 2009; Ponti and Gutierrez, 2009). Data of the cumulative amount of energy and mass required for a specific biofuel was exported from ecoinvent database v2.2 (Swiss Centre of Life Cycle Inventories, 2010) or approximated by associating the β-value of an energy resource with the cumulative degree of thermodynamic perfection of the corresponding intermediate products (Szargut and Morris, 1988; Szargut, 1990; Szargut, 2005). Data gaps were partially filled by making various assumptions. Besides, wherever possible the data were collected for the year 2008, unless as noted specifically.

4.3 Review of global biofuel production

The current global biofuel production is primarily based on the first generation/conventional technologies, *i.e.*, using sugar, starch, and vegetable oil as feed-stocks. Production of advanced biofuels, *i.e.*, biofuels derived from non-food crops and algae, has not taken place on a large scale yet. In 2008, the global production of liquid biofuels for transport was dominated by a dozen of countries: the US, Brazil, China, Canada, Australia, Japan, and some EU member states. Below we briefly discuss the situation in these countries.

4.3.1 United States

Ethanol derived from corn grains is the primary biofuel used in the US. In 2007, the US used 24% of its national corn harvest to produce bioethanol. More than 200 bioethanol production facilities have been built in the US since 1976, which produced 3.63 E+07 m^3 of ethanol in 2008. Biodiesel use has also risen, with about 2.65 E+06 m^3 of production from soya and sunflower in 2008. A Renewable Fuel Standard legislated as part of the Energy Independence and Security Act of 2007 requires 1.36 E+08 m^3 of biofuels, including both conventional and advanced biofuels in traffic fuel mix by 2022. Advanced biofuels production, as required by the Act, is expected to increase dramatically, and would exceed conventional biofuels production by 2021.

4.3.2 Brazil

Ethanol derived from sugar cane is the primary biofuel produced in and exported from Brazil which firstly widespread developed the biofuel market. In response to the first oil crisis of the 1970s, Brazil lunched the National Ethanol Program, Proálcool. Several policies were introduced to promote biofuel consumption. Price regulations were removed in the late 1990s. In 2008, the existing 248 plants produced 2.45 E+07 m^3 of ethanol, about 3.50 E+06 m^3 of which were exported to the US, Europe, Korea and Japan. Biodiesel production was at a record level in 2008 of 1.10 E+06 m^3.

4.3.3 China

The production of biofuels, primarily bioethanol in China has developed rapidly since 2000. By 2008, China had built five state certified fuel ethanol pants and reached a production capacity of fuel ethanol about 2.45 E+06 m^3, ranking as the third-largest single bioethanol producer after the US and Brazil. 80% of the fuel ethanol was made from corn, the rest from wheat. Due to the lack of eligible vegetable oils and a standard of biodiesel use, biodiesel production in China has been limited at a minimal level compared to the ethanol production. An estimated biodiesel production of 6.00 E+04 m^3 to 3.40 E+05 m^3 was reported Bacovsky *et al.* (2009), with soybean and other waste vegetable oil used as feed-stocks. However, due to the shrinking stock of inferior corn the government is seeking other biomass feed-stocks, such as cassava or sweet sorghum which may have to be imported from neighbour countries.

4.3.4 EU member states

The EU Directive 2003/30/EC (2003) requires a minimum of 2% biofuel in transport fuels beginning 2005. The updated same directive sets a 5.75% target for 2010. By 2020, the target is projected to 10%. Because the 5.75% target has not been reached so far, the EU will have to increase its biofuel production or even focus on imports to meet this goal.

The EU Directive, the Biofuel Quota Act, and other policy initiates promote the production and use of transport biofuel in Germany. Despite the peak-and-decline biofuel market because of the removal of policy incentives happened in 2007, Germany remains its leading producer in biodiesel production, and reached a production capacity of 3.18 E+06 m^3 of rapeseed-derived biodiesel in 2008. The production of bioethanol of 7.30 E+05 m^3 is mainly from sugar beet and wheat.

France is the second largest biofuel producer in the EU, encouraging production and consumption of biofuels with tax rebates and penalties. In 2008, the production capacities were 9.91 E+05 m^3 of biodiesel from rapeseed (75%) and soybean (25%) and 5.78 E+05 m^3 of bioethanol from sugar beet (80%) and wheat (20%), respectively.

For other EU member states, *viz.*, Spain, the Netherlands, the UK, Austria, Poland, Portugal, Ireland, Belgium, Denmark, Norway, and Finland, we refer to Table 4.1 for the review of their production capacities in 2008.

Table 4.1 Summary of production capacities of key biofuel producers in 2008, in E+03 m^3 /yr.

Producer	Biodiesel				Bioethanol					
	Soybean	Rapeseed	U.S.[a]	Total	Corn	Sugar cane	Wheat	Sugar beet	U.S.[a]	Total
USA	2650			2650	36300					36300
Brazil	1100			1100		24497				24497
China	60			60	1958		490			2448
Germany		3180		3180				730		730
France	248	743		991			116	462		578
Spain		926		926			578			578
Netherlands		1372		1372						0
UK		347		347	153					153
Austria			252	252					13	13
Poland			91	91					151	151
Portugal			227	227						0
Ireland		63		63			85			85
Belgium			108	108						0
Denmark			103	103						0
Norway			39	39						0
Finland				0					3	3
Canada		60	40	100	670		200			870
Australia			260	260		64	100			164
Japan	10			10						0
Total	4068	6691	1120	11879	39081	24561	1569	1192	167	66570

[a] U.S. = unspecific feed-stocks

4.3.5 Canada

The Clean Air Act passed on late 2006 also services as a biofuels policy initiative and regulates and funds the biofuel development. Canada produced about 9.70 E+05 m^3 of biofuels in 2008, more than a four-fold increase in three years. 6.00 E+04 m^3 of biodiesel was produced from rapeseed; 4.00 E+04 m^3 from unspecific feed-stocks. The production of bioethanol was 6.70 E+05 m^3 from corn and 2.00 E+05 m^3 from wheat.

4.3.6 Australia

Biodiesel production in Australia was 1.00 E+05 m^3 from tallow (animal fat), 1.60 E+05 m^3 from other unspecific feed-stocks in 2008. The bioethanol production was 1.00 E+05 m^3 from wheat and 6.4 E+04 m^3 from sugar cane and cane molasses (residues).

4.3.7 Japan

Though being a main economic power, Japan has fairly low biofuel production. The most widely used biofuel, ethyl tert-butyl ether, is totally imported. Domestic biofuel production is beginning. In 2008, 1.00 E+04 m^3 of biodiesel was produced from soybean for traffic use. And there is no ethanol produced domestically.

4.3.8 Synthesis

To sum up, as shown in Table 4.1, biofuel production capacity in 2008 across the 19 countries under consideration in the study totaled 1.19 E+07 m^3 of biodiesel and 6.66 E+07 m^3 of bioethanol. Over 99% of the production has been based on the first generation/conventional technologies.

4.4 Review of anthropogenic exergy resource demand

4.4.1 Ecosphere

As shown in Figure 4.1, solar radiation, moon gravity, and geothermal heat are three main primary energy and exergy sources supporting all the planetary processes. The exergy of solar radiation received by the Earth can be easily approximated once the solar constant, *i.e.*, the flux density of solar radiation received by the Earth, is determined and related to the β-value given by Petela (1964). Part of the exergy reaching the Earth is immediately reflected and backscattered by the atmosphere. A small percent of the incident exergy is reflected by the Earth's surface as well. Moon gravity, together with solar gravity interacts with the rotating Earth and causes tides as the motion of sea levels. Tidal exergy dissipates as friction in the shallow oceans and continental shelves, 70% of which is attributed to the moon gravity. Specific tidal exergy is equivalent to the gravitational potential energy due to the height difference between the tidal maxima and minima over the tidal record (Hermann, 2006). Geothermal energy to the ecosphere comes from three sources, *i.e.*, lithospheric heat, heat from the core, and heat from radioactive decay. Conversion of these energy flows into exergy flows depends on the Carnot efficiency that in turn is determined by the temperature of a geothermal heat flow and the temperature of the reference environment. The uncertainty of various geothermal heat flows makes the determination of global geothermal heat quite challenging. The evaluation of other exergy sources, *i.e.*, solar radiation and moon gravity, is characterized by different uncertainties due to the lack of sufficient knowledge of the dynamics of the complex ecosphere. Hence various estimations of global exergy sources are reported which are summarized in Table 4.2 (Szargut, 2003; Gong and Wall, 2001a; Chen GQ, 2005; Munk and Macdonald, 1960; Munk and Wunsch, 1998; Egbert and Ray, 1999; Hofmeister and Crisis, 2005; Hamza *et al.*, 2007; Sclater *et al.*, 1980; Pollack *et al.*, 1993).

Table 4.2 Summary of various estimations of global primary exergy sources, in MJ/yr (into A)

Primary exergy source	Reported estimation [a]	Reference	This study
Solar radiation [b]	3.33 E+18	Szargut, 2003	3.6 E+18
	3.38 E+18	Gong and Wall, 2001a	
	3.83 E+18	Chen GQ, 2005	
	3.88 E+18	Hermann, 2006	
Moon gravity	7.6 E+13	Gong and Wall, 2001a	9.5 E+13
	8.5 E+13	Munk and Macdonald, 1960	
	9.5 E+13	Chen GQ, 2005	
	1.17 E+14	Munk and Wunsch, 1998; Egbert and Ray, 1999	
Geothermal heat	9.78 E+14~1.104 E+15	Hofmeister and Crisis, 2005; Hamza *et al.*, 2007	1.198 E+15
	1.325 E+15~1.388 E+15	Sclater *et al.*, 1980;	
		Pollack *et al.*, 1993	

[a] Notations such as "E+18" mean exponents (10^{18}).

[b] The exergy input of net solar radiation to the ecosphere

Table 4.2 shows that by far the dominant primary exergy source to the ecosphere is the net solar exergy input of 3.60 E+18 MJ/yr. The other two independent primary exergy sources, *i.e.*, geothermal heat and moon gravity, which totalled to about 1.29 E+15 MJ/yr are several orders of magnitude less than that of the net solar exergy input and thus their contribution is negligible .

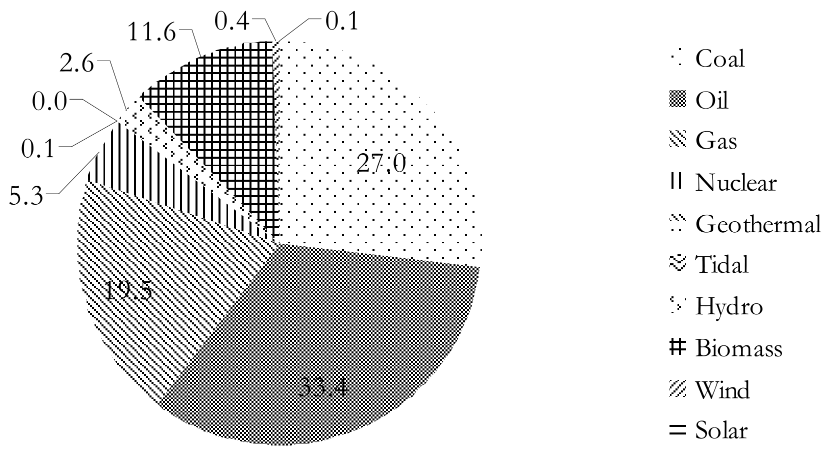

Figure 4.3 Summary of global anthropogenic demand of various exergy resources, by percentage (from A to B).

4.4.2 Anthroposphere

The exergy demand by the anthroposphere is considerably smaller than that of the ecosphere. While the literature values of metal and mineral exergy resources are not available, Table 4.3 summarizes the exergy demand of the anthroposphere (Szargut, 2005; Hermann, 2006; IEA, 2008; BP, 2010). It is indicated in Table 4.3 and Figure 4.3 that the anthroposphere mainly relies on non-renewable exergy resources, which amount to 4.15 E+14 MJ/yr and accounts for 85.2% of the global anthropogenic exergy demand. This value includes 3.89 E+14 MJ/yr from fossil fuels and 2.59 E+13 MJ/yr from nuclear fuels. It is assumed that the exergy extracted from non-renewable energy resources is completely consumed in various production and consumption processes. This corresponds to a heat of 4.15 E+14 MJ/yr added to the planetary processes.

Table 4.3 Summary of global energy flows to the anthroposphere in 2008, in MJ/yr (from A to B).

Exergy resource	Energy flow [a]	β-value [b]	Exergy consumption
Coal	1.262 E+14	1.04	1.313 E+14
Oil	1.578 E+14	1.03	1.625 E+14
Gas	1.01 E+14	0.94	9.49 E+13
Nuclear	2.59 E+13	1	2.59 E+13
Geothermal	8.8 E+11	0.71	6.25 E+11
Tidal	1.6 E+10	1	1.6 E+10
Hydro	1.26 E+13	1	1.26 E+13
Biomass	5.36 E+13	1.05	5.63 E+13
Wind	1.9 E+12	1	1.9 E+12
Solar [c]	5.4 E+11	0.93	5.0 E+11

[a] Energy flow values are from the International Energy Agency (IEA, 2008) and the British Petroleum (BP, 2010).

[b] β-values of non-renewable energy resources are from Szargut (1990); β-value of geothermal is based on a global average Carnot efficiency of 0.71 in Hermann (2006); other β-values are following the definition.

[c] Solar energy collected directly by photovoltaic panels and solar thermal panels.

4.5 Natural resource demand and heat emission

4.5.1 Natural resource demand of biofuels

The biodiesel production from soybean shares a number of processes with that from rapeseed. Inflows for the agricultural production under consideration are seeds, lime, fertilizers, pesticides, fuels for the operation of agricultural machinery, and steel for the production of agricultural machinery. Inflows for the industrial conversion are fuels, chemicals, and various feed-stocks such as soybean, rapeseed, corn, sugar cane, wheat, and sugar beet. Table 4.4 summarizes the cumulative exergy demand of non-renewable resources that is required in the supply chain of these inflows to deliver a specific type of biofuel.

Table 4.4 Summary of exergy resource demand of different biofuels ($CExD_{NRR}$), in MJ/yr (from C to D).

Biofuel	Soybean methyl ester	Rapeseed methyl ester	Corn-derived ethanol	Sugar cane -derived ethanol	Wheat-derived ethanol	Sugar beet -derived ethanol
$CExD_{NRR}$	6.13 E+10	1.00 E+11	6.62 E+11	7.36 E+10	2.82 E+10	7.97 E+09

Table 4.5 compares results of the natural resource demand of global biofuels with that of the anthroposphere. The normalization shows that the production of the first generation biofuels, *i.e.*, biodiesel and bioethanol, by key producer countries in 2008 consumed 9.32 E+11 MJ of exergy from non-renewable resources and would account for 0.23% of the total anthropogenic non-renewable resource demand.

Table 4.5 Anthropogenic natural resource demand share of global biofuels.

Biofuel	$CExD_{NRR}$, in MJ/yr	$Ex_{anthro\text{-}NRR}$ [a], in MJ/yr	$CExD_{NRR}$/ $Ex_{anthro\text{-}NRR}$
Biodiesel	1.61 E+11	4.15 E+14	0.04%
Bioethanol	7.71 E+11	4.15 E+14	0.19%
Total	9.32 E+11	4.15 E+14	0.23%

[a] $Ex_{anthro\text{-}NRR}$ = exergy of total anthropogenic demand of non-renewable resources

4.5.2 Heat emission of biofuels

Anthropogenic heat, *i.e.*, heat generated by various human activities and emitted to the ecosphere, is neglected in current global climate models, likely because it is considered as a much smaller contributor to global warming than greenhouse gases and aerosols. However, the heat that is introduced by deriving exergy from non-renewable resources would not otherwise have been added on relevant timescales, thus should constitute a climate forcing (Chaisson, 2008; Flanner, 2009). An outgoing ecospherical radiation flux of 238 W/m^2 at an equivalent blackbody temperature of 255K is reported (Chen, 2005; Peixoto, 1991). The global anthropogenic exergy demand and non-renewable exergy demand of global biofuels correspond to a heat emission to the ecosphere of 4.87 E+14 MJ/yr and 9.32 E+11 MJ/yr, respectively. With an average Earth's surface temperature of 288 K and Earth's surface area of 5.1 E+14 m^2, they generate heat flux of 0.03 W/ m^2 and 5.79 E-05 W/m^2 and entropy at a rate of 5.36 E+10 W/K and 1.03 E+08 W/K, respectively, as shown in Table 4.6. Although the anthropogenic heat is small compared to the ecospherical radiation, its addition might lead to a new equilibrium with a higher temperature (global warming). Besides, comparing to greenhouse gases that have a climate forcing of 2.9 W/m^2 (IPCC, 2007), the contribution to climate change of heat emission due to the exergy consumption of global biofuels is about 0.002% of global greenhouse warming and could be negligible at level A. If one relates the entropy production to the global net entropy generation density (1.21 W/K·m^2, reported by Chen GQ, 2005), the result indicates the entropy footprint in terms of an area of Earth's surface that is occupied by the techno-system under consideration. For global primary energy supply and global biofuel production, their entropy footprint would be 4.37 E+10 m^2 and 8.48 E+07 m^2, respectively.

Table 4.6 Summary of heat emission and entropy generation of the ecosphere, the anthroposhere, and global biofuels (from B to A).

System	Heat flux	Entropy generation rate	Temperature
	in W/m^2	in W/K	in K
Ecosphere [a]	238	6.17 E+14	255
Anthroposphere	0.03	5.36 E+10	288
Biofuels	5.79 E-05	1.03 E+08	288

[a] Chen GQ, 2005; Peixoto *et al.*, 1991

4.6 Conclusions and outlook

The study developed a global framework for the analysis of natural resource demand in order to address the question how the natural resource demand of biofuel techno-system can be analyzed to assess its environmental sustainability. The framework defines the biofuel system in terms of exergy at four levels: the foreground system, the supply chain, the anthropopsphere, and the ecosphere. Various measures of resource demand can be incorporated into the framework. Conclusions can be drawn on the basis of reviews of the natural resource demand of global biofuel production, the ecosphere, and the anthroposphere in 2008:

- First generation of biodiesel and bioethanol by key producer countries consume 9.32 E+11 MJ of exergy from non-renewable resources and account for 0.23% of the total anthropogenic non-renewable resource demand.
- The heat flux induced by global biofuel production is 5.79 E-05 W/m^2, which would reach up to 0.002% of global greenhouse warming if anthropogenic heat flux is treated as a climate forcing.
- Global biofuel production generates entropy at a rate of 1.03 E+08 W/K and would require 8.48 E+07 m^2 of Earth's surface for the disposal of entropy.

While the present study only analyzes global biofuel production in 2008, it may be extended to include time series based on various scenarios to investigate the future development of global biofuel economy in terms of the resource demand, climate impact, and its implication to the ecospherical carrying capacity.

Chapter 5

Thermodynamic resource indicators in LCA: A case study on the titania produced in Panzhihua city, southwest China

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Abstract

Purpose While life cycle assessment (LCA) has standardized methods for assessing emission impacts, some comparable methods for the accounting or impact assessment of resource use exist, but are not as mature or standardized. This study contributes to the existing research by offering a comprehensive comparison of similarities and differences of different resource indicators, in particular those based on thermodynamics, and testing them in a case study on titania (titanium dioxide pigment) produced in Panzhihua city, southwest China.

Materials and methods The system boundary for resource indicators is defined using a thermodynamic hierarchy at four levels, and the case data for titania also follow that hierarchy. Seven resource indicators are applied. Four are thermodynamics-based—cumulative energy demand (CED), solar energy demand (SED), cumulative exergy demand (CExD), and cumulative exergy extraction from the natural environment (CEENE)—and three have different backgrounds: abiotic resource depletion potential, environmental priority strategies, and eco-indicator 99. Inventory data for the foreground system has been collected through on-site interviews and visits. Background inventory data are from the database ecoinvent v2.2. Characterizations factors are based on CML-IA database covering all major methods. Computations are with the CMLCA software.

Results and discussion The scores of resource indicators of the chloride route for titania system are lower than that of the sulphate route by 10–35 % except in terms of SED. Within the four thermodynamic indicators for resources, CED, CExD, and CEENE have similar scores, while their scores are five orders of magnitude lower than the SED score. Atmospheric resources do not contribute to the SED or CEENE score. Land resources account for a negligible percentage to the SED score and a small percentage to the CEENE score. Non-renewable resources have a dominant contribution to all seven resource indicators. The global production of titania would account for 0.12 and 0.14 % of the total anthropogenic non-renewable resource demand in terms of energy and exergy, respectively.

Conclusions First, we demonstrate the feasibility of thermodynamic resource indicators. We recommend CEENE as the most appropriate one within the four thermodynamic resource indicators for accounting and characterizing resource use. Regarding the case study on the titania produced in China, all the resource indicators except SED show that the sulfate route demands more resource use than the chloride route.

5.1 Introduction

Natural resources are the ultimate inputs to our civilization and the non-substitutable basis for economic growth (Daly, 1977; Ayres, 1998). As these are available in a limited amount, the long-term well-being of both mankind and the environment cannot maintain without sound stewardship or sustainable utilization of natural resources. In human–environment systems, resource uses in parallel to emissions are an important source of environmental impacts. It has been demonstrated that a number of emission-related impacts are strongly related to resource use, in particular energy input (Huijbregts *et al.*, 2010). However, while the life cycle assessment (LCA) community has standardized methods for assessing emission impacts, some comparable methods for the accounting or impact assessment of resource use exist, but are not as mature or standardized (Baral and Bakshi, 2010). In the ILCD handbook (EC JRC, 2010a, 2010b), resource depletion is the only impact category for which no single recommended method has been identified. Examples of methods for characterizing resources in LCA are the abiotic resource depletion potential (ADP) developed by CML (Guinée *et al.*, 2002), willingness to pay developed within the environmental priority strategies (EPS) framework (Steen, 1999a, 1999b), and surplus energy developed in Eco-indicator 99 (EI99) (Goedkoop and Spriensma, 2000a, 2000b).

In addition, thermodynamic metrics such as energy, exergy, and entropy have been used as a basis for resource indicators. for instance, in the so-called life cycle exergy analysis (Gong and Wall, 1997, 2001; Wall, 2011) or exergetic LCA (Cornelissen, 1997; Cornelissen and Hirs, 2002) (see the Appendix for an elaboration on the combination of thermodynamic metrics and LCA). Thermodynamic resource indicators are applied as screening impact indicators and to give an estimation of resource use. As compared to complete LCA studies, the calculation of thermodynamic resource indicators requires fewer information on emission estimates or impact assessment factors (Huijbregts *et al.*, 2006); nevertheless, no thermodynamic resource indicator is recommended by the ILCD Handbook (EC JRC, 2010a, 2010b). Besides the LCA studies, thermodynamic resource indicators are applied in other aspects of the analysis of human-environment systems due to their physical validation and quantitative formulation (Dewulf *et al.*, 2008; Sciubba and Wall, 2007). However, different resource measures apply to different system levels in human-environment systems (Liao *et al.*, 2011). Meanwhile, there is no consensus on the most appropriate resource measure or even on what the issue is for the impact of resource use (Baral and Bakshi, 2010; EC JRC, 2010a, 2010b). Studies that compare multiple resource indicators are not uncommon (Rugani *et al.*, 2011; Caneghem *et al.*, 2010; Baral and Bakshi, 2010; Bösch *et al.*, 2007). Rugani *et al.* (2011) compare solar energy demand (SED) with cumulative energy demand (CED), cumulative exergy demand (CExD), and cumulative exergy extraction from the natural environment (CEENE) for 2326 products in the ecoinvent database v2.1. Caneghem *et al.* (2010) compare ADP, EPS, CExD, EI99, and the total resource mass for the steel. Baral and Bakshi (2010) compare CExD with ecological cumulative exergy consumption (ECEC) by applying them to transportation fuels. Bösch *et al.* (2007) compare CExD with CED, EI99, and ADP for 1,197 products in the ecoinvent database v1.2.

This study contributes to the existing research by offering a comprehensive comparison of the similarities and differences of different resource indicators, in particular those based on thermodynamics, and testing the indicators in a case study on the titania produced in Panzhihua city, southwest China. This study is focused on thermodynamic resource indicators, *i.e.*, CED, SED, CExD, and CEENE. These are also compared with ADP, EPS, and EI99. Table 5.1 summarizes the indicators used.

Table 5.1 Overview of resource indicators addressed in this study

Name	Abbr.	Unit	Levels [a]	Reference
Cumulative energy demand	CED	MJ	B+C+D	VDI 1997; Huijbregts *et al.*, 2006, 2010
Solar energy demand	SED	MJ_{se}-eq	A+B+C+D	Rugani *et al.*, 2011
Cumulative exergy demand	CExD	MJ_{ex}-eq	B+C+D	Bösch *et al.*, 2007
Cumulative exergy extraction from the natural environment	CEENE	MJ_{ex}-eq	B+C+D	Dewulf *et al.*, 2007
Abiotic resource depletion potential	ADP	kg_{sb}-eq	B+C+D	Guinée *et al.*, 2002
Environmental priorities strategies	EPS	MJ-eq	B+C+D	Steen, 1999a, 1999b
Eco-indicator 99	EI99	ELU	B+C+D	Goedkoop and Spriensma, 2000a, 2000b

[a] See Figure 5.1

5.2 Methodology

5.2.1 System boundary

The principle of system definition is that it should include all relevant processes. A diagram for resource indicators as well as titania under consideration in this study is shown in Figure 5.1. The technosphere (also called anthroposphere) is the boundary of most resource indicators, *i.e.*, CED, CExD, CEENE, ADP, EPS, and EI99; the ecosphere is the boundary of SED since it traces back the primary energy and material resources to include the planetary processes.

5.2.2 Choice of impact and indicators

In this section, we define the framework of analysis, discuss the metrics that are to be studied, and describe the data sources used.

1) General remarks

In LCA studies, four classes of indicators have been proposed for the impact assessment of resource use: (1) those based on energy or mass, *e.g.*, CED and material input per unit service; (2) those based on relation of use to deposits, *e.g.*, ADP; (3) those based on future consequences of resource extractions, *e.g.*, EPS and EI99; and (4) those based on exergy consumption or entropy generation, *e.g.*, CExD and CEENE (Finnveden and Östlund, 1997; Stewart and Weidema, 2002; Steen, 2006). The indicator of ECEC, as defined by Hau and Bakshi (2004), has been left out of consideration because of its inconsistent allocation method with CED, SED, CExD, and CEENE. Two allocation methods have been identified by Hau and Bakshi (2004) for fully and partially defined networks, respectively. While the allocation of ECEC in fully defined networks is type of standardized allocation in LCA, the allocation in partially defined networks is similar with that in emergy analysis, *i.e.*, all resource consumption of a specific process is considered to be essential for making each co-product and all co-products from the process have the total resource consumption (Rugani, 2010). Various ecospheric processes are usually partially defined networks. Thus, in practice, ECEC is implemented by using emergy-type of allocation or even is referred to as emergy, *e.g.*, in the analysis of natural resource consumption of transportation fuels by Baral and Bakshi (2010). Entropy-based indicators of resources, for example as in Gößling-Reisemann

(2008a, 2008b), have been left out of consideration due to the lack of support from on-site data or ecoinvent data.

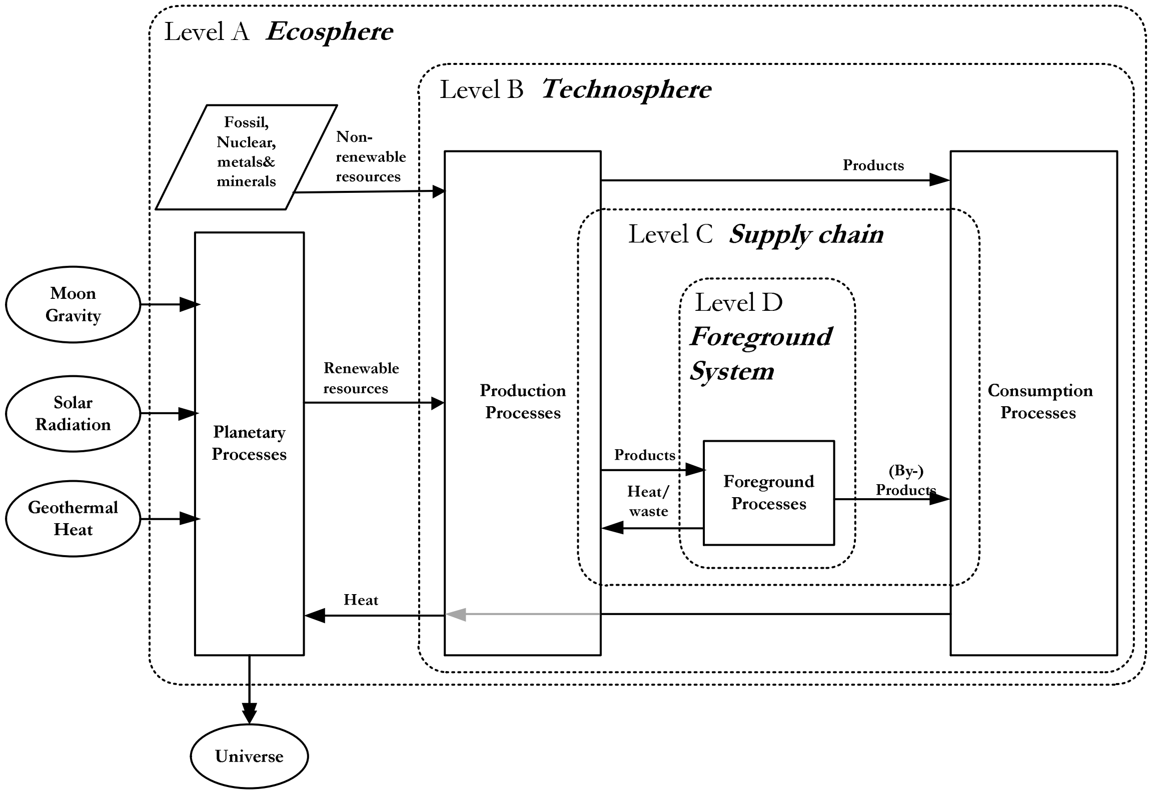

Figure 5.1 System boundary of various resource indicators. The ellipses stand for sources or sinks, the parallelogram for stocks, and the rectangles for processes.

2) Energy and energy-based indicators

Energy is defined as the ability to do work (Isaacs *et al.*, 1999)[1]. Various types of measures are used in energy analysis of various products and economic sectors. While the analysis can focus on the secondary energy requirement, *e.g.*, coke, diesel, petrol, electricity, *etc.* (Luo *et al.*, 2009), most energy analysis aims at determining the direct and indirect primary energy requirements of a product. Almost all primary energy originates from solar energy, ultimately.

The CED indicator represents the direct and indirect primary energy use (in megajoules) throughout the life cycle of a product (VDI, 1997). CED is also referred to as gross energy requirement (IFIAS, 1978), embodied energy (Costanza, 1980), or energy cost (Bullard and Herendeen, 1975). This study uses the same definition of CED as that used by Huijbregts *et al.* (2006, 2010). The SED indicator represents the direct and indirect solar energy use (in megajoule solar energy, MJ_{se}-eq) throughout the life cycle of a

[1] This statement has been challenged by one of the reviewers. He or she writes to agree that energy is often defined as such, but that "this is still not correct! To repeat a false statement many times does not make it true!" The reviewer points to a debate (Wall, 1977, 1986) where energy is described as "motion or ability of motion (*e.g.*, the disordered motions of the hot molecules in a cup of coffee); measured in joules (J)". Although we appreciate the critical attitude of the reviewer, we prefer to stick to mainstream science in the context of developing LCA while applauding the debate on such fundamentals in more dedicated journals. As a sign of the mainstream, even in thermodynamics, it suffices to point to some standard textbooks (Guggenheim, 1957; Zemansky and Dittman, 1981) where energy is always defined in relation to the work done on or by the system.

product (Rugani *et al.*, 2011). Compared with CED, SED includes the conversion from solar energy to the primary energy. SED is not the same as emergy (another form of cumulative solar energy demand; see Odum (1996)) since emergy analysis uses computation rules that differ from those of LCA. Furthermore, SED, in contrast to emergy, does not take into account human labor, information, and many ecosystem services (Rugani *et al.*, 2011).

3) Exergy and exergy-based indicators

Exergy is defined as the maximum work (*i.e.*, useful energy) which can be obtained as a system is brought into equilibrium with the reference environment. It has the same unit as energy, *viz.*, Joules. This study adopts the reference environment proposed by Szargut *et al.* (1988, 2005) with the natural environment subsystem by Gaggioli *et al.* (1977). Exergy is consumed in all real processes in proportion to the entropy being produced. Exergy applies to both energy carriers and non-energetic materials. The exergy of a resource represents the minimal work needed to form the resource. Various exergy-based indicators exist for resource accounting.

The CExD indicator represents the total exergy of all natural resources that is required throughout the life cycle of a product (in megajoules, MJ_{ex}-eq) (Bösch *et al.*, 2007). CExD is equivalent to cumulative exergy consumption defined by Szargut (2005), both used to measure the potential loss of "useful" resources. The cumulative degree of thermodynamic perfection (CDP) can be determined by associating the CExD with the specific exergy of the product (Szargut *et al.*, 1988). The CEENE indicator represents the total exergy of resources that is taken away from the ecosphere and used as "fuel and stock" for the anthroposphere (expressed in megajoules, MJ_{ex}-eq) (Dewulf *et al.*, 2007). CEENE distinguishes itself from CExD by taking the actual transformed exergy into account. The resulting exergy values of biomass and solar energy are not implemented to avoid double accounting (Dewulf *et al.*, 2007).

4) Other methods and indicators

The ADP method takes the decrease of the resource per se as the key problem. In resource accounting, ADP, as a function of natural reserves of the resources combined with their extraction rates (expressed in kilograms of antimony equivalents (kg_{sb}-eq) per unit of resource extraction), is used to characterize each extraction of elements (in metal ores and minerals) and fossil resources. The overall ADP factor of fossil resources is set equal to 4.81E-04 kg_{sb}-eq/MJ of fossil fuel (Guinée *et al.*, 2002). The ADP calculated for the ultimate reserve is used in this study.

The EPS method takes the higher production cost of the alternative resource as the key problem. It describes the environmental impacts, which are related to the development of products, as impacts to specific protection subjects, *e.g.*, resources, biodiversity, human health, *etc.* (Steen, 1999a, 1999b). In resource accounting, the impact to resource use is evaluated according to the willingness to pay to avoid negative effects. The willingness to pay for resources is set equal to the cost of the sustainable alternative of the resource, expressed in environmental load value (ELU).

The EI99 method takes the increasing energy needed for the future extraction of lower grade resource as the key problem. Similar with the EPS method, the EI99 method calculates the environmental impacts to specific protection subjects (Goedkoop and Spriensma, 2000a, 2000b). In resource accounting, the surplus energy (expressed in megajoule equivalents) needed to produce 1 kg of a fossil resource from oil shale, tar sands, or coal shale mix, or to extract 1 kg of a metal ore or mineral from a lower grade ore is used to characterize corresponding resource flows. The EI99 indicator based on an egalitarian perspective is used in this study.

Table 5.2 below summarizes the categorization of resource groups as considered by different resource indicators addressed in this study.

Table 5.2 Synthesis of resource indicators and resource groups addressed in this study

Resource group [a]	Type [b]	CED	SED	CExD	CEENE	ADP	EI99	EPS
Atmospheric	n. d.		×		×			
Fossil	NRR	×	×	×	×	×	×	×
Land	n. d.		×		×			
Metal ores	NRR		×	×	×	×	×	×
Minerals	NRR		×	×	×	×	×	×
Nuclear	NRR	×	×	×	×			×
Renewable energy	RR	×	× [d]	×	× [d]			
Water [c]	RR		×	×	×	×		

n. d. not defined, *RR* Renewable resources, *NRR* Non-renewable resources

[a] This is just one categorization. However, as pointed out by the ILCD Handbook (EC JRC 2010a), other categorizations, such as Finnveden (1998) and Guinée *et al.* (2002) split resource differently.

[b] It should be noted that in SED, the atmospheric and land resource are considered as NRR and RR, respectively.

[c] Bromine, iodine, and magnesium in water are included

[d] The value of converted solar energy and the gross caloric value of biomass (including primary forest) are not implemented in SED and CEENE to avoid double accounting. Primary forest in this study is considered as a renewable energy resource, which is the same as the consideration in SED and CEENE but different from that in impact indicators CED and CExD in the ecoinvent database v2.2

5.3 Case study

5.3.1 Case description

Titania is an important fine chemical product with a broad range of applications in paints, plastics, inks, paper, cosmetics, ceramics, rubber products, *etc.* The chloride route and the sulfate route, as two current mature routes for the commercial production of titania, are analyzed in this study as two alternatives for the titania produced in Panzhihua city, southwest China. This study is a cradle-to-gate analysis of the titania system. The functional unit in this study is defined as 1 kg of titania (titanium dioxide pigment) at plant.

Both the chloride route and the sulfate route are used in Panzhihua city, southwest China to extract titania from vanadium-bearing titaniferrous magnetite ore (V-Ti magnetite ore, 10.25% (*w/w*) of TiO_2; see Appendix Table S5. 1 for the composition of the ore). After the mining and beneficiation of V-Ti magnetite ore, the titanium ore (48.8, *w/w*, of TiO_2) can be either used directly as the feedstock for the sulfate process or it proceeds to the production of high titanium slag (94.0, *w/w*, of TiO_2). Figure 5.2 shows the flow chart of the foreground system of titania (99.0, *w/w*, of TiO_2) production. The foreground system of the sulfate route is divided into three unit processes while that of the chloride route system includes four unit processes. Appendix Tables S5.2 to S5.6 show the raw input data of every unit process. It is noted that these processes do not comprise the full life cycle of the titania since the utilization and other end-of-life processes are left out of consideration.

Beneficiated titanium ore and beneficiated iron ore are co-produced in the process "Mining and beneficiation" in both the chloride route and the sulfate route. Allocation of resource use is based on their mass. The transport distance for the beneficiated titanium ore to the titania plant is 80 km. As for the distance between the titanium slag plant and the titania plant, the value is set to zero since they are locally close to each other. The transport of other auxiliary raw materials is left out of consideration due to data unavailability.

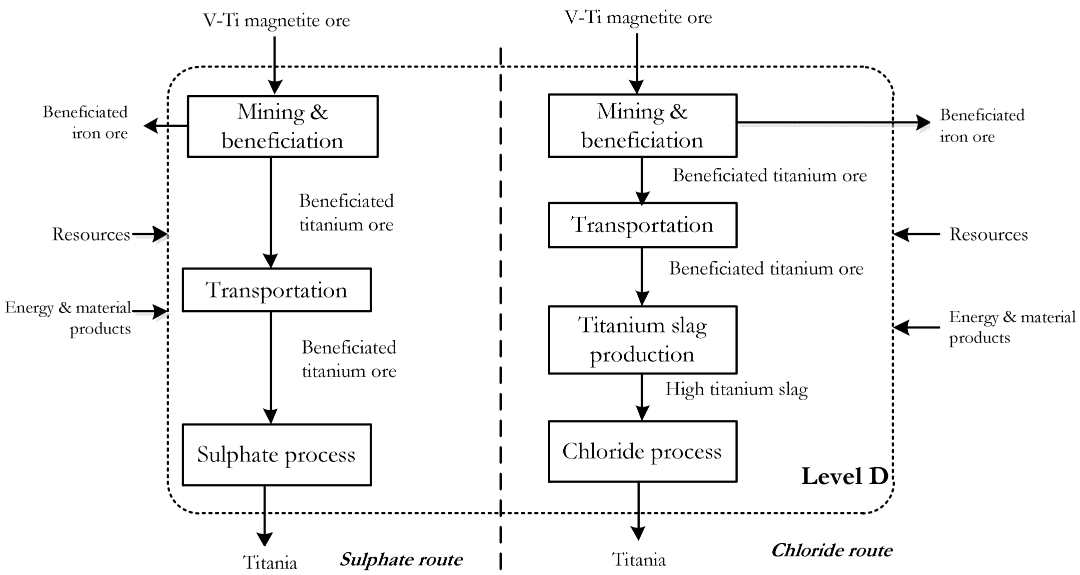

Figure 5.2 Flowchart of titania production foreground system, at level D in Figure 5.1.

5.3.2 Date source and software

In this study, only the input data and the (co-) product of each unit process are required. Data on the processes of mining and beneficiation, titanium slag production, chloride process, and sulfate process have been collected mainly through interviews and site visits at local enterprises, located in Panzhihua city, southwest China. A consistent set of data on energy and material inputs is obtained by sending them a standardized questionnaire. Table 5.3 shows the inventory of main resource and product inputs of the two routes based on our survey.

Data on road transport are derived from Yang *et al.* (2002). Background data on electricity produced in China and other energy and material product inputs are obtained from the ecoinvent database v2.2 (Swiss Centre of Life Cycle Inventories, 2010; see Appendix Table S5.7 for their corresponding dataset names).

Data on the characterization factors for CED, SED, CExD, and CEENE are obtained from Rugani *et al.* (2011) while the characterization factors for ADP, EPS, and EI99 are based on the CML-IA Database (2010) (Appendix Table S5.8). Data gaps are partially filled by making various assumptions and referring to some trivial literature (*e.g.*, see the calculation of CExD characterization factor of V–Ti magnetic ores in the Appendix). Computations are with the software CMLCA (Chain Management by Life Cycle Assessment) developed by Heijungs (2011) in this study.

Table 5.3 Main resource and product inputs needed to produce 1 kg of the titania in Panzhihua city, southwest China

No.	Input	Type	Unit	Chloride route	Sulfate route
1	V–Ti magnetite ore	Resource	kg	5.071	5.576
2	Steel ball	Product	kg	0.001	0.002
3	Anthracite	Product	MJ	10.076	-
4	Coke	Product	kg	0.693	-
5	Liquid chlorine	Product	kg	0.25	-
6	Iron powder	Product	kg	-	0.09
7	Aluminum powder	Product	kg	0.006	-
8	Oxygen	Resource	kg	0.643	-
9	Liquid caustic soda (30 %)	Product	kg	0.3	0.35
10	Sulfuric acid (98 %)	Product	kg	-	4.05
11	Saturated steam (1.3MPa)	Product	kg	5.5	8
12	Coal	Resource	kg	-	2
13	Petrol	Product	kg	0.017	0.018
14	Diesel	Product	kg	0.011	0.111
15	Process water [a]	Resource	kg	53.758	101.787
16	Electricity	Product	kWh	2.85	1.578

[a] Process water is not implemented considering the very high uncertainty of its surveyed value.

5.4 Results and discussion

5.4.1 Resource scores

Table 5.4 gives the scores of seven resource indicators addressed in this study for 1kg of titania produced via both the chloride route and the sulfate route. Within the four thermodynamic resource indicators, CED, CExD, and CEENE have similar scores with each other, while their scores are five orders of magnitude lower than the score of SED. This is mainly because the SED includes the ecospheric processes (Figure 5.1) for forming various resources. The CExD of 1 kg of the titania produced in Panzhihua city, southwest China, is 118 and 138 MJ_{ex}-eq for the chloride route and the sulfate route, respectively. Considering the specific chemical exergy of titania (11.326 MJ_{ex}/kg), this corresponds to a CDP of 0.096 and 0.082 for the chloride route and the sulfate route, respectively, which is in the lower bound of the range of CDP for normal energy and material products (0.05–0.84; Szargut *et al.* (1988)).

Table 5.4 Scores of various resource indicators of 1kg of the titania produced in Panzhihua city, southwest China

Route	CED	SED	CExD	CEENE	ADP	EPS	EI99
	(MJ)	(MJ_{se}-eq)	(MJ_{ex}-eq)	(MJ_{ex}-eq)	(kg_{Sb}-eq)	(ELU)	(MJ-eq)
Chloride route	106	7.91E+07	129	123	0.0536	1.50	8.66
Sulfate route	117	6.63E+07	151	143	0.0735	2.32	10.6

Figure 5.3 compares the resource indicators between the chloride route and the sulfate route. It shows that titania produced via the chloride route uses less resources than the sulfate route by 10–35 % except in terms of SED. The higher score of SED of the chloride route compared to the sulfate route can be explained by the fact that rather more sodium chloride as a resource flow is used in the chloride route than in the sulfate route, while the difference of other resource demands between the two routes is not so significant. Of the sodium chloride (as shown in Appendix Table S5.8), 0.364 and 0.179 kg are used in the chloride route and the sulfate route, respectively. They correspond to SED scores of 3.60E+07 and 1.77E+07 MJ_{se}-eq, respectively, which account for 45 and 27 % of the total SED in the chloride route and the sulfate route, respectively.

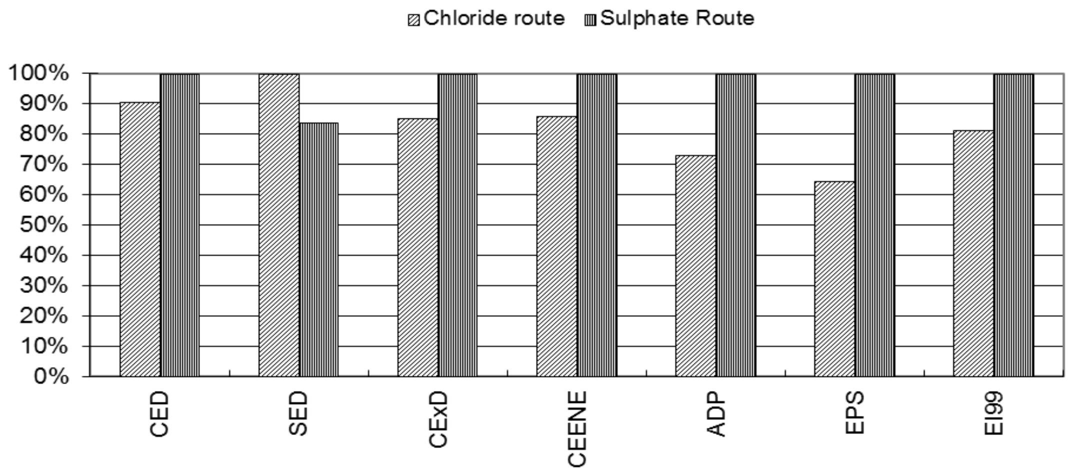

Figure 5.3 Comparison of scores of resource indicators between the chloride route and the sulfate route for the titania produced in Panzhihua city, southwest China

5.4.2 Resource contributions

The relative contribution of each resource group to the scores of different resource indicators is represented in Figure 5.4 and Figure 5.5 for the chloride route and the sulfate route, respectively. Within the seven resource groups analyzed (Table 5.1 and Table 5.2), atmospheric resources and land resources are considered in SED and CEENE only. Atmospheric resources do not contribute to the SED or CEENE score since their characterization factors are set to zero. Land resources account for a negligible percent to the SED scores (0.01 % in both the chloride and sulfate routes), and have a small contribution to the CEENE scores, *i.e.*, 8 and 6 % in the chloride route and sulfate routes, respectively. This indicates that, at least in titania system analyzed, atmospheric resources and land resources could be left out of consideration in the SED indicator despite the SED indicator being regarded to give a more comprehensive overview of the resource demand than the indicators of CED, CExD, ADP, EPS, and EI99.

In Figure 5.4 and Figure 5.5, it appears that non-renewable resources have a dominant contribution to the scores of all seven resource indicators in both the chloride and sulfate routes, while renewable energy sources have a small contribution (<2 %). Fossil resources have a relatively high contribution to the scores of CED, CExD, CEENE, ADP, and EI99 (more than 74 %) in all types of non-renewable resources. Metal ores and fossil fuels have comparable contributions to the score of EPS. This can be explained by the fact that the average willingness to pay for the production of metals ores by a mining–

crushing–grinding–leaching–precipitation process, which is considered as the sustainable alternative for the current mining practice, is several orders of magnitude higher than that for the production of sustainable alternatives for fossil resources (*e.g.*, charcoal, rapeseed, *etc.*) while the demand of metal ores is several orders of magnitudes lower than that of fossil resources (except for V–Ti magnetite ore whose EPS characterization factor is unavailable). The score of SED is dominated by the demand of metal ores (mainly V–Ti magnetite ore) and minerals (mainly sodium chloride), with contributions of 92 % in the chloride route and 89 % in the sulfate route, respectively.

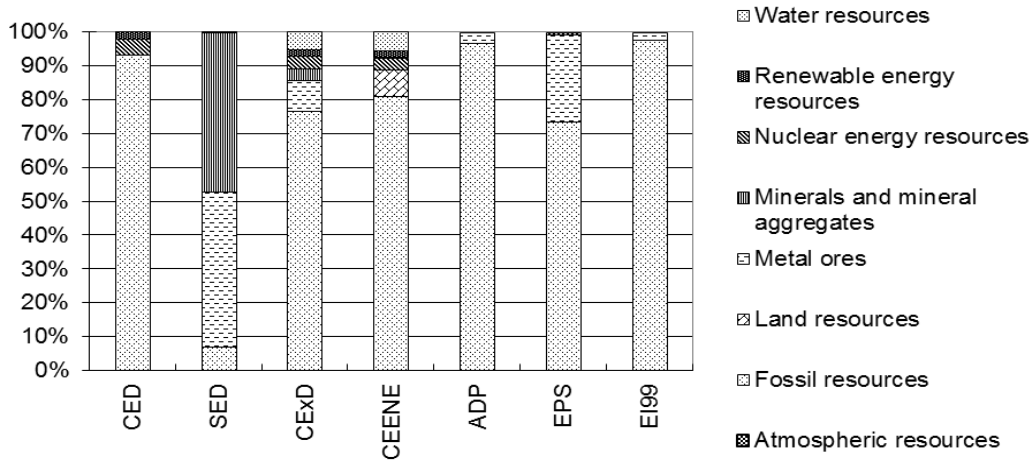

Figure 5.4 Relative contributions of resource groups to the different resource indicators (CED, SED, CExD, CEENE, ADP, EPS, and EI99) in the chloride route

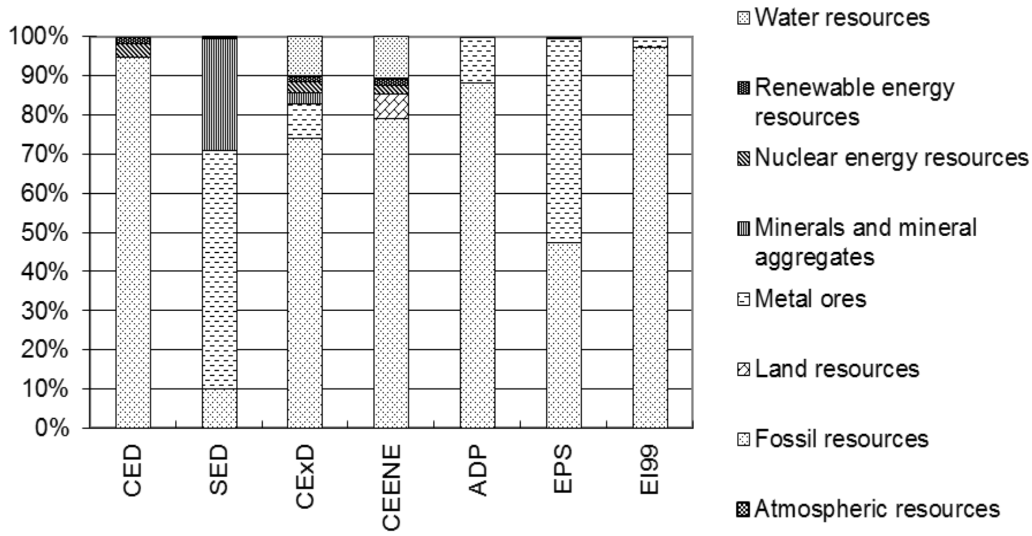

Figure 5.5 Relative contributions of resource groups to the different resource indicators (CED, SED, CExD, CEENE, ADP, EPS, and EI99) in the sulfate route

5.4.3 Sensitivity analysis of CED

There has been a debate on the question if the energy of all types of energy carriers, *viz.*, fossil, nuclear, and renewable, should be integrated into a single score. Frischknecht *et al.* (1998) recommend refraining from aggregating renewable and non-renewable energy demand because of the different nature of the resources. Furthermore, it is recognized that the demand of non-renewable energy resources is dominantly responsible for global warming and the depletion of non-renewable energy resources (Pacala and Socolow, 2004; Rosa and Ribeiro, 2001). If renewable energy sources are excluded, the cumulative non-renewable energy demand (CED_{NRR}) can be defined as: $CED_{NRR} = CED_{fossil} + CED_{nuclear}$. Table 5.5 gives the CED_{NRR} that is required in the supply chain of 1 kg of the titania produced in Panzhihua city, southwest China.

Table 5.5 Cumulative non-renewable energy demand (CED_{NRR}) of 1 kg of the titania produced in Panzhihua city, southwest China

Route	CED_{fossil} (MJ)	$CED_{nuclear}$ (MJ)	CED_{NRR} (MJ)
Chloride route	98.7	5.01	104
Sulfate route	111	3.97	115

Figure 5.6 shows the relative contribution of different non-renewable energy carriers to CED_{NRR}. It appears that normal fossil fuels, *i.e.*, hard coal, crude oil, and natural gas, have dominant contribution (more than 90 %) in both routes.

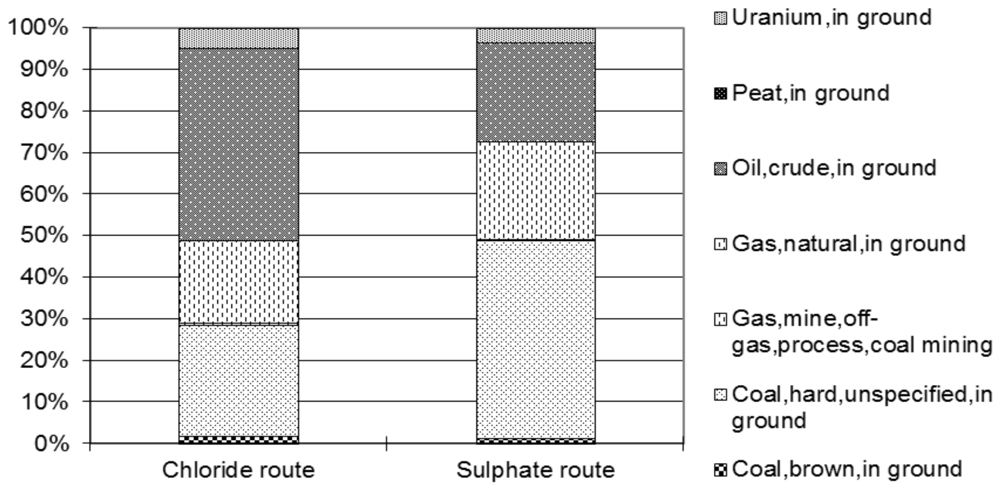

Figure 5.6 Relative contribution of non-renewable energy carriers to CED_{NRR}

5.4.4 Normalization

Similar to CED_{NRR}, the cumulative non-renewable exergy demand ($CExD_{NRR}$) can be defined as: $CExD_{NRR} = CExD_{fossil} + CExD_{nuclear} + CExD_{metals} + CExD_{minerals}$. Considering the CED_{NRR} and $CExD_{NRR}$ of 1kg of titania produced by the chloride route and the sulfate route (104–115 MJ and 120–134 MJ_{ex}-eq, respectively), the global production of titania which is reported to be 4.5E+09 kg/year for 2004 (Linak and Inoguchi, 2005)[2] would correspond to the CED_{NRR} and the $CExD_{NRR}$ of global titania of 4.67E+11–5.17E+11 MJ/year and 5.40E+11–6.03E+11 MJ_{ex}-eq/year, respectively. A total anthropogenic non-renewable energy/exergy demand, *i.e.*, the demand of non-renewable energy/exergy by all human activities in the anthroposphere, is reported to be around 4.11E+14 MJ/year and 4.15E+14

[2] While 4.5E+09 kg/year refers the total global production of titania from both chloride and sulphate routes, the percent is inaccessible in Linak and Inoguchi (2005). Other source (*cf.* http://www.cinkarna.si/en/245) reports that the global ratio between chloride route and sulphate route is approximately 56:44.

MJ_{ex}-eq/year (for the year 2008; the International Energy Agency, 2008; the British Petroleum, 2010; Liao *et al.*, 2012a)[3]. The normalization shows that the global production of titania would account for about 0.12 % of the total anthropogenic non-renewable energy demand and about 0.14 % of the total anthropogenic non-renewable exergy demand. Similar normalizations in other resource indicators can also be implemented if corresponding values of the total anthropogenic demand are available.

5.5 Conclusions and recommendation

In this study, we compared different resource indicators, in particular those based on thermodynamics. The different resource indicators have been shown to give different results in a case study on titania, although most indicators pointed in the same direction. Compared with other non-thermodynamic resource indicators, the basic added value to the impact assessment of resource use by using thermodynamic resource indicators in LCA lies in the completeness of resource scope and scientific robustness and validity, while thermodynamic resource indicators have lower environmental relevance in terms of expressing the resource scarcity and depletion (EC JRC, 2010a, 2010b). Within the four thermodynamic resource indicators addressed, SED and CEENE seem to be the most comprehensive indicators since they account for the largest number of resource groups. However, SED has different system boundaries than the other three indicators and, at least in the case of the two routes for titania, differs considerably from the other three by focusing on metal ores and minerals whose issue of scarcity per se could be better expressed via other non-thermodynamic resource indicators. Thus, we recommend CEENE as the most appropriate thermodynamic indicator for accounting and characterizing resource use, energetic and otherwise. As for the other two indicators, CED and CExD do not account for atmospheric and land resources (biomass is accounted in a different way) and focus on the energy content and exergy content of resources, respectively. CExD accounts for non-energetic materials (mainly metal ores and minerals), which are excluded in CED.

We also demonstrated the feasibility of thermodynamic resource indicators by testing them in the case study on the titania produced in Panzhihua city, southwest China. Conclusions can be drawn with regard to the case study: (1) all the resource indicators, except SED, under consideration show that the sulfate route demands more resource use than the chloride route; (2) non-renewable resources, in particular fossil resources, have a dominant contribution to all resource indicators addressed, except SED; (3) the global production of titania would account for 0.12 and 0.14 % of the total anthropogenic non-renewable resource demand in terms of energy and exergy, respectively.

It is a challenge to promote thermodynamic resource indicators. As pointed out by the ILCD Handbook: "(a thermodynamic resource indicator) does not take into account the future scarcity of a resource while it somehow considers the aspect of dispersion which is also an indicator of availability" (EC JRC, 2010a, 2010b), more efforts are needed to clarify the relevance between resources' thermodynamic properties and their scarcity for humans if thermodynamic indicators are used for the impact assessment besides the accounting and characterization of resource use. In addition, future study can refine the characterization

[3] Liao *et al.* (2012) show the calculation of $CExD_{NRR}$. The CED_{NRR} is calculated as the sum of various non-renewable energy flows whose value is reported by the International Energy Agency (2008) and double-checked according to the British Petroleum (2010). To a specific non-renewable energy flow, its CExD is determined by associating its CED with the corresponding exergy-to-energy ratio which is available in Szargut et al. (1988).

factors of minerals containing similar elements and set characterization factors to more resource flows based on reliable data, on one hand, and give more information on uncertainty, on the other hand. In this case, thermodynamic indicators would serve as more useful methods for the accounting and impact assessment of resource use.

Appendix

The combination of thermodynamic metrics and LCA

While thermodynamic analysis (energy/exergy/entropy/emergy analysis) and LCA have been developed separately, there has been a close link between LCA and energy analysis 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 the supply-chain level (level C in Figure 5.1). 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, and the third involves incorporating thermodynamic analysis into life-cycle thinking, mainly for specific multi-criteria studies. Both the first and second ways share the strategy of using thermodynamic metrics as a basis for resource indicators and thus are elaborated here.

Exergy consumption or entropy generation is used as for resource accounting and the characterization of resource depletion in life-cycle impact assessment (Wall, 1977, 1986; Ayres *et al.*, 1996, Finnveden and Östlund, 1997; Gößling-Reisemann, 2001; Stewart and Weidema, 2005; Steen, 2006). The underlying idea is that it is the physical utility, which can measured by exergy or entropy, rather than energy or matter (except for nuclear reactions), that is consumed and may denominate the issue of resource depletion (Gong and Wall, 2001; Gößling-Reisemann 2008a). By far the most commonly applied indicators of this type are cumulative exergy demand (CExD) (Bösch *et al.*, 2007) and cumulative exergy extraction from the natural environment (CEENE) (Dewulf *et al.*, 2007). CExD 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 (2005). CEENE distinguishes itself from CExD 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. 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 (Hau and Bakshi, 2004). The resource aggregation based on these indicators is appealing. However, all indicators can give counterintuitive results since they seldom address their presumption of the substitutability between various exergy resources adequately (Baral and Bakshi, 2010; Bakshi *et al.*, 2011).

Wall (1977) 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 *et al.* (1997, 2001) 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 values (Seager and Theis, 2002) or indirectly reflected determing the total exergy of resources 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. 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.

Table S5.1 The composition of V–Ti magnetite ore in Panzhihua city, Southwest China

Substance	Fe	TiO_2	V_2O_5	Cr_2O_3	S	P_2O_5	SiO_2	Al_2O_3	CaO	MgO
Content [a]	31.8	10.25	0.32	0.029	0.6	0.046	21.25	9.05	6.53	6.36

[a] content in %, *w/w*

Unit process raw input data

Table S5.2 Inputs to unit process "Mining and beneficiation", without allocation. Outputs are 1kg of beneficiated titanium ore (48.8 %, *w/w*, of TiO_2) and 10 kg of beneficiated iron ore

No	Input	Amount	Unit
1	V-Ti magnetite ore	23.32	kg
2	Steel ball	0.00649	kg
3	Process water	15.84	kg
4	Electricity	0.3278	kWh

Table S5.3 Inputs to unit process "Sulfate process". Output is 1kg of titania (99.0 %, *w/w*, of TiO2)

No	Input	Amount	Unit
1	Beneficiated titanium ore	2.63	kg
2	Sulfuric acid (98 %)	4.05	kg
3	Iron powder	0.09	kg
4	Caustic soda (30 %)	0.35	kg
5	Coal	2	kg
6	Diesel	0.099	kg
7	Steam	8	kg
8	Process water	98	kg
9	Electricity	1.5	kWh
10	Truck transport	0.21	t*km

Table S5.4 Inputs to unit process "Titanium slag production". Output is 1kg of high titanium slag (94.0 %, *w/w*, of TiO2)

No	Input	Amount	Unit
1	Beneficiated titanium ore	1.7	kg
2	Anthracite	0.21	kg
3	Metallurgical coke	0.0156	kg
4	Process water	6.36	kg
5	Electricity	1.46	kWh
6	Truck transport	0.174	t*km

Table S5.5 Inputs to unit "Chloride process". Output is 1kg of titania (99.0 %, *w/w*, of TiO2)

No	Input	Amount	Unit
1	High titanium slag	1.15	kg
2	Petroleum coke	0.67	kg
3	Liquid chlorine	0.25	kg
4	Aluminum powder	0.006	kg
5	Oxygen	0.643	kg
6	Liquid caustic soda (30 %)	0.3	kg
7	Saturated steam (1.3MPa)	5.5	kg
8	Process water	43	kg
9	Electricity	1.1	kWh

Table S5.6 Inputs to unit process "Transportation". Output is 1t*km of truck transport

No	Input	Amount	Unit
1	Gasoline	0.0851	kg
2	Diesel	0.0568	kg

Table S5.7 Main product inputs in ecoinvent database v2.2 needed to produce 1kg of titania

No	Input	Dataset name in ecoinvent v2.2	Unit	Location [a]
1	Aluminium powder	Aluminium, production mix, at plant	kg	RER
2	Anthracite [b]	Anthracite, burned in stove 5–15kW	MJ	RER
3	Caustic soda (liquid, 30 %)	Sodium hydroxide, 50 % in H_2O, production mix, at plant	kg	RER
4	Chlorine (liquid)	Chlorine, liquid, production mix, at plant	kg	RER
5	Coke	Petroleum coke, at refinery	kg	RER
6	Diesel	Diesel, at refinery	kg	RER
7	Electricity	Electricity mix	kWh	CN
8	Iron powder	Iron scrap, at plant	kg	RER
9	Petrol	Petrol, low-sulphur, at refinery	kg	RER
10	Steam (Saturated, 1.3MPa)	Steam, for chemical processes, at plant	kg	RER
11	Steel ball	Steel product manufacturing, average metal working	kg	RER
12	Sulfuric acid (98 %)	Sulphuric acid, liquid, at plant	kg	RER

[a] RER = Europe; CN = China
[b] Anthracite: heating value = 32.4 MJ/kg

CExD characterization factor of V–Ti magnetite ore

Fe, reference species: Fe_2O_3, standard chemical exergy of Fe_2O_3 = 377.8 kJ/mol = 2.361 MJ/kg
Ti, reference species: TiO_2, standard chemical exergy of TiO_2 = 906.1 kJ/mol = 11.326 MJ/kg
V, reference species: V_2O_5, standard chemical exergy of V_2O_5 = 720.1 kJ/mol = 3.957 MJ/kg
The V–Ti magnetite can be treated as a composite mainly containing Fe_2O_3 (45.43 %, *w/w*), TiO_2 (10.25 %, *w/w*) and V_2O_5 (0.32 %, *w/w*), then its exergy, *i.e.*, CExD characterization factor, is: 2.361 MJ/kg *0.4543 + 11.326 MJ/kg *0.1025 + 3.957 MJ/kg * 0.0032 = 2.25 MJ/kg

Table S5.8 LCI + CF of resource flows in the chloride route and the sulfate route

Name	Group	Chloride route	Sulfate route	Unit	Characterization factors						
					CED	SED	CExD	CEENE	ADP	EPS	EI99
Carbon dioxide, in air[resource_in air]	atmospheric	4,01E-02	4,01E-02	kg							
Oxygen	atmospheric	6,43E-01	0,00E+00	kg							
Coal, brown, in ground[resource_in ground]	fossil	1,97E-01	1,53E-01	kg	9,90E+00	1,42E+06	1,03E+01	1,03E+01	6,71E-03	4,98E-02	6,10E-01
Coal, hard, unspecified, in ground[resource_in ground]	fossil	1,44E+00	2,86E+00	kg	1,91E+01	1,42E+06	1,97E+01	1,97E+01	1,34E-02	4,98E-02	2,04E+00
Gas, mine, off-gas, process, coal mining[resource_in ground]	fossil	1,47E-02	8,96E-03	Nm^3	3,98E+01		3,74E+01				
Gas, natural, in ground[resource_in ground]	fossil	5,37E-01	7,10E-01	Nm^3	3,83E+01	1,47E+06	3,60E+01	3,83E+01	1,87E-02	9,16E-01	3,26E+00
Oil, crude, in ground[resource_in ground]	fossil	1,05E+00	6,01E-01	kg	4,58E+01	2,32E+06	4,65E+01	4,62E+01	2,01E-02	5,06E-01	3,49E+00
Peat, in ground[resource_biotic]	fossil	7,49E-06	1,77E-05	kg	9,90E+00	3,53E+05	1,03E+01	1,02E+01			
Sulfur, in ground[resource_in ground]	fossil	5,07E-07	1,50E-06	kg		4,45E+06	1,90E+01	1,89E+01	1,93E-04	1,00E-01	
Carbon, in organic matter, in soil[resource_in ground]	land	1,16E-06	1,03E-06	kg							
Occupation, arable, non-irrigated[resource_land]	land	4,01E-05	5,18E-05	m^2a		6,17E+04		6,81E+01			
Occupation, construction site[resource_land]	land	2,51E-04	3,20E-04	m^2a		6,17E+04		6,81E+01			
Occupation, dump site, benthos[resource_land]	land	5,07E-04	3,86E-04	m^2a							
Occupation, dump site[resource_land]	land	1,66E-02	1,26E-02	m^2a		6,17E+04		6,81E+01			
Occupation, forest, intensive, normal[resource_land]	land	9,69E-02	9,29E-02	m^2a		6,17E+04		6,81E+01			
Occupation, forest, intensive, short-cycle[resource_land]	land	2,01E-05	1,79E-05	m^2a		6,17E+04		6,81E+01			
Occupation, forest, intensive[resource_land]	land	3,61E-04	5,33E-04	m^2a		6,17E+04		6,81E+01			
Occupation, industrial area, benthos[resource_land]	land	4,14E-06	3,32E-06	m^2a							
Occupation, industrial area, built up[resource_land]	land	7,26E-04	2,99E-03	m^2a		6,17E+04		6,81E+01			
Occupation, industrial area, vegetation[resource_land]	land	3,48E-04	1,06E-03	m^2a		6,17E+04		6,81E+01			
Occupation, industrial area[resource_land]	land	8,80E-03	4,02E-03	m^2a		6,17E+04		6,81E+01			
Occupation, mineral extraction site[resource_land]	land	2,42E-03	1,60E-03	m^2a		6,17E+04		6,81E+01			
Occupation, permanent crop, fruit, intensive[resource_land]	land	2,80E-05	2,51E-05	m^2a		6,17E+04		6,81E+01			
Occupation, shrub land, sclerophyllous[resource_land]	land	7,05E-05	8,58E-05	m^2a		6,17E+04		6,81E+01			
Occupation, traffic area, rail embankment[resource_land]	land	3,13E-04	6,77E-04	m^2a		6,17E+04		6,81E+01			
Occupation, traffic area, rail network[resource_land]	land	3,46E-04	7,48E-04	m^2a		6,17E+04		6,81E+01			
Occupation, traffic area, road embankment[resource_land]	land	9,73E-04	9,72E-04	m^2a		6,17E+04		6,81E+01			
Occupation, traffic area, road network[resource_land]	land	9,76E-04	1,05E-03	m^2a		6,17E+04		6,81E+01			
Occupation, urban, discontinuously built[resource_land]	land	1,63E-07	1,25E-07	m^2a		6,17E+04		6,81E+01			
Occupation, water bodies, artificial[resource_land]	land	1,16E-02	9,76E-03	m^2a		6,17E+04		6,81E+01			
Occupation, water courses, artificial[resource_land]	land	6,74E-04	5,04E-04	m^2a		6,17E+04		6,81E+01			
Transformation, from arable, non-irrigated, fallow[resource_land]	land	6,29E-07	1,94E-07	m^2							
Transformation, from arable, non-irrigated[resource_land]	land	7,39E-05	9,56E-05	m^2							

Transformation, from arable[resource_land]	land	2,39E-06	9,26E-07	m^2
Transformation, from dump site, inert material landfill[resource_land]	land	2,55E-06	6,84E-06	m^2
Transformation, from dump site, residual material landfill[resource_land]	land	1,14E-05	9,93E-06	m^2
Transformation, from dump site, sanitary landfill[resource_land]	land	1,13E-07	3,63E-07	m^2
Transformation, from dump site, slag compartment[resource_land]	land	7,37E-09	1,57E-08	m^2
Transformation, from forest, extensive[resource_land]	land	6,69E-04	6,86E-04	m^2
Transformation, from forest, intensive, clear-cutting[resource_land]	land	7,19E-07	6,38E-07	m^2
Transformation, from forest[resource_land]	land	1,45E-03	9,21E-04	m^2
Transformation, from industrial area, benthos[resource_land]	land	1,56E-08	2,17E-08	m^2
Transformation, from industrial area, built up[resource_land]	land	5,64E-09	8,25E-09	m^2
Transformation, from industrial area, vegetation[resource_land]	land	9,62E-09	1,41E-08	m^2
Transformation, from industrial area[resource_land]	land	3,70E-06	4,22E-06	m^2
Transformation, from mineral extraction site[resource_land]	land	1,67E-05	1,63E-05	m^2
Transformation, from pasture and meadow, intensive[resource_land]	land	6,03E-08	7,79E-08	m^2
Transformation, from pasture and meadow[resource_land]	land	2,96E-05	3,41E-05	m^2
Transformation, from sea and ocean[resource_land]	land	5,07E-04	3,86E-04	m^2
Transformation, from shrub land, sclerophyllous[resource_land]	land	1,74E-05	1,97E-05	m^2
Transformation, from tropical rain forest[resource_land]	land	7,19E-07	6,38E-07	m^2
Transformation, from unknown[resource_land]	land	4,44E-04	3,58E-04	m^2
Transformation, to arable, non-irrigated, fallow[resource_land]	land	7,34E-07	4,21E-07	m^2
Transformation, to arable, non-irrigated[resource_land]	land	7,40E-05	9,57E-05	m^2
Transformation, to arable[resource_land]	land	3,83E-05	4,31E-05	m^2
Transformation, to dump site, benthos[resource_land]	land	5,07E-04	3,86E-04	m^2
Transformation, to dump site, inert material landfill[resource_land]	land	2,55E-06	6,84E-06	m^2
Transformation, to dump site, residual material landfill[resource_land]	land	1,14E-05	9,93E-06	m^2
Transformation, to dump site, sanitary landfill[resource_land]	land	1,13E-07	3,63E-07	m^2
Transformation, to dump site, slag compartment[resource_land]	land	7,37E-09	1,57E-08	m^2
Transformation, to dump site[resource_land]	land	1,35E-04	1,01E-04	m^2
Transformation, to forest, intensive, clear-cutting[resource_land]	land	7,19E-07	6,38E-07	m^2
Transformation, to forest, intensive, normal[resource_land]	land	6,59E-04	6,75E-04	m^2
Transformation, to forest, intensive, short-cycle[resource_land]	land	7,19E-07	6,38E-07	m^2
Transformation, to forest, intensive[resource_land]	land	2,41E-06	3,55E-06	m^2
Transformation, to forest[resource_land]	land	1,62E-05	1,95E-05	m^2
Transformation, to heterogeneous, agricultural[resource_land]	land	5,97E-05	4,03E-05	m^2
Transformation, to industrial area, benthos[resource_land]	land	2,10E-07	3,58E-07	m^2
Transformation, to industrial area, built up[resource_land]	land	1,65E-05	6,32E-05	m^2

Transformation, to industrial area, vegetation[resource_land]	land	8,09E-06	2,34E-05	m^2						
Transformation, to industrial area[resource_land]	land	1,70E-04	6,73E-05	m^2						
Transformation, to mineral extraction site[resource_land]	land	1,40E-03	8,81E-04	m^2						
Transformation, to pasture and meadow[resource_land]	land	2,38E-06	3,30E-06	m^2						
Transformation, to permanent crop, fruit, intensive[resource_land]	land	3,94E-07	3,53E-07	m^2						
Transformation, to sea and ocean[resource_land]	land	1,56E-08	2,17E-08	m^2						
Transformation, to shrub land, sclerophyllous[resource_land]	land	1,41E-05	1,71E-05	m^2						
Transformation, to traffic area, rail embankment[resource_land]	land	7,28E-07	1,57E-06	m^2						
Transformation, to traffic area, rail network[resource_land]	land	8,00E-07	1,73E-06	m^2						
Transformation, to traffic area, road embankment[resource_land]	land	6,55E-06	6,84E-06	m^2						
Transformation, to traffic area, road network[resource_land]	land	1,33E-05	1,47E-05	m^2						
Transformation, to unknown[resource_land]	land	2,76E-06	7,17E-06	m^2						
Transformation, to urban, discontinuously built[resource_land]	land	3,24E-09	2,49E-09	m^2						
Transformation, to water bodies, artificial[resource_land]	land	7,75E-05	6,57E-05	m^2						
Transformation, to water courses, artificial[resource_land]	land	7,79E-06	5,85E-06	m^2						
Volume occupied, final repository for low-active radioactive waste[resource_in ground]	land	1,77E-08	1,39E-08	m^3						
Volume occupied, final repository for radioactive waste[resource_in ground]	land	4,40E-09	3,46E-09	m^3						
Volume occupied, reservoir[resource_in water]	land	5,54E-02	4,67E-02	m^3a						
Volume occupied, underground deposit[resource_in ground]	land	8,15E-08	4,87E-08	m^3						
Aluminium, 24% in bauxite, 11% in crude ore, in ground[resource_in ground]	metal ores	5,18E-03	1,60E-03	kg	3,26E+06	5,73E+00	4,70E-01	1,09E-09	4,93E-01	2,38E+00
Cadmium, 0.30% in sulfide, Cd 0.18%, Pb, Zn, Ag, In, in ground[resource_in ground]	metal ores	4,26E-08	1,05E-07	kg	1,98E+10	8,58E+00		1,57E-01	2,91E+04	
Chromium, 25.5% in chromite, 11.6% in crude ore, in ground[resource_in ground]	metal ores	2,95E-04	1,15E-03	kg	9,10E+07	5,43E+00	1,60E+00	4,43E-04	8,49E+01	9,17E-01
Cinnabar, in ground[resource_in ground]	metal ores	9,70E-07	4,75E-07	kg	2,44E+10	2,90E+00	2,88E+00	9,22E-02	5,30E+04	1,66E+02
Cobalt, in ground[resource_in ground]	metal ores	1,11E-09	4,12E-09	kg	7,91E+07	1,93E+02	1,18E+00	1,57E-05	2,56E+02	
Copper, 0.99% in sulfide, Cu 0.36% and Mo 8.2E-3% in crude ore, in ground[resource_in ground]	metal ores	2,85E-05	1,05E-04	kg	5,77E+07	1,53E+02	1,58E+01	1,37E-03	2,08E+02	3,67E+01
Copper, 1.18% in sulfide, Cu 0.39% and Mo 8.2E-3% in crude ore, in ground[resource_in ground]	metal ores	1,57E-04	5,76E-04	kg	5,77E+07	1,43E+02	1,58E+01	1,37E-03	2,08E+02	3,67E+01
Copper, 1.42% in sulfide, Cu 0.81% and Mo 8.2E-3% in crude ore, in ground[resource_in ground]	metal ores	4,17E-05	1,53E-04	kg	5,77E+07	7,32E+01	1,58E+01	1,37E-03	2,08E+02	3,67E+01
Copper, 2.19% in sulfide, Cu 1.83% and Mo 8.2E-3% in crude ore, in ground[resource_in ground]	metal ores	2,08E-04	7,66E-04	kg	5,77E+07	3,35E+01	1,58E+01	1,37E-03	2,08E+02	3,67E+01
Gallium, 0.014% in bauxite, in ground[resource_in ground]	metal ores	3,23E-12	2,56E-12	kg	1,04E+07	4,50E+03		1,46E-07	2,12E+02	
Gold, Au 1.1E-4%, Ag 4.2E-3%, in ore, in ground[resource_in ground]	metal ores	1,24E-09	6,21E-09	kg	2,97E+08	3,46E+05		5,20E+01	1,19E+06	
Gold, Au 1.3E-4%, Ag 4.6E-5%, in ore, in ground[resource_in ground]	metal ores	2,28E-09	1,14E-08	kg	2,97E+08	4,82E+05		5,20E+01	1,19E+06	
Gold, Au 1.4E-4%, in ore, in ground[resource_in ground]	metal ores	2,73E-09	1,36E-08	kg	2,97E+08	4,50E+05		5,20E+01	1,19E+06	

Gold, Au 2.1E-4%, Ag 2.1E-4%, in ore, in ground[resource_in ground]	metal ores	4,16E-09	2,08E-08	kg	2,97E+08	2,95E+05		5,20E+01	1,19E+06	
Gold, Au 4.3E-4%, in ore, in ground[resource_in ground]	metal ores	1,03E-09	5,16E-09	kg	2,97E+08	1,47E+05		5,20E+01	1,19E+06	
Gold, Au 4.9E-5%, in ore, in ground[resource_in ground]	metal ores	2,47E-09	1,24E-08	kg	2,97E+08	1,29E+06		5,20E+01	1,19E+06	
Gold, Au 6.7E-4%, in ore, in ground[resource_in ground]	metal ores	3,83E-09	1,91E-08	kg	2,97E+08	9,40E+04		5,20E+01	1,19E+06	
Gold, Au 7.1E-4%, in ore, in ground[resource_in ground]	metal ores	4,32E-09	2,16E-08	kg	2,97E+08	8,87E+04		5,20E+01	1,19E+06	
Gold, Au 9.7E-4%, Ag 9.7E-4%, Zn 0.63%, Cu 0.38%, Pb 0.014%, in ore, in ground[resource_in ground]	metal ores	2,59E-10	1,29E-09	kg	2,97E+08	5,81E+04		5,20E+01	1,19E+06	
Indium, 0.005% in sulfide, In 0.003%, Pb, Zn, Ag, Cd, in ground[resource_in ground]	metal ores	8,70E-10	1,88E-09	kg	2,37E+08	2,77E+03		6,89E-03	4,87E+04	
Iron, 46% in ore, 25% in crude ore, in ground[resource_in ground]	metal ores	1,84E-02	2,38E-02	kg	7,07E+06	2,52E+00	3,62E-01	5,24E-08	9,61E-01	5,10E-02
Lead, 5.0% in sulfide, Pb 3.0%, Zn, Ag, Cd, In, in ground[resource_in ground]	metal ores	9,11E-06	1,04E-05	kg	2,83E+08	4,29E+00	3,58E+00	6,34E-03	1,75E+02	7,35E+00
Lithium, 0.15% in brine, in ground[resource_in ground]	metal ores	4,69E-12	3,51E-12	kg						
Manganese, 35.7% in sedimentary deposit, 14.2% in crude ore, in ground[resource_in ground]	metal ores	4,94E-05	1,34E-04	kg	2,08E+08	4,44E+00	1,01E+00	2,54E-06	5,64E+00	3,13E-01
Molybdenum, 0.010% in sulfide, Mo 8.2E-3% and Cu 1.83% in crude ore, in ground[resource_in ground]	metal ores	3,87E-06	1,42E-05	kg	4,12E+08	2,09E+02	1,75E+01	1,78E-02	2,12E+03	4,10E+01
Molybdenum, 0.014% in sulfide, Mo 8.2E-3% and Cu 0.81% in crude ore, in ground[resource_in ground]	metal ores	5,47E-07	2,01E-06	kg	4,12E+08	4,56E+02	1,75E+01	1,78E-02	2,12E+03	4,10E+01
Molybdenum, 0.022% in sulfide, Mo 8.2E-3% and Cu 0.36% in crude ore, in ground[resource_in ground]	metal ores	5,49E-07	1,56E-06	kg	4,12E+08	1,45E+03	1,75E+01	1,78E-02	2,12E+03	4,10E+01
Molybdenum, 0.025% in sulfide, Mo 8.2E-3% and Cu 0.39% in crude ore, in ground[resource_in ground]	metal ores	2,01E-06	7,35E-06	kg	4,12E+08	8,92E+02	1,75E+01	1,78E-02	2,12E+03	4,10E+01
Molybdenum, 0.11% in sulfide, Mo 4.1E-2% and Cu 0.36% in crude ore, in ground[resource_in ground]	metal ores	1,10E-06	3,12E-06	kg	4,12E+08	6,39E+02	1,75E+01	1,78E-02	2,12E+03	4,10E+01
Nickel, 1.13% in sulfide, Ni 0.76% and Cu 0.76% in crude ore, in ground[resource_in ground]	metal ores	4,25E-07	9,84E-07	kg	1,18E+08	5,61E+01	2,51E+01	6,53E-05	1,60E+02	1,63E+01
Nickel, 1.98% in silicates, 1.04% in crude ore, in ground[resource_in ground]	metal ores	8,05E-04	2,78E-03	kg	1,18E+08	6,06E+01	2,51E+01	6,53E-05	1,60E+02	1,63E+01
Pd, Pd 2.0E-4%, Pt 4.8E-4%, Rh 2.4E-5%, Ni 3.7E-2%, Cu 5.2E-2% in ore, in ground[resource_in ground]	metal ores	1,94E-09	6,87E-09	kg	7,25E+07	1,30E+04	6,48E+00	6,34E-03	1,75E+02	1,35E+00
Pd, Pd 7.3E-4%, Pt 2.5E-4%, Rh 2.0E-5%, Ni 2.3E+0%, Cu 3.2E+0% in ore, in ground[resource_in ground]	metal ores	4,67E-09	1,65E-08	kg	7,25E+07	4,89E+04	6,48E+00	6,34E-03	1,75E+02	1,35E+00
Pt, Pt 2.5E-4%, Pd 7.3E-4%, Rh 2.0E-5%, Ni 2.3E+0%, Cu 3.2E+0% in ore, in ground[resource_in ground]	metal ores	4,80E-11	1,38E-10	kg	2,18E+08	2,51E+04	4,10E+00	2,22E+00	7,43E+06	
Pt, Pt 4.8E-4%, Pd 2.0E-4%, Rh 2.4E-5%, Ni 3.7E-2%, Cu 5.2E-2% in ore, in ground[resource_in ground]	metal ores	1,72E-10	4,93E-10	kg	2,18E+08	9,48E+04	4,10E+00	2,22E+00	7,43E+06	
Rh, Rh 2.0E-5%, Pt 2.5E-4%, Pd 7.3E-4%, Ni 2.3E+0%, Cu 3.2E+0% in ore, in ground[resource_in ground]	metal ores	4,00E-11	1,30E-10	kg	7,07E+08	5,44E+04	9,26E+00		4,95E+07	
Rh, Rh 2.4E-5%, Pt 4.8E-4%, Pd 2.0E-4%, Ni 3.7E-2%, Cu 5.2E-2% in ore, in ground[resource_in ground]	metal ores	1,25E-10	4,06E-10	kg	7,07E+08	2,05E+05	9,26E+00		4,95E+07	
Rhenium, in crude ore, in ground[resource_in ground]	metal ores	8,94E-11	6,49E-10	kg	5,26E+09	1,62E+04	8,69E+00	6,03E-01	7,43E+06	
Silver, 0.007% in sulfide, Ag 0.004%, Pb, Zn, Cd, In, in ground[resource_in ground]	metal ores	2,77E-08	1,37E-07	kg	2,64E+08	9,61E+01		1,18E+00	5,40E+04	
Silver, 3.2ppm in sulfide, Ag 1.2ppm, Cu and Te, in crude ore, in ground[resource_in ground]	metal ores	1,98E-08	9,79E-08	kg	2,64E+08	1,03E+04		1,18E+00	5,40E+04	

Silver, Ag 2.1E-4%, Au 2.1E-4%, in ore, in ground[resource_in ground]	metal ores	1,83E-09	9,04E-09	kg	2,64E+08	5,06E+03		1,18E+00	5,40E+04	
Silver, Ag 4.2E-3%, Au 1.1E-4%, in ore, in ground[resource_in ground]	metal ores	4,17E-09	2,06E-08	kg	2,64E+08	5,94E+03		1,18E+00	5,40E+04	
Silver, Ag 4.6E-5%, Au 1.3E-4%, in ore, in ground[resource_in ground]	metal ores	4,09E-09	2,02E-08	kg	2,64E+08	8,26E+03		1,18E+00	5,40E+04	
Silver, Ag 9.7E-4%, Au 9.7E-4%, Zn 0.63%, Cu 0.38%, Pb 0.014%, in ore, in ground[resource_in ground]	metal ores	2,70E-09	1,33E-08	kg	2,64E+08	9,96E+02		1,18E+00	5,40E+04	
Tantalum, 81.9% in tantalite, 1.6E-4% in crude ore, in ground[resource_in ground]	metal ores	2,18E-08	1,08E-07	kg	9,89E+07	3,94E+05		4,06E-05	1,98E+03	
Tellurium, 0.5ppm in sulfide, Te 0.2ppm, Cu and Ag, in crude ore, in ground[resource_in ground]	metal ores	2,97E-09	1,47E-08	kg	2,97E+10	4,07E+01		5,94E+05		
Tin, 79% in cassiterite, 0.1% in crude ore, in ground[resource_in ground]	metal ores	9,89E-07	4,77E-06	kg	9,89E+08	6,30E+02	3,63E-01	1,62E-02	1,19E+03	6,00E+02
TiO2, 54% in ilmenite, 2.6% in crude ore, in ground[resource_in ground]	metal ores	7,59E-05	1,04E-04	kg	3,82E+07	2,42E+01	1,69E+00	2,79E-08	9,53E-01	
TiO2, 95% in rutile, 0.40% in crude ore, in ground[resource_in ground]	metal ores	1,44E-10	6,53E-10	kg	3,82E+07	1,58E+02		2,79E-08	9,53E-01	
V-Ti magnetite ore	metal ores	5,07E+00	5,58E+00	kg	7,07E+06	2,25E+00				2,90E-02
Zinc, 9.0% in sulfide, Zn 5.3%, Pb, Ag, Cd, In, in ground[resource_in ground]	metal ores	1,54E-04	4,92E-04	kg	4,24E+07	6,79E+00	1,14E+01	5,38E-04	5,71E+01	2,00E+00
Zirconium, 50% in zircon, 0.39% in crude ore, in ground[resource_in ground]	metal ores	2,98E-08	1,49E-07	kg	1,87E+07	1,61E+02		5,44E-06	1,25E+01	
Anhydrite, in ground[resource_in ground]	minerals	5,97E-09	1,64E-08	kg	9,89E+07	6,00E-02	1,58E-01			
Barite, 15% in crude ore, in ground[resource_in ground]	minerals	6,78E-03	4,19E-03	kg	9,89E+07	4,20E+00	1,28E-01			
Basalt, in ground[resource_in ground]	minerals	1,10E-04	4,24E-04	kg	1,46E+05	2,80E-01	3,10E-01			
Borax, in ground[resource_in ground]	minerals	6,52E-09	1,69E-08	kg	9,89E+07		2,35E-01	4,27E-03	5,00E-02	
Calcite, in ground[resource_in ground]	minerals	4,15E-02	4,56E-02	kg	5,50E+06	1,00E+02	1,84E-01			
Chrysotile, in ground[resource_in ground]	minerals	1,06E-05	5,16E-06	kg	1,25E+06	1,40E-01	1,06E-01	2,02E-09	5,64E+00	3,13E-01
Clay, bentonite, in ground[resource_in ground]	minerals	5,82E-04	5,26E-04	kg	1,98E+06	5,90E-02	1,09E-01			
Clay, unspecified, in ground[resource_in ground]	minerals	1,53E-02	5,75E-02	kg	1,98E+06	5,70E-01	1,06E-01			
Colemanite, in ground[resource_in ground]	minerals	2,44E-06	8,73E-06	kg	9,89E+07		2,69E-01	1,37E-03	2,08E+02	3,67E+01
Diatomite, in ground[resource_in ground]	minerals	2,70E-11	3,72E-11	kg	1,25E+06	1,50E-01	4,05E+00			
Dolomite, in ground[resource_in ground]	minerals	5,49E-05	1,08E-04	kg	5,50E+06	8,20E-02	1,26E-01			
Feldspar, in ground[resource_in ground]	minerals	5,22E-10	1,08E-09	kg	1,25E+06	1,40E-01	1,03E-01			
Fluorine, 4.5% in apatite, 1% in crude ore, in ground[resource_in ground]	minerals	3,96E-06	5,82E-06	kg	1,25E+06	6,30E+01	2,60E-01		4,86E+00	
Fluorine, 4.5% in apatite, 3% in crude ore, in ground[resource_in ground]	minerals	1,76E-06	2,58E-06	kg	1,25E+06	2,10E+01	2,60E-01		4,86E+00	
Fluorspar, 92%, in ground[resource_in ground]	minerals	1,33E-04	1,73E-04	kg	9,89E+07	1,50E-01	4,40E-01			
Granite, in ground[resource_in ground]	minerals	1,18E-12	3,93E-12	kg	4,90E+05	6,80E-02	9,04E-02			
Gravel, in ground[resource_in ground]	minerals	1,86E-01	3,07E-01	kg	1,25E+06	6,80E-02	9,04E-02			
Gypsum, in ground[resource_in ground]	minerals	1,60E-07	1,41E-07	kg	9,89E+07	4,50E-02	1,50E-01			
Kaolinite, 24% in crude ore, in ground[resource_in ground]	minerals	4,92E-06	4,21E-06	kg	1,25E+06	2,63E+00	5,70E-02			
Kieserite, 25% in crude ore, in ground[resource_in ground]	minerals	1,81E-08	1,82E-08	kg	9,89E+07	2,52E+00	2,72E-01			
Magnesite, 60% in crude ore, in ground[resource_in ground]	minerals	2,68E-04	3,46E-04	kg	9,89E+07	1,05E+00	1,15E-01			
Metamorphous rock, graphite containing, in ground[resource_in ground]	minerals	7,66E-06	2,25E-06	kg	1,42E+06	1,09E+00	3,42E+01			

Olivine, in ground[resource_in ground]	minerals	2,27E-09	6,41E-09	kg		1,25E+06	7,80E-01	4,79E-01		
Phosphorus, 18% in apatite, 12% in crude ore, in ground[resource_in ground]	minerals	7,42E-06	1,09E-05	kg		1,25E+06	1,58E+01	2,60E-02	5,52E-06	4,47E+00
Phosphorus, 18% in apatite, 4% in crude ore, in ground[resource_in ground]	minerals	1,58E-05	2,33E-05	kg		1,25E+06	5,25E+00	2,60E-02	5,52E-06	4,47E+00
Sand, unspecified, in ground[resource_in ground]	minerals	1,82E-06	2,26E-06	kg		4,95E+06	6,80E-02	3,10E-02		
Shale, in ground[resource_in ground]	minerals	1,69E-08	4,66E-08	kg		2,36E+06	5,70E-01	8,20E-02		
Sodium chloride, in ground[resource_in ground]	minerals	3,64E-01	1,79E-01	kg		9,89E+07	2,50E-01	2,48E-01	5,50E-08	
Sodium nitrate, in ground[resource_in ground]	minerals	8,36E-13	2,63E-12	kg		1,25E+06			5,50E-08	
Sodium sulphate, various forms, in ground[resource_in ground]	minerals	3,23E-05	4,66E-05	kg		9,89E+07	1,50E-01	1,27E-01	5,50E-08	
Stibnite, in ground[resource_in ground]	minerals	2,81E-12	3,87E-12	kg		2,49E+09		7,34E+00	1,00E+00	9,58E+03
Sylvite, 25 % in sylvinite, in ground[resource_in ground]	minerals	2,82E-06	9,70E-06	kg		1,25E+06	9,90E-01	2,68E-01	1,60E-08	1,00E-02
Talc, in ground[resource_in ground]	minerals	6,49E-07	6,66E-07	kg		1,25E+06	3,90E-02	5,70E-02		
Ulexite, in ground[resource_in ground]	minerals	1,66E-07	1,78E-07	kg		9,89E+07		2,17E-01		
Vermiculite, in ground[resource_in ground]	minerals	1,36E-06	1,90E-06	kg		1,25E+06	3,90E-02	1,10E-01		
Uranium, in ground[resource_in ground]	nuclear	8,95E-06	7,09E-06	kg	5,60E+05	9,53E+07	5,60E+05	4,69E+05		1,19E+03
Energy, gross calorific value, in biomass, primary forest[resource_biotic]	renewable energy	8,03E-05	7,13E-05	MJ	1,00E+00		1,05E+00			
Energy, gross calorific value, in biomass[resource_biotic]	renewable energy	4,08E-01	4,18E-01	MJ	1,00E+00		1,05E+00			
Energy, kinetic (in wind), converted[resource_in air]	renewable energy	8,40E-02	6,64E-02	MJ	1,00E+00	1,47E+03	1,00E+00	4,00E+00		
Energy, potential (in hydropower reservoir), converted[resource_in water]	renewable energy	1,79E+00	1,48E+00	MJ	1,00E+00	2,73E+04	1,00E+00	1,25E+00		
Energy, solar, converted[resource_in air]	renewable energy	1,14E-03	9,02E-04	MJ	1,00E+00		9,30E-01			
Wood, hard, standing[resource_biotic]	renewable energy	2,04E-05	1,47E-05	m^3						
Wood, primary forest, standing[resource_biotic]	renewable energy	7,45E-09	6,61E-09	m^3						
Wood, soft, standing[resource_biotic]	renewable energy	1,57E-05	2,48E-05	m^3						
Wood, unspecified, standing[resource_biotic]	renewable energy	4,20E-11	9,39E-11	m^3						
Bromine, 0.0023% in water[resource_in water]	water	1,31E-09	1,07E-09	kg					4,39E-03	
Iodine, 0.03% in water[resource_in water]	water	3,37E-10	2,80E-10	kg					2,50E-02	
Magnesium, 0.13% in water[resource_in water]	water	1,29E-08	2,66E-08	kg					2,02E-09	
Water, cooling, unspecified natural origin[resource_in water]	water	1,13E-01	8,65E-02	m^3		5,44E+05	5,00E+01	5,00E+01		
Water, lake[resource_in water]	water	1,43E-03	2,00E-03	m^3		2,22E+05	5,00E+01	5,00E+01		
Water, river[resource_in water]	water	1,05E-02	1,12E-02	m^3		3,09E+05	5,00E+01	5,00E+01		
Water, salt, ocean[resource_in water]	water	1,42E-03	1,28E-03	m^3						
Water, salt, sole[resource_in water]	water	8,32E-04	4,73E-04	m^3						
Water, turbine use, unspecified natural origin[resource_in water]	water	7,95E+00	6,28E+00	m^3						
Water, unspecified natural origin[resource_in water]	water	5,68E-03	2,02E-01	m^3		5,44E+05	5,00E+01	5,00E+01		
Water, well, in ground[resource_in water]	water	6,11E-03	6,38E-03	m^3		1,10E+06	5,00E+01	5,00E+01		

Chapter 6

Answers to research questions and reflection

6.1 Introduction

Evaluating technologies may pose the biggest challenges to IE and related sustainability sciences. This thesis has developed a hierarchical thermodynamic framework for the environmental sustainability analysis of technologies, from small (titania production) to large (global biofuels). The framework defines techno-systems at four levels, *viz.*, the ecosphere, the anthroposphere, the supply chain, and the foreground system.

This concluding chapter provides an integration of the preceding four chapters, which were written as independent journal papers, into a coherent thesis. First, I will answer the four sets of research questions that were formulated in Chapter 1. Next, I will give my reflection and discussion on the thermodynamic perspective. Finally, I will discuss the further development of thermodynamic analysis for sustainability.

6.2 Answers to research questions

The objective of this thesis is to offer insights into the potential offered by thermodynamics in the environmental sustainability analysis of technologies in the Anthropocene. To this end, four main sets of research questions have been raised, with answers as below:

Q1. What is the relevance of thermodynamics for environmental sustainability analysis of technologies? Can we link the key laws of thermodynamics to the development and use of technologies?

Answer: The environmental dimension of the sustainability of technologies is manifested in physical exchanges between technologies and between a techno-system and the ecosphere. These physical exchanges are expressed as energy flows and conversions from a thermodynamic perspective as demonstrated in the thermodynamic framework for sustainability analysis (Chapter 2). The thermodynamic framework models the physical reality of the ecosphere as the sum of techno-systems and the natural environment. A techno-system converts material and energy resources into products and services, which can be at the level of the foreground system or the supply chain of the techno-system, the anthroposphere, or the ecosphere. Its environment is the rest of the universe which is not thermodynamically affected by the techno-system. The thermodynamic structure of the techno-system is a conversion of inflows of high entropy raw materials and low entropy energy carriers into outflows of low entropy products and high entropy waste. The depletion of materials and energy resources and the generation of wastes and pollutants, as two major problems of technologies from the point of view of environmental sustainability, are explicitly represented in the model developed in this thesis, though the harmful nature of pollutants, like their toxicity, is not covered. This model converts the description of technologies into indicators representing their environmental sustainability in terms of (thermodynamics-based) resource consumption (Chapters 3, 4, and 5), resource renewability (Chapter 3), physical profit (Chapter 3), system efficiency (Chapter 3), and heat emission (Chapter 4). All the preceding chapters have shown that taking account of thermodynamics is a necessity when analyzing environmental sustainability of technologies. Without it, major options and constraints in technology development cannot be specified and specific techno-systems cannot be judged in this perspective.

Q2. What are the major thermodynamic metrics and methods that can be used for environmental sustainability analysis of technologies? Can we find a practical way to link the basic concepts of energy transformations within the boundaries of the first and second laws of thermodynamics?

Answer: Energy and exergy are shown to be the major thermodynamic metrics for environmental sustainability analysis of technologies (Chapters 2 and 3). Emergy, on the basis of energy definition, is another major thermodynamic metric (Chapter 3). Although being also one such metric, entropy is left out of consideration in this thesis because entropy is energy per kelvin and temperature is not relevant as such in this thesis. Energy analysis, exergy analysis, emergy analysis as well as entropy analysis are common methods for the environmental sustainability analysis of technologies. The role and applications of these major thermodynamic metrics and methods are reviewed in a sustainability analysis of broader human-environment systems which includes technologies (broadly defined) and their functioning to show how these metrics can be used in a practical manner. The quantitative relationship between the thermodynamic metrics is not self-evident so a quantified specification of the metrics based on a clear mathematical and conceptual formulation, as for example regarding boundary flows and stock changes, should clarify the relationship (Chapter 2). These thermodynamic metrics provide a basis to convert inflows of material and energy resources for a technology, *e.g.*, the bioethanol produced from corn stover in the U.S. (Chapter 2) into environmental sustainability indicators.

Q3. How can thermodynamics be integrated with LCA and MFA to achieve a better understanding of technologies at different system levels? Can we link the thermodynamic analysis to functional systems and to the main material flows in the anthroposphere?

Answer: Our research confirmed that combining thermodynamic analysis with the main modeling approaches in IE – LCA, MFA as well as environmentally extended IOA – is both feasible and useful. (Chapter 2). There are three ways to integrate thermodynamics with LCA as reviewed, *viz.*, employing thermodynamic metrics in life cycle impact assessment of resource depletion, using thermodynamic metrics to approximate environmental impact, and incorporating thermodynamic analysis into life cycle thinking for multi-criteria studies. Material and energy flow analysis is presented as the most common framework to integrate thermodynamics with MFA. Thermodynamics can also be integrated with MFA in other, more *ad hoc* ways, such as in the investigation of the natural resource demand of global biofuels (see *e.g.*, Chapter 4). Exergy is used as a measure of resources. Various estimations of primary exergy sources to the ecosphere, *i.e.*, solar radiation, moon gravity, and geothermal heat, are summarized. The global anthropogenic exergy demand is estimated by linking energy flows from the ecosphere to the anthroposphere with their exergy-to-energy ratio. Natural resource demand of different first generation liquid biofuels (biodiesel and bioethanol) is determined using cumulative exergy demand. Flows of heat emitted to the ecosphere by the supply chain and the foreground production of global biofuels as well as by the anthroposphere are also determined. Employing thermodynamic metrics in life cycle impact assessment of resource depletion has been illustrated as a way to integrate thermodynamics and LCA (Chapter 5). The pros and cons of seven life cycle impact assessment indicators are investigated by comparing four recently implemented thermodynamic resource indicators with three non-thermodynamic resource indicators and testing their feasibility in the case of titania produced in China.

Q4. How can we apply thermodynamic analysis integrated with LCA and MFA to support decision-making on environmental sustainability? To what extent does the thermodynamic analysis overlap with the sustainability concepts covered in the impact categories of LCA, or is it an add-on, or can it help classify diverging mechanisms? Can we get to grips more effectively with the resource issues currently on the agenda?

Answer: There are three ways in which thermodynamic analysis enriches the analysis based on LCA and MFA. The first is by referring to the performance of a specific technology in terms of certain environmental concerns, *e.g.*, natural resource depletion and climate change (Chapter 4). The problem of natural resource depletion is commonly reflected in thermodynamic analysis, LCA, and MFA, for instance, via cumulative exergy extraction from the natural environment, abiotic resource depletion, and material input per service unit, respectively. Among these three indicators, cumulative exergy extraction from the natural environment as the thermodynamic one has the highest completeness of resource scope. Thermodynamic analysis reflects heat emission of technologies as one mechanism of climate change. This supplements global warming through the emission of greenhouse gases as another mechanism covered by LCA. The second is by assessing the sustainability of a specific technology against some indicators, *e.g.*, resource renewability and system efficiency. For instance, the lower cumulative degree of thermodynamic perfection of bioethanol compared to that of diesel indicates that bioethanol technology is less efficient in delivering energy/exergy than conventional energy technology (Chapter 3). These indicators are not an explicit part of the standard impact categories of LCA. The third is by comparing technology alternatives, such as the chloride route and the sulfate route, for titania production (Chapter 5). The comparison is based on the developed framework, where thermodynamic indicators represent resource properties and other non-thermodynamic indicators characterize resource scarcity.

6.3 Reflection and discussion

6.3.1 The thermodynamic perspective: evaluation of environmental sustainability problems

The thermodynamic perspective effectively addresses the environmental problem of the depletion of materials and energy resources, while providing limited added value in terms of evaluating that of the generation of wastes and pollutants. The potential to cause instability to the ecosphere due to the generation of wastes and pollutants can be quantified based on their exergy value or the abatement exergy loss but the impact of environmental pollutants on human and ecological health, *e.g.*, toxicity, cannot be measured based on exergy or other thermodynamic metrics. Environmental sustainability in this aspect is to be assessed more effectively using other tools such as specific LCA impact categories, or substance oriented risk assessment.

6.3.2 The thermodynamic framework: resolution of environmental sustainability analysis

The spatial and temporal resolution in the hierarchical thermodynamic framework developed and applied in this thesis can be further refined to improve its relevance in supporting decision-making on environmental sustainability. Environmental sustainability is a concern about what ought to be, or ought to be avoided, in the future. Making a decision on environmental sustainability needs knowledge about not only the present situation but also what would be possible situations in the future. Be it predictions, projections, or descriptive scenarios, the most relevant analysis includes, among others, time series and description of the evolution of technologies while the thermodynamic framework applied as such mainly includes snapshot-type of analysis, which is determined by thermodynamics primarily as an equilibrium science *per se*. In addition, the spatial differentiation of technologies, as an important factor to improve the precision of the results, should be considered when scaling up a specific local technology. For instance, the electricity input to the titania production in China is not the same as that to the global situation (Chapter 5). The solar radiation to the corn production and the corn grain yield in the State of Iowa in the U.S. are different from that in the Province of Ontario in Canada (Chapter 4).

6.3.3 The thermodynamic mechanism: one aspect of technology complexity

The developed model accurately represents the thermodynamic mechanism of technologies, while further case studies, including dynamic ones, may reflect the complexity of technology to a wider extend as well as in greater depth. Techno-systems as well as the ecosphere are complex adaptive systems. This thesis applies thermodynamic analysis mainly as static linear models and the causality of the interactions between techno-systems is pre-assumed typically by fixing transformation ratios to represent the system behavior, as usual in LCA, MFA as well as environmental extended IOA. This makes it quite challenging to link a specific technology as a full system into higher-level systems analysis, be it in the context of environmental sustainability analysis or others, since causality is ossified and the dynamics caused by other non-thermodynamic constraints and real-life feedbacks are left out of consideration. Examples include the limits to land availability and other feed back mechanisms in the biofuel case studies. In addition, how the anthroposphere as the sum of techno-systems evolves from one regime to another is not easy to explain by only applying the thermodynamic mechanism. Thermodynamics sets constraints on options, and can indicate the relative performance of techno-systems but does not specify the dynamic drivers. These are mainly social in nature, covering cultural, institutional, political, and economic mechanisms.

6.3.4 The dimensions of thermodynamic analysis: metric and level

The developed model provides a framework which is able to incorporate major thermodynamic metrics and relationships. As thermodynamic models should reflect physical reality as accurately as possible, the quantitative relationship between energy and the other metrics should be clarified when these metrics are to be used together. This relies on semantical and mathematical definitions of theses metrics, which will help define the two dimensional (scale level and metric) linear sequence of various types of thermodynamic analysis within the framework as illustrated in Chapter 3. The metric dimension in principle can distinguish energy, entropy, and exergy. The entropy dimension and the application of exergy at the level of the ecosphere may be examined in future research. While emergy has been shown to be based on energy, the system boundary and the time frame difference between these two concepts should be formulated quantitatively. For instance, some gas deposits may have formed already hundreds of billions years ago, partly based on solar radiation and partly of geothermal heat from the condensation of the earth and from nuclear reactions. This does not help much in the sustainability analysis for our future generations.

6.4 Further development of thermodynamic analysis for sustainability

Based on the work conducted in this thesis, some interesting research lines to explore further can be identified.

1) Thermodynamic analysis should be developed further so as to better inform sustainability decision-making. Changed technologies, and their market volumes, are considered as solutions for un-sustainability and are supposed to limit the level of influence of the Anthropocene. However their implementation will have both positive and negative environmental, economic, and social impacts. Economic and social aspects of sustainability have not been treated in this thesis. They may be analyzed according to a set of coherent rules in terms of system boundaries, data quality, *etc.* and

analytical methods at all levels discerned. An IE-type of approach is a necessity since problem-shift should be avoided when making system-level decisions.

2) The developed thermodynamic framework should be extended to answer questions that go beyond the scope of sound stewardship of natural resources. For instance, is large-scale implementation of emerging energy technologies limiting or enlarging the level of influence of the Anthropocene? Thermodynamic measures may give one answer. How can we better embed these outcomes in the sustainability discussion, with broader applicability to different technologies? We may then consider further energy technologies besides biofuels, *e.g.*, solar photovoltaics, solar thermal, geothermal, wind, hydro, wave, tidal, and nuclear fusion and fission. Climate mechanisms such as greenhouse gas emissions, heat emission, albedo change, land use change, *etc.*, should be covered together for a full analysis of the impact on the climate system. In addition, system analysis approaches at a higher level than IE, *e.g.*, earth system analysis, might be introduced to give reference climate threshold more directly since climate modeling is better covered there.

3) The case studies should be strengthened to enable better results of environmental sustainability analysis. On the one hand the thermodynamic model of a case technology should be as specific as possible. For instance, in the case of bioethanol, individual plants in the State of Iowa use co-produced electricity as process energy rather than purchasing from the national grid. This should be reflected in the model. On the other hand more data should become available. Examples of the missing data, as shown in the case of global biofuels and titania, include the global metal and mineral exergy resources consumption and the total anthropogenic demand of non-renewable resources in the indicator of solar energy demand. In the practice of thermodynamic analysis, modeling specification and data comprehensiveness is interrelated and balanced via making assumptions. For instance, the case study of bioethanol has been done by assuming that fossil fuel inputs to the transportation in the U.S. are not considered, although this assumption may have little effect in the global model. The uncertainty due to modeling assumptions should be analyzed better.

These three items seem most worthwhile directions for the further development of thermodynamic analysis of sustainability.

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SUMMARY

Introduction

Since the onset of the Industrial Revolution around 1800, humans have substantially influenced the ecosphere, to a degree that is comparable to that associated with major changes in the geological past. It is clear that we may view the current era as being sufficiently different from other parts of the Holocene to refer to it as the Anthropocene. In the 'Anthropocene', humans have been pursuing economic growth and creating wealth in an unsustainable way. Transforming such unsustainable economies requires changes to technologies which are related to various physical and social aspects of sustainable development, including natural resources of energy and materials and which are subject to the most complex forms of thermodynamic analysis. The energy basis of the Industrial Revolution already indicates that thermodynamics can offer an important – though not the only possible – perspective on technologies. The anthroposphere, which comprises the entire range of technologies, is the interface between physical and symbolic realities in the conceptual modeling of Industrial Ecology (IE) and is thus the focus of IE. As such, technologies and sustainable development are interrelated from a thermodynamic perspective, with IE as a major point of access for studying the relationship.

Research questions

Against the background of increasing sustainability problems in the Anthropocene, this thesis aims to offer insights into the potential offered by thermodynamics in the environmental sustainability analysis of technologies. Four main sets of research questions have been formulated in this thesis:

- Question set 1. What is the relevance of thermodynamics for environmental sustainability analysis of technologies? Can we link the key laws of thermodynamics to the development and use of technologies?
- Question set 2. What are the major thermodynamic metrics and methods that can be used for environmental sustainability analysis of technologies? Can we find a practical way to link the basic concepts of energy transformations within the boundaries of the first and second laws of thermodynamics?
- Question set 3. How can thermodynamics be integrated with life cycle assessment (LCA) and material flow analysis (MFA) to achieve a better understanding of technologies at different system levels? Can we link the thermodynamic analysis to functional systems and to the main material flows in the anthroposphere?
- Question set 4. How can we apply thermodynamic analysis integrated with LCA and MFA to support decision-making on environmental sustainability? To what extent does the thermodynamic analysis overlap with the sustainability concepts covered in the impact categories of LCA, or is it an add-on, or can it help classify diverging mechanisms? Can we get to grips more effectively with the resource issues currently on the agenda?

Materials and methods

Focusing on product technology, the studies reported in this thesis have developed a hierarchical thermodynamic framework for environmental sustainability analysis of technologies. The framework defines techno-systems at four levels, *viz.* the ecosphere, the anthroposphere, and individual technologies, the latter being further subdivided into a foreground system and a supply chain. The methodological

framework is elaborated in a literature review of thermodynamic analysis for human–environment systems (Chapter 2) and applied to three case studies on specific technologies (bioethanol, global biofuels, and titania in Chapters 3 to 5).

- The literature review (Chapter 2) focuses on the role and applications of thermodynamic analysis in IE as well as its related processes in human-–environment systems, in order to identify the limitations and challenges of thermodynamic analysis in current IE research.
- The bioethanol case study (Chapter 3) presents an environmental sustainability assessment of bioethanol produced from corn stover in the U.S. against four thermodynamics-based indicators, *viz.* resource consumption, resource renewability, physical profit, and system efficiency, by applying energy analysis, exergy analysis, and emergy analysis.
- The global biofuel case study (Chapter 4) illustrates how the natural resource demand as well as the climate impact of the heat emissions that arise when biofuel technology is implemented at a global level can be analyzed to assess its environmental sustainability by integrating thermodynamics and MFA.
- The titania case study (Chapter 5) demonstrates the feasibility of thermodynamic resource indicators in LCA, *viz.* cumulative energy demand, solar energy demand, cumulative exergy demand, and cumulative exergy extraction from the natural environment, by testing them for the case of titania produced in China, and comparing them with some scarcity-oriented resource indicators.

Answers to research questions

The thesis provides answers to the research questions by presenting the present state of development of thermodynamics, and applying available approaches to the case studies:

Answer to Question set 1: The depletion of materials and energy resources and the generation of wastes and pollutants, as two major problems of technologies from the point of view of environmental sustainability, are explicitly represented in the thermodynamic model developed in this thesis. This model converts the description of technologies into indicators representing their environmental sustainability in terms of (thermodynamics-based) resource consumption, resource renewability, physical profit, system efficiency, and heat emission. This thesis has shown that taking account of thermodynamics is a necessity when analyzing the environmental sustainability of technologies. Without this analysis, thermodynamic options and constraints cannot be specified and specific technology systems cannot be judged in this perspective.

Answer to Question set 2: Energy, exergy, and emergy have been shown to be the major thermodynamic metrics for environmental sustainability analysis of technologies. These thermodynamic metrics provide a basis to convert inflows of material and energy resources for a technology into environmental sustainability indicators. Energy analysis, exergy analysis, emergy analysis as well as entropy analysis are common methods for environmental sustainability analysis of technologies. The role and applications of these major thermodynamic metrics and methods are reviewed in a sustainability analysis of broader human–environment systems to show how these metrics and methods can be used in a practical manner.

Answer to Question set 3: Our research confirmed that combining thermodynamic analysis with the main modeling approaches in IE – LCA, MFA as well as environmentally extended input-output analysis – is both feasible and useful. There are three ways to integrate thermodynamics with LCA, *viz.* employing thermodynamic metrics in life cycle impact assessment of resource depletion, using thermodynamic metrics to approximate environmental impact, and incorporating thermodynamic analysis into life cycle thinking for multi-criteria studies. Material and energy flow analysis is presented as the most common framework to integrate thermodynamics with MFA, but thermodynamics can also be integrated with MFA in other, more *ad hoc* ways (see *e.g.* Chapter 4).

Answer to Question set 4: There are three ways in which thermodynamic analysis enriches the analysis based on LCA and MFA. The first is by referring to the performance of a specific technology in terms of certain environmental concerns, *e.g.*, natural resource depletion and climate change. The second is by assessing the sustainability of a specific technology against some indicators, *e.g.*, resource renewability and system efficiency. The third is by comparing technology alternatives, such as the chloride route and the sulphate route, for titania production.

Reflection and discussion

- The thermodynamic perspective effectively addresses the environmental problem of the depletion of materials and energy resources, while providing limited added value in terms of evaluating that of the generation of wastes and pollutants.
- The spatial and temporal resolution in the thermodynamic framework can be further refined to improve its relevance in supporting decision-making on environmental sustainability.
- The thermodynamic framework accurately represents the thermodynamic mechanism of technologies, while further case studies, including dynamic ones, may reflect the complexity of technology to a wider extent as well as in greater depth.
- The thermodynamic framework is able to incorporate major thermodynamic metrics and relationships. The quantitative relationship between energy and the other metrics should be clarified when these metrics are to be used together.

Recommendations for further development

- Thermodynamic analysis should be developed further so as to better inform sustainability decision-making.
- The thermodynamic framework should be extended to answer questions that go beyond the scope of sound stewardship of natural resources.
- The case studies should be strengthened to enable better results of environmental sustainability analysis.

SAMENVATTING

Introductie

Sinds het begin van de Industriële Revolutie rond 1800, heeft de mens heeft de mens de ecosfeer substantieel beïnvloed, in een mate die vergelijkbaar is met grote veranderingen in het geologisch verleden. Het is duidelijk dat het huidige tijdperk verschilt van andere delen van het Holoceen en aangeduid kan worden als het Anthropoceen. In het Anthropoceen streven mensen naar economische groei en creëren rijkdom op een niet-duurzame wijze. Het transformeren van niet-duurzame economieën vereist andere technologieën. Technologieën zijn gerelateerd aan verschillende fysieke en sociale aspecten van duurzame ontwikkeling, met inbegrip van natuurlijke hulpbronnen van energie en materialen, en kunnen bestudeerd worden met de meest complexe vormen van thermodynamische analyse. De energetische basis van de Industriële Revolutie geeft al aan dat thermodynamica een belangrijk maar niet exclusief perspectief kan bieden op technologieën. De antroposfeer, die het totaal van alle technologieën omvat, vormt de interface tussen de fysieke en de symbolische werkelijkheid bij de conceptuele modellering van Industriele Ecologie (IE) en vormt daarom de focus van IE. In die zin zijn technologieën en duurzame ontwikkeling met elkaar verbonden vanuit een thermodynamisch oogpunt, met IE als een van de belangrijkste ingangen voor het bestuderen van die relatie.

Onderzoeksvragen

Tegen de achtergrond van de toenemende problemen met duurzaamheid in het Anthropoceen, heeft dit proefschrift tot doel inzicht te verschaffen in de potentie van de thermodynamica bij de analyse van de duurzaamheid van technologieen uit milieuoogpunt. Vier centrale groepen van onderzoeksvragen zijn in dit proefschrift geformuleerd:

- Q1: Wat is de relevantie van de thermodynamica voor de duurzaamheidsanalyse van technologieën uit milieuoogpunt? Kunnen we de hoofdwetten van de thermodynamica koppelen aan de sturing van ontwikkeling en gebruik van technologieën?
- Q2. Wat zijn de belangrijkste thermodynamische kentallen en methoden die gebruikt kunnen worden voor de duurzaamheidsanalyse van technologieën? Hoe kunnen we de basisbegrippen van de energie-transformaties op een praktische manier formuleren binnen de begrenzingen van de eerste en tweede hoofdwet van de thermodynamica?
- Q3. Hoe kan de thermodynamica worden geïntegreerd met levenscyclusanalyse (LCA) en materiaalstroomanalyse (MFA) om technologieën op verschillende systeemniveaus beter te kunnen begrijpen? Kunnen we de thermodynamische analyse koppelen aan functiesystemen en aan de belangrijkste materiaalstromen in de antroposfeer?
- Q4. Hoe kan de thermodynamische analyse - geïntegreerd met LCA en MFA -toegepast worden voor de ondersteuning van een op duurzaamheid gerichte besluitvorming? In hoeverre overlapt de thermodynamische analyse met duurzaamheidsconcepten in de effectcategorieën van de LCA, of is die analyse additioneel, of kan zij helpen bij het ordenen van verschillende mechanismen? Kunnen we een betere grip krijgen op het onderwerp van natuurlijke hulpbronnen, inclusief grondstoffen?

Materialen en methoden

Gericht op product-technologieën, is in dit proefschrift een thermodynamisch hierarchisch kader ontwikkeld voor duurzaamheidsanalyse van technologieën op milieugebied. Het kader definieert technosystemen op vier niveaus, te weten de ecosfeer, de antroposfeer, en een individuele technologie, die verder wordt opgesplitst in de voorgrondtechnologie en de supply chain. Het methodologisch kader wordt uitgewerkt in een literatuurstudie van thermodynamische analyse voor mens-milieu systemen (hoofdstuk 2) en vervolgens toegepast op drie case studies van technologieën (bio-ethanol, mondiale biobrandstoffen, en titanium, in de hoofdstukken 3 tot 5)

- Het literatuuronderzoek (hoofdstuk 2) richt zich op de rol en toepassingen van thermodynamische analyse in IE en de bijbehorende processen in mens-milieu-systemen, om de beperkingen en uitdagingen van de thermodynamische analyse in het huidige IE onderzoek te lokaliseren.
- De bio-ethanol case studie (hoofdstuk 3) presenteert een milieu-beoordeling van de duurzaamheid van bio-ethanol geproduceerd uit maïsstro in de VS op basis van vier thermodynamisch gebaseerde indicatoren, te weten grondstofgebruik, grondstofvernieuwbaarheid, fysieke winst, en systeemefficiëntie door toepassing van energie-analyse, exergie-analyse en emergie-analyse.
- De case study naar mondiale biobrandstoffen (hoofdstuk 4) laat zien hoe de vraag naar natuurlijke hulpbronnen en klimaateffecten door warmte-emissies van biobrandstof-technologie geanalyseerd kan worden voor een duurzaamheidsbeoordeling, door de integratie van thermodynamica en MFA.
- De titaniumanalyse (hoofdstuk 5) toont de toepasbaarheid van thermodynamische indicatoren in LCA, te weten de cumulatieve energievraag; de zonne-energie vraag; de cumulatieve exergievraag, en cumulatieve exergieextractie uit de natuurlijke omgeving, door ze toe te passen op de productie van titaanoxide in China, met vervolgens een vergelijking met een aantal schaarste-gerichte grondstofindicatoren.

Antwoorden op onderzoeksvragen

Met de presentatie van de state-of-the-art thermodynamische begrippen en door de toepassing van de huidige benaderingen in de case studies, beantwoordt het proefschrift de onderzoeksvragen:

Antwoord op Q1: De uitputting van grondstoffen en energiedragers en het genereren van afval en verontreinigende stoffen, als twee grote problemen van de technologieen in de duurzaamheidsanalyse, worden expliciet weergegeven in het thermodynamisch model zoals ontwikkeld in dit proefschrift. Dit thermodynamisch model levert de beschrijving van technologieën in termen van indicatoren die (thermodynamica-gebaseerd) hun milieuduurzaamheid aangeven in termen van verbruik van natuurlijke hulpbronnen, vernieuwbaarheid van grondstoffen, fysieke winst, energetisch rendement van het systeem, en warmteafgifte. Dit proefschrift heeft aangetoond dat het noodzakelijk is om milieuduurzaamheid van technologieën te analyseren met behulp van de thermodynamica. Zonder deze analyse kunnen thermodynamische opties en beperkingen niet goed worden gespecificeerd en kunnen specifieke technologiesystemen kunnen niet vanuit dit perspectief worden beoordeeld.

Antwoord op Q2: Energie, exergie, evenals emergie vormen de belangrijkste thermodynamische kentallen bij de een duurzaamheidsanalyse van technologieen. Deze thermodynamische kentallen vormen een basis voor de omzetting van de instroom van materiaal en energiedragers van een technologie in duurzaamheidsindicatoren. Energieanalyse, exergieanalyse, emergieanalyse en entropieanalyse vormen tezamen de basis voor deze duurzaamheidsanalyse van technologieën. De rol en toepassingen van deze centrale thermodynamische kentallen en methoden zijn bezien in de duurzaamheidsanalyse van bredere mens-milieu-systemen, om te tonen hoe deze metrieken en methoden op een praktische manier zijn te gebruiken.

Antwoord op Q3: Het blijkt dat de combinatie van thermodynamische analyse met de belangrijkste modelmatige benaderingen in IE - LCA en MFA, en ook de input-output analyse met milieuextensies –

zowel mogelijk als nuttig is. Er zijn drie manieren om thermodynamica te integreren met LCA, door het gebruik va de thermodynamische kentallen in de LCA-effectbeoordeling van grondstoffenuitputting; door ze te gebruiken als benadering voor andere milieueffecten; en door de integratie van thermodynamische analyse in het levenscyclusdenken bij multi-criteria studies. Materiaal- en energiestroomanalyse vormt het meest overeenkomende kader voor de integratie van thermodynamica met MFA. Thermodynamica kan tevens met MFA worden geïntegreerd op een meer *ad hoc* wijze (zoals in hoofdstuk 4).

Antwoord op Q4: Er zijn drie manieren waarop de thermodynamische analyse de analyse met LCA en MFA verrijkt. De eerste is door aan te geven hoe een specifieke technologie functioneert met betrekking tot bepaalde milieuproblemen, zoals grondstoffenuitputting en klimaatverandering. De tweede is de beoordeling van de duurzaamheid van een specifieke technologie in relatie tot een aantal indicatoren, zoals hernieuwbaarheid van grondstoffeng en efficiëntie van het systeem. De derde vergelijkt alternatieve technologieën, zoals de chlorideroute en sulfaatroute voor de productie van titaandioxide.

Reflectie en discussie

- Het thermodynamische perspectief heeft betrekking op het milieuprobleem van de uitputting van grondstoffen en heeft slechts een beperkte toegevoegde waarde bij de evaluatie van de generatie van afval en verontreinigende stoffen.
- De detaillering en het schaalniveau in ruimte en tijd in het thermodynamische kader zoals ontwikkeld en toegepast in dit proefschrift kan verder verfijnd worden om de relevantie bij de ondersteuning van duurzaamheidsbesluitvorming verder te verbeteren.
- Het thermodynamisch kader kan ook de thermodynamische mechanismen van technologieën goed weergeven, terwijl meer case studies, ook dynamische, de complexiteit van technologieën beter weer zullen kunnen geven in breedte en diepte.
- Het thermodynamische kader omvat de belangrijkste thermodynamische kentallen en relaties. De kwantitatieve relatie tussen energie en de andere kentallen moet worden verduidelijkt wanneer deze kentallen samen worden gebruikt.

Aanbevelingen voor verdere ontwikkeling

- Ontwikkel de thermodynamische analyse verder om duurzaamheidsbesluitvorming beter te informeren;
- Breid het thermodynamisch kader verder uit om ook vragen te kunnen beantwoorden die verder gaan dan rentmeesterschap over natuurlijke hulpbronnen;
- Versterk case studies voor betere resultaten bij duurzaamheidsanalyse.

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