Chapter 10: Exergy and cumulative exergy use analysis

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Abstract

Exergy is a thermodynamic metric that represents the amount of useful energy one can obtain out of an object in a given reference environment. The exergy concept is used in several applications: from the analysis of industrial processes to economic, sustainability and ecosystem analysis. In this chapter, the focus is on cumulative exergy consumption (CExC) methods used in sustainability assessment. Since these methods account consistently for the total resource intake, they are often used as measure for environmental impacts, mainly of resource consumption.

10.1. What is exergy

To be able to define and evaluate sustainability goals, there is a need for sustainability metrics. These metrics are traditionally called indicators, with exergy being one of them. Exergy relates to the second law of thermodynamics. While the first law of thermodynamics states that mass and energy cannot be created or disappear, the second law states that all spontaneous processes create entropy. Entropy is commonly understood as a measure of disorder, indicating a quality loss of the input energy. Due to entropy generation, the energy that can be made available from the outputs is less than the energy that can be made available from the inputs, although the total energy of the outputs equals the total energy of the inputs. This quality degradation is quantifiable by the loss of exergy, as illustrated in Figure 10.1 [1][2].

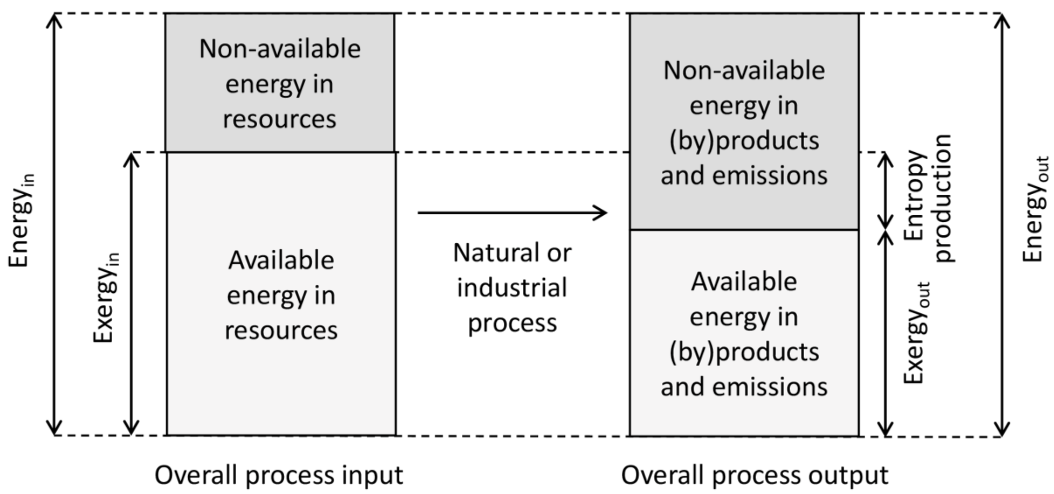

Figure 10.1: Analysis of a process based on the two laws of thermodynamics. The first law states that all energy going into the process is equal to the energy leaving the process. The second law states that the available energy or exergy embodied in products, by-products and emissions is lower than the exergy entering the system, because of exergy loss, i.e. entropy production. Source: Reprinted with permission from Renewables-based Technology, 2006, Dewulf et al., Copyright 2006, Wiley

As a counterpart to entropy, the concept of exergy was introduced by Gibbs in 1873: the case of available energy. Several years later, in 1953, the Slovenian Zoran Rant suggested the term "exergy" to indicate this available energy. The Greek prefix 'ex' refers to external work, while the prefix 'en' in energy refers to internal work. In 1988, Szargut introduced a modern definition of exergy, which is still applicable today: "Exergy is the amount of work obtainable when a system is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interaction only with the above mentioned components of nature" [3][4]. An important aspect stated in previous definition is that exergy is a metric dependent on the reference environment, i.e. the natural surroundings. When the system and the surroundings reach equilibrium, zero exergy is obtained. The link with entropy is the following: the absolute value of exergy loss due to irreversible processes is equal to the entropy production multiplied with the temperature of the surroundings [2].

10.2. Calculation of exergy

The exergy of a system can be split up into different aspects, the most important ones being: the potential exergy due to its position in a given body force field, the kinetic exergy related to its velocity with respect to a fixed reference frame, the physical exergy specified by its pressure and temperature being different from the surroundings, and the chemical exergy linked with its composition being different from the surroundings. Other possible forms of exergy are electric exergy, nuclear exergy and radiation exergy. Prior to calculation of exergy, the natural surrounding needs to be defined by its characteristics and composition, as done by Szargut [2][4].

Physical exergy can be calculated from the specific physical enthalpy h and the specific physical entropy of the systems s, at the initial state temperature T_i and pressure P_i and at reference state temperature T_0 and pressure P_0 of the environment respectively, see equation (10.1).

$$Ex_{ph} = (h_i - h_0) - T_0(s_i - s_0) \tag{10.1}$$

Kinetic exergy, potential exergy, electrical exergy and nuclear exergy have the same value as the corresponding energy terms. For radiation exergy, the exergy-to-energy ratio β is given in equation (10.2), with T the actual temperature and T_0 the environmental temperature. In case of solar irradiation, the actual temperature T is the temperature of the sun, resulting in an exergy-to-energy ratio of 0,9327 [2][5].

$$\beta = 1 + \frac{1}{3}\left(\frac{T_0}{T}\right)^4 - \frac{4}{3}\left(\frac{T_0}{T}\right) \tag{10.2}$$

The calculation of chemical exergy is more complex. For each chemical element in the resource material, one predefines a reference compound in the natural environment, e.g. SiO_2 for Si and O_2 for O. These reference compounds are the most probable products of the interaction of the elements with other common compounds in the natural environment and show typically high chemical stability. The exergy value of the reference compounds is governed by geochemical data: its relative occurrence in the natural environment; this exergy value is the available energy which can be obtained when bringing the reference compound to its reference concentration. Exergy values for reference compounds at standard conditions, e.g. 1 mol per litre for aqueous compounds or 1 atmosphere for gases, are tabulated in the work of Szargut. The exergy of non-reference substances can be calculated as the sum of the standard Gibbs free energy ΔG_r^0 of the reaction needed to convert this substance to reference compounds at standard conditions, and the chemical exergy of these reference compounds (Ex_{ch}^0). This is shown in equation (10.3), with v_k the number of moles of the kth reference compound. Suffix ^{0} denotes that the reference system is assumed to be at standard environmental temperature T_0 (usually 298.15K) and pressure (usually 1 atmosphere) [6].

$$Ex_{ch} = \Delta G_r^0 + \sum_k v_k Ex_{ch,k}^0 \tag{10.3}$$

For the chemical exergy of a system, which is a collection of compounds, the mixing exergy needs to be added. This mixing exergy term is shown in equation (10.4), with R the universal gas constant, x_i the mole fraction of species in the mixture, T_0 the standard environmental temperature and γ_i the activity coefficient. Values for activity coefficients can be found in literature. They may be greater or smaller than unity for real solutions, and are unity for ideal solutions [5].

$$Ex_{mix} = RT_0 \ln(\gamma_i x_i) \tag{10.4}$$

Additionally for organic compounds, the chemical exergy can be calculated through different techniques: the group contribution method, the exergy-to-energy ratio (β) method and the macronutrient method. In the first method, the molecular structure is subdivided in several functional groups (e.g. -COOH, $-CH_2-$,…) for which exergy values are predefined, all contributing to the total exergy. This method can be used when chemical compounds have been specified and their relative percentages are available. In the second method, β-values are used to link energy streams with their exergy content, mostly used for solid or liquid organic fuels, e.g. wood. The β-value is obtained out of the elementary contents of carbon, oxygen, hydrogen and nitrogen. The lower heating value is used as an energy value. This method can only be used if these data are available. If the necessary data for both methods is available, De Vries [7] says it is preferable to consider the more accurate group contribution method over the β-method. In the macronutrient method, the composition in terms of carbohydrates, proteins, lipids, ash and water is identified [8]. For each of these macronutrients an exergy value is calculated, e.g. for proteins based on their respective average amino acid composition, and then based on the shares of macronutrient fractions, a total exergy value is calculated. This method is evidently only applied for biomass streams.

Bendoricchio and Jorgensen [9] introduced an additional aspect to the exergy value of biotic organisms, namely the exergy content addressed by the genetic information stored in the organism. The formula for the calculation of exergy of the genetic information is given in equation (10.5), with T_0 the standard environmental temperature, N the number of components in the ecosystem, c_i the concentration of the ith component and P_i the probability to find the genetic code [10][2].

$$Ex_{info} = RT_0 \sum_{i=2}^{N} c_i ln(P_i) \tag{10.5}$$

Component $i = 1$ is detritus (dead organic matter), and components from $i = 2$ are taxa (commonly species). The equation starts from $i = 2$ because detritus has no genetic structures. Bendoricchio and Jorgensen [9] defined the exergy content of living organisms as the sum of this exergy of genetic information and the chemical exergy. Later on, this exergy content was named eco-exergy by Susani [10]. There has been criticism on this approach, because it would strongly overestimates the amount of exergy really stored in information and is not thermodynamically sound.

10.3. Applications of exergy

10.3.1. Use in industrial system analysis

As mentioned in the introduction, the exergy concept found its origin in thermodynamic engineering. Therefore, *industrial systems analysis* has probably been the most common application of exergy. In technical literature, exergy analysis has been extensively used to characterize the thermodynamic efficiency of industrial processes [3]. Exergetic efficiency is here defined as the ratio between the output and input flows, both quantified in exergy, see equation (10.6).

$$\eta = \frac{\sum Ex_{outputs}}{\sum Ex_{inputs}} \tag{10.6}$$

A distinction can be made between the simple efficiency and rational efficiency. Simple efficiency is the ratio of all the outputs (products, heat, waste and exergy loss) over the exergy of the needed inputs, while rational efficiency is the exergy of the desired outputs (products) over the exergy of the needed inputs [5]. The rational efficiency of a process makes it possible to indicate how efficient the inputs are transformed towards products, and not towards waste and lost work (Figure 10.2).

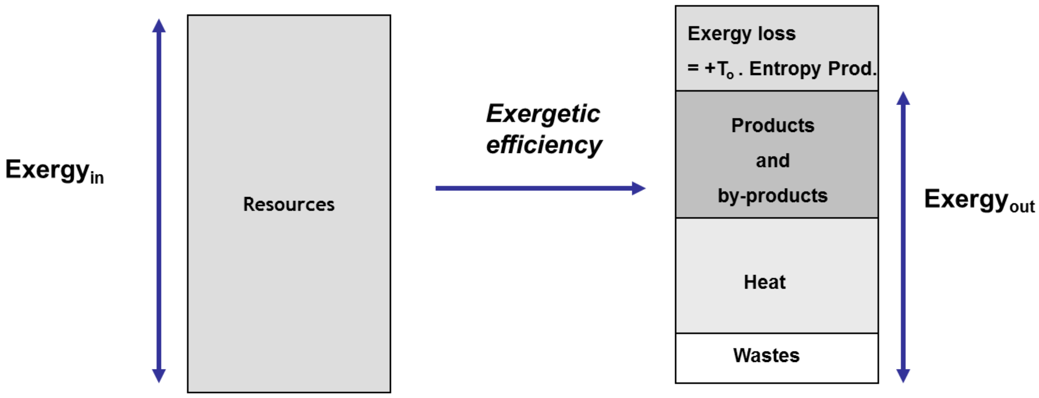

Figure 10.2. Exergetic efficiency of a process or system. Source: Reprinted with permission from Environmental Science & technology, 42, Dewulf et al., 2008, Copyright 2008, American Chemical Society

In literature, exergy analysis has been applied in many case studies, typically situated at process level: e.g. analysis of biomass gasification [11], solar energy technologies [12], coal-based thermal power plants [13], desalination processes [14], combined heat and power plants [15], etc. Exergy analysis allows one to find the particular hotspots in exergy use or loss of the studied process or system. With this knowledge, the system can be improved through better usage of exergy and thus less entropy production.

For example in the study of Huysveld et al. [16], the exergy efficiency of the feed production system for fish farming was investigated. In one step/process of this system, rice husk is burned to cook the feed ingredients. The efficiency of the overall system could be improved by improving latter step, where an exergetically inefficient combustion of 24% occurs. By using a better boiler installation with a cogeneration unit, one could improve the efficiency up to 35%.

Extensions of exergy analysis exist in which the complete supply chain of the considered process is taken into account. These extensions are called 'cumulative exergy consumption (CExC) methods'. CExC is defined as the sum of the exergy contained in all natural resources entering the supply chain of the selected process [4][2]. This approach is closely related to cumulative energy consumption analysis. However, unlike energy, exergy is a non-conserved property, making it possible to evaluate both the quantity and the quality of resources. Efficiency can here be expressed as the ratio of the exergy contained in the final product to the CExC, see equation (10.7).

$$\eta = \frac{\sum Ex_{outputs}}{CExC} \qquad (10.7)$$

10.3.2. Use in sustainability analysis

The concept of CExC has evolved from pure technical analysis to *sustainability assessment* by using the CExC methods as a proxy for the environmental impacts. The exergy concept is not only used to assess the environmental impact of resource intake, which will be discussed in detail in section 10.4, but also to quantify the impact of *emissions*. Because emissions are not in thermodynamic equilibrium with their environment, they have an exergetic value. This can be used to express the emissions' environmental impact. However, the exergy value of emissions is not necessarily linked to the impact on the ecosystem and human health. For example, the exergy contents of benzene and toluene are not very different, but their environmental impacts are obviously different. To quantify the impact of emissions in exergetic terms, different approaches have been developed [17][18]. In the approach of Dewulf and Van Langenhove [19], the exergy loss in nature and in society due to health effects is calculated to measure the effect of emissions.

10.3.3. Use in economic analysis

Exergy has also been linked with economics. The combination of thermodynamics and economics is referred to as "thermoeconomics", a term coined by Tribus and Evans [20]. In its most basic form, thermoeconomics assigns monetary values to exergy streams by writing monetary balances on components or subsystems of a system, making it possible to achieve a better production management [21][2]. The Extended Exergy Accounting (EEA) method of Sciubba [22] does the opposite by giving an exergetic value to the immaterial monetary costs: capital, labour and environmental remediation. The exergy content of a product (Ex) is defined as the sum of the CExC, the capital equivalent exergy (Ex_c), the labour equivalent exergy (Ex_l) and the environmental remediation equivalent exergy (Ex_{env}), as shown in equation (10.8).

$$Ex = CExC + Ex_c + Ex_l + Ex_{env} \quad (10.8)$$

The exergetic value of labour in a society can be computed as the total (yearly averaged) exergetic resource input divided by the number of working hours. Analogously, the exergetic value of the capital of a country can be computed as the total exergetic resource input into that country, divided by the global monetary circulation. The exergetic value of environmental remediation can be calculated as the exergetic cost, e.g. of a wastewater treatment plant, required to convert an emitted pollutant into a set of substances with zero environmental impact [22]. In literature, EEA has been applied to several societies, e.g. Italy [23], Turkey [24] and Norway [25].

10.3.4. Use in natural system analysis

Exergy is also used in the field of system ecology. In ecosystems, an increase in exergy corresponds to an increase in terms of biomass and genetic complexity. As an ecosystem develops, it will capture and storage more exergy. The more exergy captured, the more effective ecosystems dissipate their exergy, i.e. present a larger buffering capacity against destructive exergy flows like radiation, wind, rain etc. For example, forest ecosystem buffer against sunlight and rain with their canopy structure. This has led to two axioms for ecosystem development: maximizing exergy storage and maximizing exergy dissipation [26]. A first set of indicators for measuring the integrity of ecosystem was derived by Odum [27]. Ever since, several ecological indicators have been developed. Bendoricchio and Jørgensen [9] calculated the exergy content of an ecosystem from the exergy stored in its various compounds. To address the genetic complexity and diversity aspect of these biotic compounds or organisms, they introduced the eco-exergy concept (see earlier) [2][26][28].

10.4. Cumulative exergy use analysis

As mentioned in the previous section, cumulative exergy consumption or CExC methods are applied in environmental sustainability analysis as impact methodologies related to resource use. One could address this environmental impact at different steps of the impact pathway. At step 1, the natural resources as such are accounted for, and at further steps, the impact of resource depletion is quantified. Methods at step 1 are also called resource accounting methods (RAM). The philosophy behind the RAM methods is that "the less resources consumed, the better, for the same functional unit". The CExC methods are RAM methods, situated at the first step in the impact pathway [29]. Being based on exergy, they make it possible to account for both the quality and quantity of extracted resources. Indeed, the two aspects underlying all consumptive processes are both quantified: the first aspect simply defines the resource quantity, while the second aspect defines the extent to which resource extraction removes resource quality [30].

In the work of Swart et al. [29], the existing cumulative exergy methods are summarized: the Cumulative Exergy Demand (CExD) [31], the Cumulative Exergy Extraction from the Natural Environment (CEENE) [32], the Industrial Cumulative Exergy Consumption (ICEC) and the Ecological Cumulative Exergy Consumption (ECEC) [33]. These methods have been used in several case studies, e.g. in resource use analysis of bioethanol production [34], production of transportation fuels [35] and production of pharmaceutical ingredients [36].

For example in the study of Huysveld et al. [16], the CEENE method was applied to obtain a complete cradle-to-gate life cycle profile of the resource use required for production of 1 kg Pangasius. The production chain starts at the hatcheries, where juvenile fish are grown. After a certain period, these juveniles are sold to farms where they are fed with feed manufactured at feed mills to grow further until they are harvested. In Figure 10.3, a Sankey diagram of the CEENE values of all the inputs to the foreground system and of the exergy flows within the foreground systems is presented. The thickness of a flow is proportional to its amount of exergy. It can be noticed that the largest CEENE input comes from the feed ingredients (51.5%), in particular from soybean meal, rice bran and wheat grains. The feed supply chain thus plays a key role in the resource footprint of Pangasius farming.

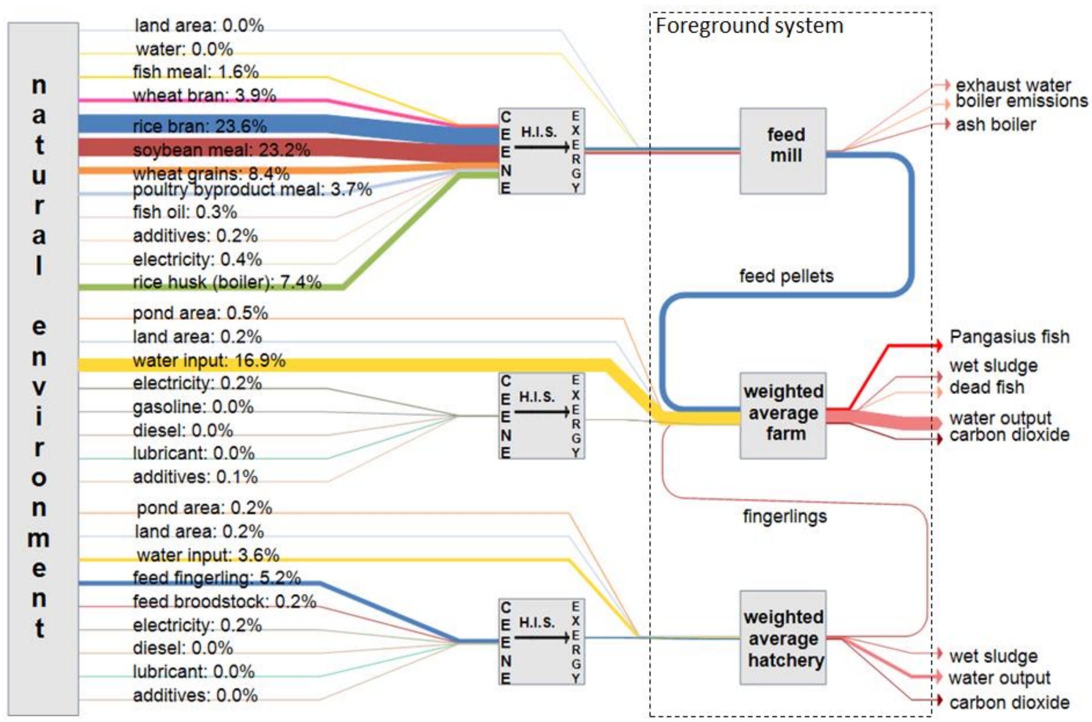

Figure 10.3. Sankey diagram of the weighted average cradle-to-gate life cycle. Thickness of a flow is proportional to its amount of exergy. The total CEENE per kg Pangasius is 305 gigajoules of exergy. H.I.S.= human-industrial system supplying products and services to the foreground system. Source: Reprinted with permission from Journal of Cleaner Production, 51, Huysveld et al. 2013, Copyright 2013, Elsevier

The main difference between the first 3 methods (CExD, CEENE, ICEC) and the last method (ECEC) is their system boundary. This is schematically presented in Figure 10.4. The ECEC method considers its boundary at the planetary ecosystem which supports life in general, called the ecosphere, containing the atmosphere, biosphere, hydrosphere and lithosphere [37]. The main exergy source supporting the ecosphere is solar radiation, together with geothermal heat and tidal energy from moon gravity. The technosphere (also called antroposphere) is the part of the ecosphere that is modified by man for use in human activities. The supply chain of inputs is a subsystem of the technosphere, converting natural resources from the ecosphere into products that are used to deliver services. The system boundary of CExD, ICEC and CEENE is equal to that of the technosphere, i.e. these methods assess the amount of natural resources in exergy withdrawn by the technosphere from the ecosphere. ECEC goes one step further by accounting also for the processes occurring in the ecosphere to produce goods and services [38]. This system boundary is similar to the emergy concept [39], as will be explained further on.

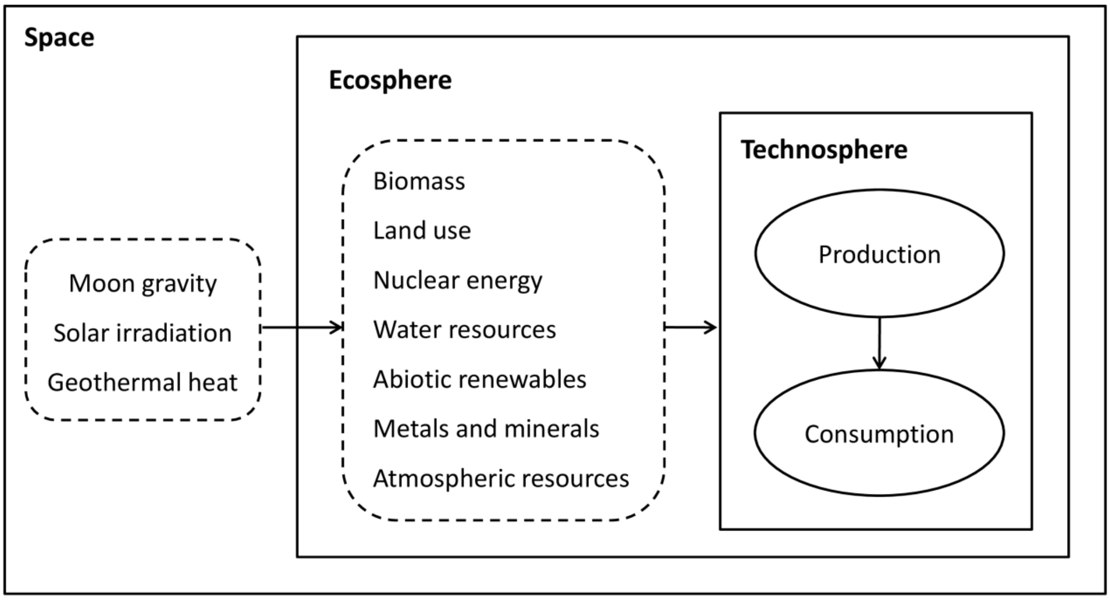

Figure 10.4. Different system boundaries. Direct inputs of solar irradiation, geothermal heat and moon gravity (tidal energy) occur also in the technosphere and are considered part of the group 'abiotic renewables'. Source: Adapted with permission from International Journal of Life Cycle Assessment, 17, Liao et al. 2012, Copyright 2012, Springer

We will priory discuss the methods that have the technosphere as system boundary (CExD, ICEC and CEENE). First, it is important to have a clear definition of what natural resources are. Udo de haes et al. [40] define them as “objects of nature which are extracted by man from nature and taken as useful input to man-controlled processes, mostly economic processes”. Natural resources can be split into different categories. Here, we will refer to the categorization of Dewulf et al. [41]: fossil fuels, minerals, metals, nuclear energy, water resources, land resources, abiotic renewable energy (i.e. wind, hydropower, tidal, wave and geothermal energy) and atmospheric resources. Regarding land resources, there are two ways to account for them: (1) by the amount and type of the biomass harvested; and (2) by the area and time needed to produce the biomass (land occupation). To avoid double counting, one way of accounting has to be chosen [32][42].

In both CExD and ICEC, land resources are accounted for by the exergy content of the harvested biomass. In the first version of CEENE (CEENE v1.1) on the other hand, land resources are accounted for by their land occupation. To do so, the solar irradiation available for photosynthesis was used as a proxy [32]. Furthermore, inflow of solar exergy and exergy of harvested biomass products as such are not accounted for in the CEENE method, since they are included in the land occupation, this to avoid double counting. For example, land occupation for feed ingredients is the main reason (62%) why CEENE input for feed pellets and thus Pangasius is so high, see Figure 10.3. This showcases the relevance of accounting for land occupation.

The CEENE method was further improved concerning land resources by Alvarenga et al. [42] In this second version of CEENE (CEENE v2.0), a distinction was made between land resources from natural systems and from human-made systems, see Figure 10.5. A system can be considered natural if its biomass production is maintained with no or negligible human intervention, e.g. primary forest. From these natural systems, extracted biomass resources are accounted for by their exergy content. In human-made systems, land area has been transformed from natural to human-made environment, e.g. forest plantations. Here, the biomass yield is not extracted from nature, since it is produced within the human-made system. What is actually extracted from nature is the land area. Therefore, the land area occupation needed for biotic resource production is accounted for in human-made system.

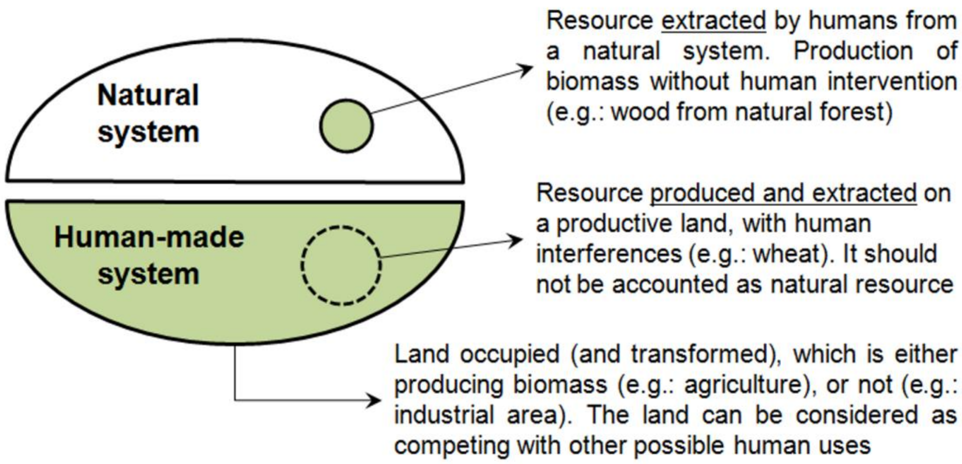

Figure 10.5. Schematic representation of land resources from two different systems. Source: Reprinted with permission from International Journal of Life Cycle Assessment, 18, Alvarenga et al. 2013, Copyright 2013, Springer

To do so, the natural potential net primary production (NPP) was used as a proxy, which is the amount of NPP a land area would produce if it was not occupied by humans. Since the natural potential NPP is a result of local natural conditions such as solar exergy, soil quality, temperature, rainfall etc., it is a better proxy than the solar exergy of CEENE v1.1. Site-specific characterization factors were obtained making spatially-differentiated impact assessment of land occupation possible [42]. This was illustrated by Alvarenga et al. [42] by analyzing nine biomass products from Ecoinvent, see Figure 10.6. The results show that land resources have a large influence on the final impact of these products. It can be noticed that site-generic characterization factors can underestimate the impact, e.g. palm fruit from Malaysia, or overestimate the impact, e.g. potatoes from the USA, compared to site-specific values.

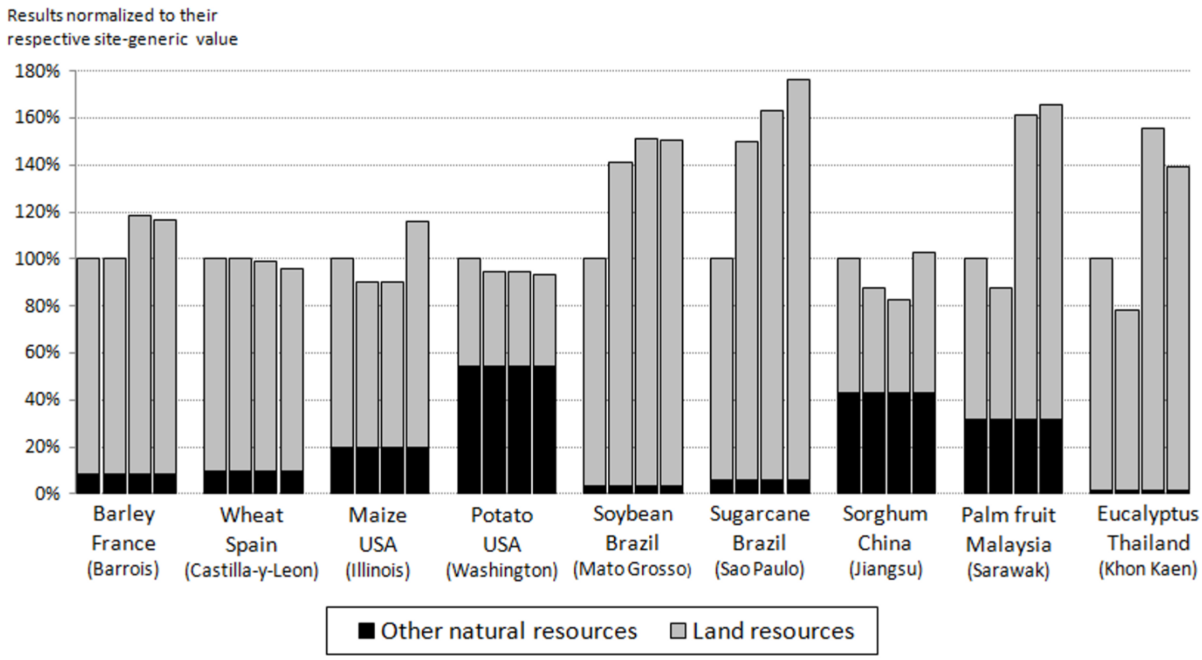

Figure 10.6. Comparison between site-generic (outer left bars), site-dependent at continent level (middle left bars), site-dependent at country level (middle right bars) and site-dependent land occupation characterization factors of the CEENE methodology at regional level (outer right bars) for nine biomass products. Source: Reprinted with permission from International Journal of Life Cycle Assessment, 18, Alvarenga et al. 2013, Copyright 2013, Springer

The main difference between CExD and ICEC are the databases to which they have been operationalized. Life Cycle Inventory databases (LCI, see Chapter XX) can be based on different inventory models: process-models or input-output (IO)-models. A thorough explanation of these models can be found in the work of Heijungs and Suh [43]. The CExD method is operationalized to the process-based Ecoinvent database [31], while the ICEC method is operationalized to the IO-based United States (US) 1997 database. Also ECEC has been operationalized to the US 1997 database [44]. The CEENE method is operationalized to both the process-based Ecoinvent database [32, 42] and the IO-based Exiobase database [45]. Exiobase is a world IO-database, covering the whole globe, while the US 1997 is a national IO-database.

The ECEC method on the other hand has the ecosphere as system boundary. As mentioned earlier, this method is closely related to the emergy concept, in which a certain amount of solar energy is attributed to geothermal heat and tidal waves in order to be able to count in terms of solar energy [39]. The emergy of a product is the available solar energy (i.e. solar exergy) used for its creation [46]. However, the emergy methodology also covers additional methodological assets which have led to a lot of criticism [3]. In the ECEC method, Hau and

Bakshi [33] try to account for the exergy that was needed to produce natural resources by natural systems (i.e. embodied exergy) by assigning them emergy values from literature. Although some of the controversial aspects of emergy are avoided in the ECEC method, its use to assess the impact of natural resource consumption is sometimes questioned [29][40].

In the study of Liao et al. [38], the CExC methods are compared with other resource-related impact methods, i.e. the Cumulative Energy Demand (CED) [47], the Solar Energy Demand (SED) [48], the Abiotic Depletion Potential (ADP) [49], Environmental Priorities Strategies (EPS) [50][51] and Ecoindicator 99 (EI99) [52]. CED and SED are both cumulative energy consumption methods, based on the first law of thermodynamics. Like the CExC methods, they are situated at the first step in the impact pathway by accounting consistently for resource use, i.e. RAM. The system boundary of CED is the technosphere, while the system boundary of SED is the ecosphere. The other impact methods (ADP, EPS and EI99) are situated at the second and third step in the impact pathway, evaluating resource scarcity at midpoint and endpoint level. An overview of the methods is giving in Table 10.1, showing which resource categories they consider.

Table 10.1. Overview of the methods and considered resource types. The grey colored column are the cumulative exergy consumption methods. ICEC considers the same resources as CExD. (*land use is accounted for in case of human-made system, and biomass in case of natural systems). Source: Adapted with permission from International Journal of Life Cycle Assessment, 17, Liao et al. 2012, Copyright 2012, Springer (open access article)

Resources	CExD	ECEC	CEENE	CED	SED	ADP	EPS	EI99
Land use			X*		X			
Biomass	X	X	X*	X				
Fossil fuels	X	X	X	X	X	X	X	X
Nuclear energy	X	X	X	X	X		X	
Metal & minerals	X	X	X		X	X	X	X
Water resources	X	X	X		X	X		
Abiotic renewables	X	X	X	X	X			
Atmosp. Resources			X		X			

Liao et al. [38] concluded that the added value of resource impact assessment with thermodynamics-based resource accounting methods lies in the completeness of the resource scope and scientific robustness and validity. On the other hand, they have lower environmental relevance in terms of resource depletion. Of all these thermodynamics-based methods, CEENE and SED consider the largest number of resource groups, and are put forward as the better ones. Liao et al. [38] recommend CEENE as the most appropriate thermodynamics-based method for accounting resource use because of its mere utilitarian perspective: CEENE considers the contribution of resources to the technosphere, while SED considers the efforts spent by the ecosphere in generating resources, leading to considerably different results.

10.5. Conclusions

This chapter has illustrated that exergy is a strong thermodynamic tool in several fields of application: in industrial engineering, it is used to characterize the efficiency of processes; in natural system analysis, it is used to measure the integrity of ecosystems; in economics, it is applied to achieve a better production management; in sustainability analysis, it is used to quantify the environmental impact of emissions and resource intake. The latter is done using CExC methods. These methods sum up all the exergy contained in the natural resources required along the life cycle of a system. CExD, CEENE and ICEC account for the resources extracted by the technosphere from the natural environment, while ECEC and SED consider the efforts spent by the ecosphere, including the natural environment, in generating resources. Finally, these methods are compared with other resource-related impact methodologies: although they have lower environmental relevance in terms of resource depletion, they offer a more complete resource range and a higher scientific validity.

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